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A baseline geochemical survey of Gibraltar to aid socio-economic development. A method using a Geographical Information System.

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Abstract

The urban environment is affected by a wide variety of anthropogenic activities which tend to increase metal concentrations in soils. Heavy metal concentrations in urban soils are influenced by a combination of factors including geology, historical and current industrial land use, transportation routes and urban regeneration. These factors must be taken into account in future planning development. Gibraltar is situated at the southern tip of Spain, and the extreme density of the population exerts considerable pressure on land use. Therefore future planning is of the utmost importance as the population of about 33,000 is concentrated on an area of 6.4 km^2.

A geochemical survey of Gibraltar has been carried out to establish current baseline data for a wide range of elements in surface soils and dusts to identify areas with metal concentrations which exceed soil guideline values and world means. Soil samples (0-15cm) have been taken from as wide a range of exposed sites as possible, from both bare and vegetated soils, in order to provide optimum geographical distribution. The main aims were to investigate geochemical associations and the spatial distribution of heavy metals within the urban environment and the nature reserve so as to make recommendations to the Government concerning sustainable development. House dusts and street dust samples were also taken, to allow the investigation of any possible migration of metals between different environmental media, in order to assess any potential risks to environmentally sensitive receptors including the residential population.

The "total" elemental concentrations of 26 elements were determined by ashing in a nitric perchloric acid mixture followed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analysis. A chemical sequential extraction technique was used to assess partitioning of elements within the soil phase, thereby giving an indication into any potential bio availability. This was also applied to dusts samples. Although it is understood that the phases applicable to soils and sediments are unlikely to be found as such in dust samples, a series of sequential extractions can give valuable information concerning the extractability, and thus mobility, of metals in the dusts. Geochemical associations in soils and dusts have been identified using factor analysis. Geostatistical models and geographic information systems (GIS) have been used to assess the spatial distributions of elements in relation to geographical factors, such as the underlying geology, urban topography, current and former land use. The GIS database allows spatial operations as well as statistical analysis to be made on the dataset whilst delivering the results in an "easy to use" graphical user interface.

Areas with metal concentrations exceeding soils guideline values were identified in locations close to former and/or current industrial sites. The concentration of metals in soils and dusts in Gibraltar is heterogeneous and site specific, therefore a portion of the variability found between different sites is not spatially related. This enhanced the likelihood of errors when predicting concentration surfaces using GIS. Interpolation techniques are generally not suited to areas with distinctly varying topologies such as those found in Gibraltar.

Various methods for calculating current baseline concentrations for Gibraltar (defined as 95% of the expected range of background concentrations) have been investigated. Their use as an aid in the identification of areas with increased metal concentrations enhances the use of risk assessments and allows future policy regulations to be implemented. The implications of this research are discussed in terms of its effects on land use management and the future socio-economic development of Gibraltar within the EU.

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Affirmation

This is to declare that the work presented here is my own work.

Abbreviations

mg/kg	milligrams per kilogram equivalent to ppm
ppm	parts per million
ppb	parts per billion
DIW	deionised water
Analar®	trade name for the grade of reagents used
IDL	instrumental detection limit
ADL	analytical detection limit
NIST CRM	National Institute of standards. Certified reference material. A substance with an accurately known concentration used to calibrate and estimate analytical accuracy
HRM	house reference material, a substance used to assess instrumental drift
LOI	loss on ignition; an estimate of the content of organic carbon in a
soil pH	acidity or alkalinity of a substance
CEC	CEC is the sum total of exchangeable cations that a soil can absorb, expressed in c mole kg^{-1}.
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
MOD	Ministry of Defence
GOG	Government of Gibraltar
DEFRA	Department of Environment, Food and Rural Affairs
EA	Environment Agency
URNR	Upper Rock Nature Reserve
EPA	Environmental Protection Act
DETR	Department of the Environment, Transport and the regions
ICRCL	Interdepartmental Committee for the Redevelopment of Contaminated Land
CLEA	Contaminated Land Exposure Assessment
SGV	Soil Guideline Values
PI	Pollution Index
EQS	Environmental Quality Standards
ESSG	European Soil Sampling Guidelines
IDW	Inverse Distance Weighting
RA	Risk Assessment
GIS	Geographic Information System
GIT	Geographic Information Technologies
GPS	Global positioning system
ESRI	Environmental Systems Research Institute, INC.
ArcView®	Software GIS product used in project developed by ESRI
SPSS®	Statistical Package for the Social Sciences
SD	standard deviation
N	number of samples/measurements
GM	GM stands for Geometric Mean
GSD	Geometric Standard Deviation

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CHAPTER 1

Introduction

1.1 Outline

In 1973 E.F Schumacher stated *"Among material resources, the greatest, unquestionably, is the land...the land carries the topsoil and the topsoil carries an immense variety of living beings, including man".*

Physical degradation of the soil is one of the main environmental issues being addressed today. Concern that human activities are unsustainable has resulted in reports such as "Our Common Future" by the World Commission on Environment and Development and in the formation of a United Nations Commission on Sustainable Development responsible for carrying out Agenda 21 (Barnaby, 1987). Despite this however, relatively little work has been carried out on the sustainability of the earth's land surface and its life support systems (Plant *et al.*, 2001).

Pollution is very often a by-product of development. The wastes generated from social and industrial progress have meant that the normal regenerative capability of the natural environment has now been stretched beyond its limits and contamination is fast changing the natural environment. Soil contamination is now affecting remote areas through air pollution, and in many regions, past anthropogenic activities such as mining have left a legacy of contamination, which will affect present and future generations. Furthermore, the processes controlling the natural chemistry of the metallic elements, and their residence time in the rock-soil-plant-human chain are still not completely understood. Metals in soils occur in many chemical and mineral forms and these impose a controlling influence on their solubility, bioavailability and potential for migration into surface and ground waters. Major and trace elements rarely occur in isolation in the environment. The associations and interactions between elements and other components in the environment are known to influence their availability to organisms and can also (depending on the element in question) ultimately lead to toxicity.

The principle aims of this work are to undertake a detailed geochemical survey of Gibraltar, investigate any risks to the atypical flora and fauna and to make

recommendations to the local government concerning sustainable development. The objectives of this baseline survey are to establish the extent and magnitude of the variations in major and trace elements in soils and dusts in order to assess the impact of industrial, commercial and urban development on the natural geochemical landscape of a very compact area.

This study continues from a reconnaissance soil geochemical survey conducted during a five month MSc project undertaken by the author of this thesis. The further work presented here forms part of an ongoing study undertaken during three years as part of a baseline geochemical survey of Gibraltar. This ongoing study includes further sampling of soils (116 extra soil samples) as well as the creation of a dust dataset for Gibraltar (83 street and 80 house dust samples). Subsequent laboratory analysis included the acid digestion of the new samples obtained and a sequential chemical extraction procedure applied to selected samples (chapter 4). The latter technique was not used during the reconnaissance work. To aid the interpretation of the analytical data obtained, a sampling and analytical quality control scheme was applied to the entire dataset which included samples from the reconnaissance study. The application of new data analytical techniques which include the use of bivariate and multivariate statistics is another part of this study which did not form part of the initial reconnaissance. Additionally, the suitability of GIS and geo-statistical methods of analyses are investigated as regards their suitability for data presentation and interpretation.

The implications of this analysis will also be discussed in terms of effects on the future socio-economic development of Gibraltar. Guideline values for Gibraltar will be suggested for future geochemical research to assist in future land use and environmental assessment and for deciding the need for more detailed investigation. Element concentrations in home environments in different areas of Gibraltar have been investigated and will be discussed with a view to evaluating and verifying any risks to the population from exposure to certain potentially toxic elements and species. Geographic Information Systems (GIS) are being used to create a database to assess the spatial distributions of elements in relation to the underlying geology, topography, as well as historical and present land use. GIS will assist with the future modelling of spatial trends whilst delivering the results in an "easy to use" graphical user interface (GUI).
The extreme density of the population of Gibraltar, which is situated at the southern tip of Spain, exerts considerable pressure on land use and thus future planning is of the utmost importance. The population of c.33000 is concentrated on an area of 6.4 km^2. The

increasing developments on reclaimed land appear to be solving the constant housing shortage, which has inhibited the general development of Gibraltar for decades. However, it is becoming increasingly apparent, that as further development plans arise, the urgency for a detailed geochemical survey of Gibraltar is needed in order to ensure efficient land use management. Land is one of the most precious and finite resources of Gibraltar; therefore it deserves extreme care in its use and preservation.

1.2 Background to the research

Development is an ongoing process, which has often led to the degradation of the soil. This is particularly evident through our use and need for land. The impact of urbanisation and industrialisation on soils is evident in the United Kingdom and Europe. This problem is expected to become progressively important at a global level as cities around the world expand to accommodate the growing population of the world. The demand for land suitable for development often exceeds the supply, especially in urban areas. Reclamation and redevelopment of previously used sites can help to make good the shortfall, but such land may have been contaminated by its former uses. While this does not mean that it is unsafe or unusable, the contamination may need to be taken into account by those buying, selling or developing on such land (ICRCL, 1987).

It is important for the purpose of this study to differentiate between the terms "contamination" and "pollution". Alloway (1999) describes them as follows: "Contamination" is used where a substance is present in an environment as a result of human activity but is producing no apparent harmful effects, whereas the term "pollution" is used when the substance in question is causing a harmful effect. These definitions refer to the possibility of harm occurring as a means of differentiating between contamination and pollution. The UK definition of contaminated land as defined in Part IIA of the 1990 Environmental Protection Act (DEFRA, 2000b) notes that *Land is only "contaminated land" where it appears, by reason of substances in, on or under the land, that: significant harm is being caused or there is a significant possibility of such harm being caused; or pollution of controlled waters is being, or is likely to be, caused.*

Contamination can also be described as that exceeding natural background levels. Thus, for example, if the background concentration of Pb in soil was 300 mg/kg, then anything above this would be contaminated. In this way contamination is site specific, and not an

used as regards health, that is to say where levels of contamination have risen to the extent that biological problems are being, or likely to be, experienced. The reason for relating these definitions on a site-specific basis is because confusion can arise when discussing a level of pollution in a certain location, if in another location the background level is higher than the quoted pollution levels in the first place.

The terms "background", "baseline", "elevated" and "deficient" are used throughout this work to assess and interpret the data obtained. It is therefore important clearly to define these words. Background data is a term used when referring to element concentrations in natural media without human influence, in other words, a pristine environment (Kabata-Pendias, 1992; Brooks *et al.*, 1995). Baseline data however, is a term which expresses an expected range (not a single value) of element concentrations around a mean in a normal sample medium. It is not generally a true background concentration and defined as 95% of the expected range of background concentrations (Kabata- Pendias *et al.*, 1992; Chen *et al.*, 1999; Dudka *et al.*, 1995).

Concentrations defined as elevated refer to values which exceed recognized soil guidelines or in the absence of soil guideline values, concentrations which are greater than established world means for a given soil type or parent geological material. Similarly, concentrations defined as low in this work relate to those which fall below established world mean values and/or soil guideline values.

In this work, areas that are defined as having elevated concentrations are according to the above definition. This does not in any way imply or suggest that such areas may be contaminated or polluted. Areas with particularly high or low concentrations in comparison to the overall trends in the dataset will be discussed in terms of concentrations falling within different percentile ranges (see Chapters 6 and 7). When these values happen to coincide with the above definitions for low or elevated values, this will be stated. Should an area be considered to be contaminated or polluted as per the definitions provided above, this will also be stated.

Stating and defining the terminology to be used when assessing elemental concentrations in soils or any other environmental media is important because elevated levels of trace metals may be toxic to biological systems (WHO[1], 1989; Royal Commission, 1983).

[1] WHO= World Health Organisation

However, some elements such as copper and zinc are essential for the maintenance, growth and repair of tissues both in animals including humans as well as in plant systems. Other elements such as cadmium and lead are non-essential; the body does not require them although they may be tolerated at very low levels and toxic at higher concentrations.

The distribution of chemical elements over the surface of the earth is controlled by physicochemical parameters that are investigated through the study of geochemistry (Plant and Raiswell, cited in Thornton, 1983). In an evaluation of soil contamination it is very important to have an understanding of the physical processes that influence the dispersion of soil pollutants. The concentration and distribution of elements in soils are controlled by factors such as the composition of the parent material, weathering, climate as well as relief and drainage conditions within the soil. Soils in most parts of the world, but particularly in the western nations, have for centuries been exposed to varying degrees of contamination from various chemicals (Alloway, 1996). The distribution of chemicals and metals in soils has to some extent been governed by the activities of humans, for example, metalliferous mining, metal smelting, waste disposal, fossil fuel combustion and sports activities such as various shooting sports. The above examples are responsible for the distribution of elements into the soils via dispersion by water and atmospheric deposition of particles, sorption of gases from the atmosphere, and placement, for example, dumping, injection and surface spreading (Alloway, 1996). Metals are however naturally present in the geosphere, atmosphere, hydrosphere and biosphere.

A consideration of metals that occur naturally in rocks is necessary before the results of geochemical analyses of soil can be interpreted. Metals are natural components of the environment; their distribution is the result of the weathering of rocks, which possess varying amounts of metal concentrations. Thornton (1995) tabulates metal content in rocks. For example, course-grained sandstone contains very small amounts of copper and cobalt, whereas marine black shales contain large amounts of molybdenum, selenium and cadmium. Potentially toxic amounts of metals in soils may be derived from the weathering process of these metal rich rocks. The bioavailability of metals within the soil is controlled both by the chemical speciation/mineralogy of the element in question as well as the soil properties. The latter include physical properties, such as particle size and permeability, and chemical properties for example: pH (acid soils result in the majority of metals being more bioavailable), redox conditions (oxidation-reduction

conditions affecting the speciation of elements) and the cation exchange capacity (CEC)[1.1].

Soil, water and air are major environmental media. The importance and distinctive attributes of soil as a resource lie in the ability to act as a sink and as a filter to a wide array of chemicals, thus preventing the flow of chemicals into ground water. Soil also acts as a bioreactor where organic pollutants can be, and are, decomposed (Alloway, 1996). Soils differ greatly in their properties depending on the rock type and conditions in which they were formed, and their age. Soils vary in the amount of water they hold as also in their depth, chemistry, physical structure and organic matter content. Any variations in these attributes will affect the chemistry of surface and ground waters, types of flora and fauna, the fertility of the soil and perhaps most importantly whether it acts as a sink or as a source of chemical elements.

"Environmental geochemistry is concerned with the complex interactions in the system geosphere-hydrosphere-atmosphere-biosphere or rock-soil-water-air-life. It encompasses the factors influencing the sources, dispersion and distribution of elements in the environment, their pathways into soils, foodstuffs and water supplies, and their influence on plant and animal life" (Thornton, 1993).

1.3 A Geochemical Investigation

The ultimate purpose of any geochemical investigation is to describe the variation of an analyte's concentration in environmental media. Analysing the entire sphere of influence is not feasible, so a series of samples are collected which are intended to encompass collectively the entire chemical variation present in that media (Ramsey, 1997). Therefore, in the majority of cases, the incentive for conducting a geochemical analysis (or any type of analysis) is not just to acquire data, but to solve a problem, to locate a source, to test a theory, or to see if a sample satisfies some predetermined quality standard (Gill and Ramsey, 1997).

Geochemical analyses are performed to ascertain the concentration of either a particular element of interest (referred to as an analyte), or a suite of elements (analytes) sharing a particular concentration range or behaviour (Gill and Ramsey, 1997). Figure 1.1 illustrates the steps to be followed in this geochemical investigation.

[1.1]CEC is the sum total of exchangeable cations that a soil can absorb, expressed in c mole kg^{-1}.

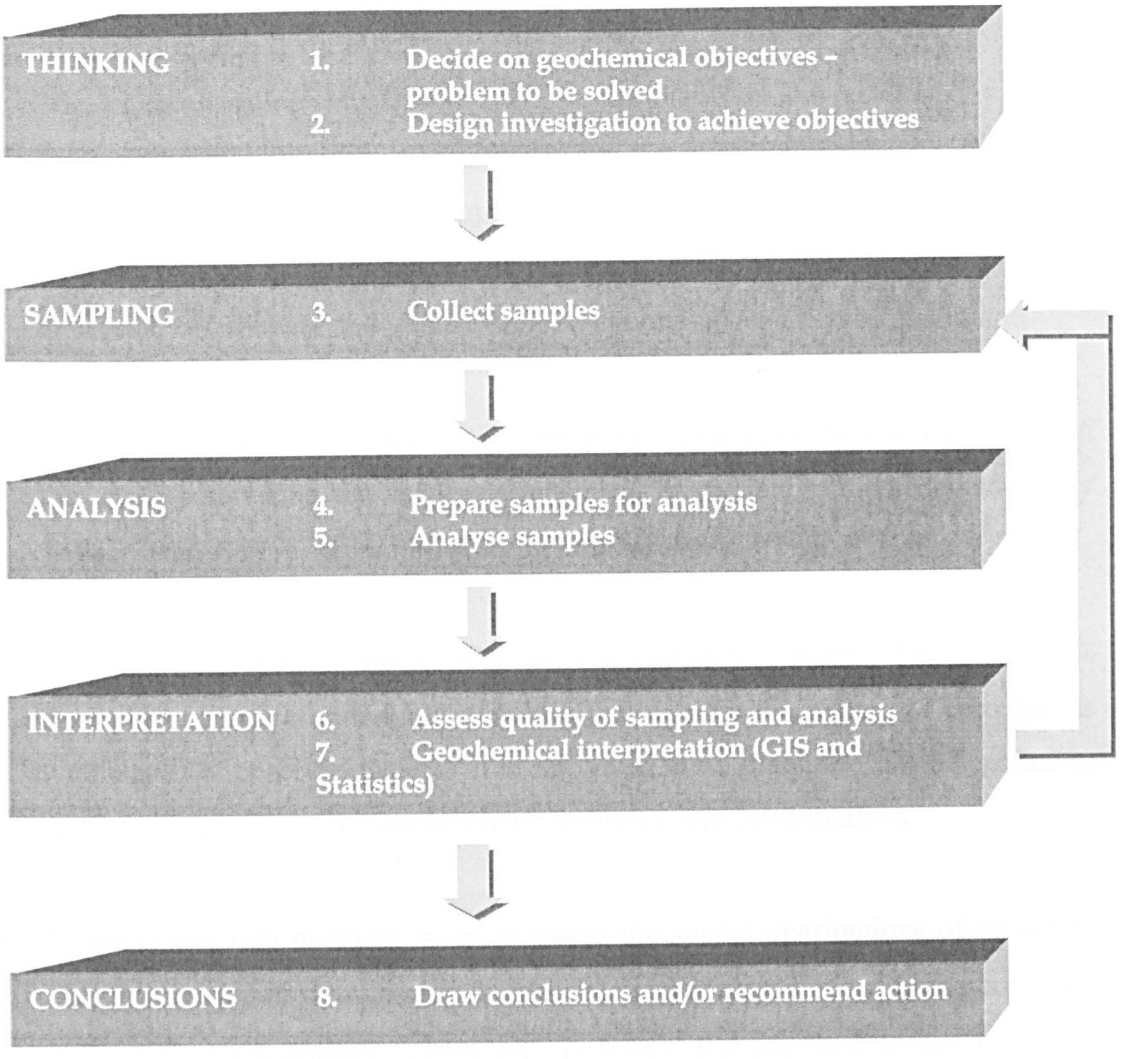

Figure 1.1 Model of a generalised geochemical investigation
Source: modified from Ramsey (1997)

A geochemical analysis entails verifying not only the concentrations themselves but also the uncertainties ("errors") that are associated with them, as these restrict the conclusions that can objectively be drawn from the data (Gill and Ramsey, 1997).

The underlying principle of the current investigation is to obtain baseline data for a number of different elements, so that the relative importance of indoor and outdoor sources of exposure to the population and to the ecosystem may be determined and reported accurately together with their spatial distribution in the surface environment.

1.4 Aims and Objectives

The detailed aims and objectives of the project are set out below:

- To undertake a detailed geochemical survey of Gibraltar and to examine total metal concentrations using a variety of soils from urban, rural and military areas.

- To establish baseline values.

- To establish the extent and magnitude of the variations in major and trace elements in soils and dusts (street and house dusts) in order to assess the impact of industrial, commercial and urban development on the geochemical landscape.

- To identify the principal factors affecting trace metal mobility and availability in the urban soils using the sequential chemical extraction method, developed by Tessier *et al.* (1979) and modified by Li *et al.* (1995a).

- To carry out Factor Analysis (FA) on the complete dataset. Factor analysis attempts to identify underlying variables that explain the pattern of correlations within a set of observed factors. It is employed in an attempt to identify pollution sources and to apportion natural versus anthropogenic contributions.

- To develop a GIS database so as to assess the spatial distributions of elements. This will be done by comparing the geochemical maps produced to features such as the underlying geology, topography, historical and present land use as well as in relation to natural elemental associations.

- To deliver a GIS database to the Government of Gibraltar, which they can use to assess land use changes in different locations and to investigate sources of contamination to the environment and to assist with future land use planning and conservation.

- To investigate how the urban geochemistry of Gibraltar relates to issues concerning land use management and sustainable development.

1.5 Thesis layout

The presentation of the research conducted for this thesis has been divided into four sections. Part A discusses the purpose and scope of the research questions tackled in this work. It includes this introduction together with a literature review and site description.

Chapter 2 reviews the literature within the field of geochemical analysis which directly relates to the research title, and the aims and objectives of this work. Chapter 3 is comprised of a detailed description of Gibraltar. All factors, both natural and anthropogenic which are believed to have some bearing on the findings and outcomes of this work are discussed.

Part B (materials and methods) of this thesis reviews and discusses the methodologies and tools available for geochemical investigations. A summary of the available methods for the statistical and spatial analysis of geochemical data have been given in chapter 4. Chapter 5 provides a detailed description of the methodologies which were applied to work carried out in this project.

Part C deals with Results and Evaluation. The uncertainties of sampling and analysis and quality control resulting from the research are discussed in chapter 6. The results of the dataset are displayed in chapter 6. The distribution of data are assessed and exploratory statistical analysis is discussed for the three datasets (soils, house dusts and street dusts). Chapter 7 deals with the spatial interpretation of the dataset. It discusses the tools used to further evaluate the dataset. The results from the bivariate, multivariate and GIS analysis are given and discussed in these two chapters.

The final section Part D discusses the interpretation of the urban geochemical data as they relate to issues concerning land use management and sustainable development in Gibraltar. It also discusses the limitations encountered during this research and the main findings and overall conclusions. Recommendations for future work are also outlined.

CHAPTER 2

Literature Review

2.1 Introduction

Chemical elements are natural components of rocks, soils, air, water and biological materials. The distribution of these elements in and between the different environmental media is controlled by physicochemical parameters that have become increasingly better understood as a result of progress in geochemistry (Plant and Raiswell, cited in Thornton, 1983; Thornton, 1998). Environmental geochemistry is therefore concerned with the complex interactions of elements in the rock-soil-water-air-life system (Thornton, 1993).

This chapter presents an overview of the different aspects within environmental geochemistry, which relate to and affect element distributions within the urban environment.

2.2 Development of Geochemistry

The roots of Geochemistry lay mainly in the 19th century but it unfolded into its multifaceted complexity during the 20th century. During that era, the two essential prerequisites for the growth of geochemistry were the discovery of the chemical elements and the development of sensitive and accurate methods for the analysis of rocks and minerals (Faure, 1991).

Many definitions exist which explain the different aspects of geochemical research. Fersman (1922), cited in Wedepohl (1969) defined geochemistry as follows: "Geochemistry studies (a) the quantitative distribution of the chemical elements in the earth's crust and their dispersion and local concentration; (b) the combinations of different elements in the different parts of the earth's crust and their distribution in space and time under the influence of different chemical processes; (c) the migration of elements and the laws of such migration as determined by different thermodynamic

conditions of their environment; and (d) the behaviour of chemical elements either in the environment of the earth's crust or as compounds and particularly as crystals. In brief, geochemistry studies the history of the chemical elements in the earth's crust and their behaviour under different thermodynamic and physicochemical natural conditions". Hawkes and Webb (1962) later defined the science of geochemistry in a less lengthy but equally comprehensive definition as: "geochemistry involves the relative abundance of the elements in the earth, the study of the distribution and migration of the individual elements in the various parts of the earth and the principles governing their abundance, association, distribution and migration".

The field of **environmental geochemistry** has developed rapidly in the past forty years in response to the need for understanding the behaviour of chemicals in soils, as well as in ground and surface waters. This came about as a result of the increase in world population, economic growth, resource development and the general increased awareness of pollution and the implementation of the ensuing regulations. Since this science was first developed in the 1960s and 1970s, it has evolved to provide critical understanding and data essential to predict contaminant migration from waste sources through soil and ground water, and to provide the basis for preventative and remediation technologies (Johnson, 1997).

A large portion of the current research in environmental geochemistry is centred on the further explanation of the mechanisms and kinetics of adsorption reactions of metals and of organic compounds. The fate of elements in soils is a popular area of research, and understanding the adsorption mechanisms will aid the development of more accurate mathematical expressions for adsorption, as well as decreasing the reliance on empirical measurements (Johnson, 1997).

2.2.1 Definitions of terminology

To avoid the confusion that can occur in the literature in relation to certain terminology some definitions are provided. The term "heavy metals" is used for metals with a density >6 g cm^{-3} which occur naturally in rocks, although concentrations are often elevated as a result of contamination. It is also used for metals that are associated with potential toxicity. Heavy metals belong to the metal

group known as "trace metals" because they collectively make up <1% of the rocks in the earth's crust (Alloway, 1996). Certain trace metals in small concentrations are necessary for the healthy growth of plants and animals, but in large concentrations can lead to toxicity and even death. These metals are referred to as "essential trace metals" or "micronutrients" (Thornton, 1995). Essential trace metals for plants include: B, Cu, Fe, Mn, Mo, Si, Sn and V. Essential trace metals for animals include: Cr, Co, Cu, F, Mn, Mo, Ni, Se, Si, Sn, V and Zn. The most important heavy metals with regard to potential hazards are: As, Cd, Cr, Hg, Pb and Zn (Alloway, 1996).

The terms "accuracy" and "precision" when used in the chemical analyses of elements and subsequent assessment of the reliability of data, can also lead to confusion. Accuracy is the nearness of the measured observation to a true value, regardless of whether the error is systematic or random. Bias is described as a systematic deviation of accuracy. Precision is a measure of the random error of a measurement (the dispersion of individual measurements, which may be accurate or inaccurate) (section 4.8.2). It is the closeness of agreement between results obtained by repeating an analytical procedure several times under the same conditions (Gill and Ramsey, 1997). Stating that an analysis is precise, is simply a qualitative statement about the random error associated with the analysis, not about how close the result is to the true value (Gill and Ramsey, 1997). High precision thus means small random error. Basically, it can be expressed as the reproducibility and repeatability of analytical results, based on the same conditions and under no special circumstances under which the measurements are replicated (Ramsey, 1992 b).

2.3 Soil geochemistry

Soil is the geochemically and biochemically complex material which forms at the interface between the earth's crust and the atmosphere (Alloway, 1996). Soils are heterogeneous, open dynamic systems comprised of solid, liquid and gaseous phases whose properties are governed by the nature of the parent material, by the climate, landscape and biota all acting through time (Sposito, 1984). The distribution of elements in the surface environment is the result of erosion processes on the underlying parent materials. These processes, whether they are physical or chemical weathering, govern the gradual transformation of hard, relatively inert, often non-

porous rocks to soil which in turn is soft, porous and chemically active (Thornton, 1995). Initially, soils that are developed *in situ* will have a trace element composition, which can be directly related to the geological parent material. With time however, this composition will digress gradually under the influence of pedogenetic processes, which are in turn influenced by climate, vegetation, micro-organisms, topography and depending on geographic location and anthropogenic influence. In soils where the parent material has been redistributed by alluvial transport, the influence of the underlying geology will have been modified or even masked (Thornton, 1995). The soil system is subject to short-term fluctuations, such as variations in the moisture status, pH and redox conditions. It is simultaneously undergoing gradual variations in response to changes in land use and environmental factors. These changes in soil properties will in turn affect the form and bioavailability of metals and need to be taken into account in decisions on the management of polluted soils (Alloway, 1995).

2.4 The distribution of elements in the natural environment

The prime natural source of elements in the environment is a result of geochemical associations combined with the process of weathering. Understanding the natural associations of elements can assist in the interpretation of anthropogenic anomalies. Goldschmidt (1954) classified elements into various groups on the basis of their distribution patterns. He used the terms siderophile, chalcophile, lithophile, atmosphile and biophile to describe elements that have an affinity for metallic iron, for sulphide, silicate, the atmosphere and life forms respectively (Table 2.1) (Goldschmidt, 1954). These groupings represent an approximate qualitative indication of natural associations and offer partial explanations for geological behaviour of elements and mineral assemblages in rocks and soils (Wedepohl, 1969; Levinson, 1980; Li, 1993).

The trace element content of soils corresponds closely to that of the different contributing rock types. The three main rock types are based on their generic origin: igneous, sedimentary and metamorphic. These range widely in their metal content.

Table 2.1 The Goldschmidt classification of elements

Siderophiles	Chalcophile	Lithophile	Atmophile	Biophile
Fe, Co, Ni, Pt, Au, Mo, Sn, (Pb), (Sb), Ge, C, P, Ru, Rh, Re, Os, Ir, (W)	Pb, Cu, Ag, Zn, Cd, Ba, In, Tl, As, Sb, Bi, S, Se, Te, (Ge), (Sn), (Fe), (Mo), (Re), (Au)	B, Al, Sc, Ti, Zr, Hf, Th, (C), (P), V, Nb, Ta, O, Cr, W, U, (Fe), Mn, F, Cl, Br, I, (H), (Tl), (Ga), (Ge), (N)	H, N, (C), (O), (F), (Cl), (Br), (I)	H, C, N, O, P, (Na), (Mg), S, (Cl), (K), (Ca), (Fe), (B), (F), (Si), (Mn), (Cu), (I)
Elements are associated to iron compounds	Elements are associated to sulphides and sulphide ores,	Elements are associated to silicates and found in the silicate lattice; group I and II	Elements are associated to the natural gasses and inert gases	Elements are associated to organic matter

(elements in parentheses belong primarily in another group)

Source: Wedepohl (1969), Levinson (1980), Li (1993)

For example, coarse-grained sandstones contain very small amounts of the nutritionally essential metals Cu, Co and Zn. Contrastingly, marine black shales frequently contain large amounts of Mo, Se and Cd, while basic ultra rocks such as serpentine may contain significant quantities of Cr and Ni. Because the geology of Gibraltar is comprised of sedimentary rocks, the origin and formation of sedimentary rocks is described in greater detail in this section.

2.4.1 Sedimentary rocks

Sedimentary rocks are formed at or near the earth's surface through the accumulation and lithification of sediment (detrital rock) or by precipitation from solution at normal surface temperatures (chemical rock). These rocks result from the weathering of igneous rocks (Krauskopf, 1995; Brownlow, 1996). Sedimentary rocks are the most common rocks exposed on the Earth's surface but form only a small part of the entire crust, which is largely dominated by igneous and metamorphic rocks. The processes of physical and chemical weathering break down these source materials into the following components (Hawkes and Webb, 1962; Fergusson, 1990; Krauskopf, 1995):

1. *Small fragments* of the source rock (gravel, sand, or silt size) that may be identifiable rock fragments or individual minerals
2. *New minerals* produced by weathering processes (mainly clays)
3. *Dissolved portions* of the source rock (dissolved salts in river and ocean water)

The accumulation of these materials (fragmental material, clays, and dissolved salts) leads to the formation of sediments on the earth's surface. Sediments may form by (Hawkes and Webb, 1962; Fergusson, 1990; Krauskopf, 1995):

1. *Mechanical accumulation* (wind, water) for example gravel and sand deposits in a river or sand dunes in a desert;
2. *Chemical precipitation*, for example salt and calcite precipitation in shallow seas and lakes;
3. *Activity of organisms*, for example carbonate accumulation in coral reefs (organic precipitation), or accumulation of organic matter in swamps (coal precursor).

Sedimentary rocks are formed when these primary sediments coagulate by means of cementation and compaction. Several different types of sedimentary rocks can be classified based on mineral composition, and origin of the sediment. The main classes are: Clastic Sedimentary Rocks, (conglomerates, sandstones and mudstones/shales) and Chemical and Biochemical Sedimentary Rocks, (limestone/dolostone, evaporates and carbonaceous rocks) (Krauskopf, 1995).

Clastic sedimentary rocks are made up of fragments of other rocks, namely igneous, metamorphic and sedimentary. These are then subdivided (according to grain size) into conglomerates (grain size >2 mm), sandstone (between 2 mm and 0.0625 mm), and shale (mudstones). Sandstones make up around 30% of all sedimentary rocks. The most abundant mineral in sandstones is typically quartz, as it is the hardest of the rock forming minerals and most resilient to abrasion during transport. Shales or mudstones is made up of consolidated mud (clay), and account for 70% of the sedimentary rocks on earth. Chemical and organic sedimentary rocks are another main group of sediments in addition to clastic sediments. They form through

inorganic or organically mediated mineral precipitation, and from biological activity. Certain conditions are needed for these rocks to form, for example small clastic sedimentation (to dilute chemical and organic input), high temperatures and high evaporation (cause supersaturation, and high organic activity e.g. in reefs, tropical swamps).

Limestones are the most common type of chemical sediment. They consist principally of the mineral calcite ($CaCO_3$), and can form by inorganic precipitation in addition to organic activity. Classifications of limestones exist that are similar to those of clastic rocks. Dolostones consist of the carbonate mineral dolomite [$CaMg(CO_3)_2$], and arise in relatively the same settings as limestones. Most of the dolostones in the sedimentary record are due to post-depositional replacement of calcite by dolomite (Mg for Ca exchange by Mg-rich pore waters) (Krauskopf, 1995; Mitchell, cited in Bear, 1964). Carbonaceous sedimentary rocks make only a small fraction of sedimentary rocks. They include those that contain abundant organic matter in various forms and are important energy resources. Coal, for example is a carbonaceous rock that consists of the altered (due to increased pressure and temperature) remains of trees and other plant material.

2.4.1.1 The Origin of Sedimentary Rocks

Sedimentary rocks are subjected to modification by a number of processes. Weathering is the first of these processes. It produces the materials that a sedimentary rock is composed of through physical (freezing, thawing) and chemical processes (dissolution of minerals, formation of new minerals, clays) occurring between the atmosphere, hydrosphere and earth surface rocks. The second process is transportation, which moves the materials to their present destination. During this process the sediment particles are transported by wind, water and gravity. They are then sorted by size and density and are smoothed through abrasion. The sorting which occurs during transport is important because it results in the conglomerates, sandstones and shale rock types. Deposition is the third process in the creation of sediments. It occurs in a setting (the sedimentary environment) that has a particular amalgamation of physical, chemical and biological circumstances. Finally, after the sediment has settled, compaction and cementation take place and a sedimentary rock

is formed. Compaction results from the weight of younger sediments that get piled on top of older sediments (rearrangement of particles, packing, dewatering). Minerals precipitated from the pore waters in these sediments cement together adjacent sediment grains, forming a coherent solid rock (Hawkes and Webb, 1962; Fergusson, 1990; Mitchell, cited in Bear, 1964).

2.4.1.2 Significance of Sedimentary Rocks

The common rock forming minerals may vary in their susceptibility to weathering and as a result, the forming of the first sedimentary rocks can be richer in secondary minerals and bioessential elements (Mitchell, cited in Bear, 1964). Clays and shales account for 70% of all sedimentary rocks and they are found to have considerably high concentrations of many elements due to their large specific surfaces with high cation exchange capacities (West, 1981). Other sedimentary rocks including sandstones and limestones have lower concentrations of metals (Table 2.2). In sandstones this is a result of being formed from more resistant igneous rocks and minerals, which possess a low concentration of most elements and very little capacity to absorb metals (West, 1981). A large variety of resources is extracted from sediments and sedimentary rocks, for example most of the iron ore in the world is mined from Precambrian sedimentary rocks, the largest lead-zinc-silver and copper deposits occur in sedimentary rocks (mostly Precambrian, especially Proterozoic), and the largest gold and uranium deposits also are located in sedimentary rocks as well (Archean to Proterozoic in age) (Mitchell, cited in Bear, 1964). Bauxite, the main ore for aluminium production is basically a fossil soil (also a sediment) that formed in tropical climates (Hawkes and Webb, 1962; Fergusson, 1990).

2.4.2 Weathering processes in soils

Weathering is the disintegration and decomposition of rocks through the exposure to the earth's atmosphere (Oliver, 1973). The contact of certain rocks and minerals with the atmosphere changes their equilibrium and makes them vulnerable to erosion. Landform evolution is therefore based to a major extent, on the denudation processes. Weathering combines the processes of destruction and synthesis. Figure 2.1 shows the pathways that occur under moderately acid conditions in humid temperate regions.

The weathering processes are complex because of the clear multitude of causative factors, and isolated because of the apparent dominance of chemistry over physics and of the subordination of gravitational forces to intermolecular ones (Oliver, 1973). It should also be noted however, that although three types of weathering are described, (physical, chemical and biochemical), in most cases, rock disintegration is the result of a complex interaction of all three processes.

Table 2.2 Typical concentrations of some heavy metals in sedimentary rocks (mg/kg).

Element	Sedimentary rocks		
	Limestone	Sandstone	Shales/clays
Ag	0.12	0.25	0.07
As	1	1	13 (<900)
Au	0.002	0.003	0.0025
Cd	0.028	0.05	0.22 (<24)
Cr	11	35	90 (<500)
Cu	5.5	30	39
Fe	15000	-	48000
Hg	0.16	0.29	0.18
Mg	26000	-	16000
Mn	620	460	850
Ni	7	9	68
Pb	5.7	10	23
Zn	20	30	120

Source: adapted from Alloway (1995) and Wedepohl (1991).

No chemical weathering takes place without a certain amount of physical stress, and the disintegration of rocks by thermal expansion does not occur without the chemical processes associated with the presence of water (Oliver, 1973). Also, in the presence of the sparsest vegetation, chemical weathering is replaced in part by biochemical processes (Oliver, 1973). Mechanical or physical weathering results from the molecular stresses imposed upon the material exposed at the surface. Strahler (1973), cited in Oliver (1973), states that the surface modification process can be considered in terms of the response of surface materials to both gravitational and molecular stresses. Types of mechanical weathering include frost shattering, or freeze-thaw process. The temperature range alternates around 0°C, causing the contraction and

expansion within the crevices and joints in the rocks. Salt crystallisation, pressure release, thermal expansion and insolation weathering, all come under the heading of mechanical weathering.

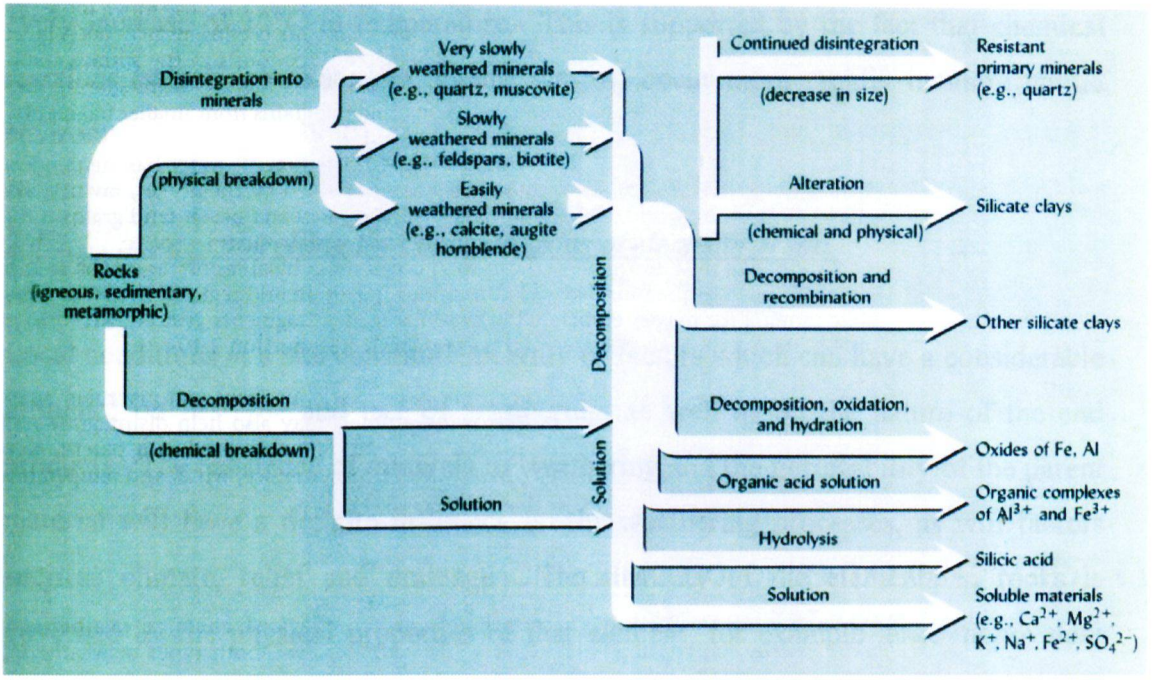

Figure 2.1 Weathering processes in soils.

Source: adapted from Brady and Weil (1999)

These types of weathering depend mostly on the temperature fluctuations around freezing point, they will not occur if the temperature is too cold or too warm, and similarly, if it is too dry (no moisture to freeze) or too wet. Biochemical weathering takes place when organic material which is both growing and/or decaying through the influence of flora or micro fauna, produces an elaborate set of biochemical processes which can considerably increase weathering rates. Chelation and cation root exchanges are examples of this type of weathering (Chorley, 1984). Another weathering process occurs when roots of plants or trees grow along the joints or bedding plain and widen the cracks, sometimes causing pieces of rock to fall off. Similarly, the burrowing of animals can have the same effect.

Chemical weathering is the process, which has received most attention in literature, as it is of major importance in the surface modification of a landscape. Oliver (1973) describes it as the modification of minerals to meet a condition of equilibrium in relation to prevailing atmospheric conditions. The rate at which chemical weathering

occurs depends upon the prevailing temperature conditions. Therefore, the chemical condition, which occurs within a given location, is dependent on the climatic conditions in that area. Chemical weathering increases as temperatures and rainfall totals increase. It has been stated that the rate of chemical weathering doubles with every increase of 10°C in temperature. This is supported by the fact that chemical reactions (which are related to organic wastes) occur more rapidly in more humid environments (Peltier, 1950).

2.4.2.1 Factors controlling the concentrations of elements in soil.

Local conditions at a site constitute an array of factors which can have a considerable influence on the type and rate of weathering, as well as on the nature of the end products. The resistance of minerals to weathering and the permeability of the parent material will have a definite influence on the weathering processes, as will factors such as climate, relief and drainage. The mobility of the elements in rocks is governed by the physical properties of that element, for example large monovalent elements are more mobile than elements with small radii because the latter attract a large hydration ring and are less able to fit onto adsorption sites (Hawkes and Webb, 1962). The larger cations are found to be the most mobile elements weathered from the parent material. Hawkes and Webb (1962) list the decreasing mobility of major elements in the following order Mg>Ca>Na>K>Si>Al=Fe and trace elements decreasing in the order Mn>Ni>Ti>Cr>V. Elements such as Li, Fe, Mn, P and S are mobilised in the soil once dissociated from the primary mineralogy and form part of major soil forming constituents (Deer *et al.*, 1992).

Contents of the major elements Na, K, Mg, Ca, P and S in soil are based on the original concentration of the parent material. Sodium, Mg and P are soluble and mobile in oxidising conditions. Magnesium is associated with clays and oxides. Calcium concentrations in soil are influenced by carbonate formation and rainfall. Calcium rich aluminosilicates weather in acid oxidising conditions and have a major influence on soil pH. Cations and metal ions are incorporated into the structure of secondary carbonates forming complex textures (Hawkes and Webb, 1962; Kabata-Pendias and Pendias, 2001; Deer *et al.*, 1992; Alloway, 1995 and Adriano, 2001).

The content of the trace elements La, Ti, Be, Co, V, Li, Sr, Ba, Mn and Fe in the soil is governed by the solubility of the primary mineralogy. Trace elements commonly substitute for Fe and Mg in the silicate lattice and become associated with the ferromagnesian minerals (silicates high in Fe and Mg such as olivine, pyroxene augite, hornblende and biotite), whilst other trace elements are associated with Ca and K (Alloway, 1995). Titanium and La are resistant to weathering and not mobile in soil, the content of these elements in soil is derived from the parent material. Beryllium is relatively immobile in soil and its concentration is correlated to the clay content of the soils. Cobalt is fairly immobile and is associated with secondary Fe and Mn oxides. The concentration of V is associated with the parent material as well as with oxides in the soil forming processes. Lithium is very mobile in oxidising acid conditions becoming associated with clay minerals (Alloway, 1995). Strontium is generally mobile and is associated with the secondary carbonate phase, clays and organic matter. Barium is found in K rich rocks feldspars and mica, is easily weathered and mobile in soils and is associated with clay and Fe-Mn oxides (Kabata-Pendias and Pendias, 2001; Deer *et al.*, 1992 and Adriano, 2001). The content of Fe in soil is partitioned into primary minerals, clay minerals, organic compounds and Fe oxides. Iron oxides are products of weathering and are an important phase in the complexation of trace metals and other cations because Fe and Mn oxides have a high sorption capacity for trace elements (Alloway, 1995).

The content of the heavy metals Cr, Ni, Cu, Zn, Cd, Pb and As in soil is the result of the *combined* effects from the underling parent material, the redistribution within the soil profile and associations made within the soil phase, as well as inputs from anthropogenic sources. Chromium concentrations are high in soils formed over shales and clays. Chromium is fairly resistant to weathering but when dissolved, it becomes strongly associated with Fe oxides (Alloway, 1995). The content of nickel in soil depends very much on the nature of the parent material. The most important factor determining the distribution of Ni between the soil solid and solutions phases appears to be pH, while factors such as clay content and the amount of Fe and Mn oxides in the soil are of secondary importance (McGrath, 1996). Copper is one of the most essential elements for animals and plants. It is relatively immobile in soil because of its association with soil organic matter, Fe and Mn oxides, soil silicate clays and other minerals (Alloway, 1995).

Total Zn content of soils is largely dependent on the composition of the parent material. In oxidising acid conditions Zn is mobile and associated with oxides and hydroxides in acid soil and organic mater in alkaline soil (Kiekens, cited in Alloway, 1995). Cadmium shows an almost universal association with Zn, with a Zn/Cd ratio that does not deviate by much more than a factor of 2 from an average of 500 to 1 in igneous, metamorphic and sedimentary rocks (Hawkes and Webb, 1962). It is very mobile in oxidising acid conditions. Cadmium mobility is influenced by pH and it tends to be more mobile in soils and thereby more available to plants than other heavy metals. Adsorption mechanisms are very important in the dynamics of Cd in soils. Alloway (1995) has shown that soils containing free $CaCO_3$ can sorb Cd and reduce its bioavailability. It was found that calcite had a high affinity for Cd and gave a linear isotherm at low Cd concentrations (Alloway, 1995). Lead has a strong tendency to be adsorbed on to particles of clay or organic matter, and in this form is largely immobile and biologically inert (Thornton *et al.*, 2001). The main compartments for Pb in soil are the soil solution, the adsorption sites of the clay-humus exchange complex, precipitated forms, secondary Fe and Mn oxides and alkaline earth carbonates, the soil humus and silicate lattices. The sum of the total exchangeable cations that a soil can absorb is referred to as cation exchange capacity (CEC) (Brady, 1999). pH and CEC are believed to be the main soil properties involved in the immobilisation of Pb and soil organic matter is more important in this process than precipitation as the carbonate or sorption by hydrous oxides (Davies, 1994). Arsenic has often been used as an indicator element during mineral prospecting to identify mineral deposits. It is a good indicator because of its association with a wide variety of mineral deposits (Alloway, 1995). In oxidising environments, the mobility of As is controlled by the co-precipitation with Fe oxides, whilst in Fe poor or partially reducing environments, As can be relatively mobile, as suggested by high average content in water relative to rock (Hawkes and Webb, 1962).

2.4.3 Formation of Soils

Soils are responsible for a variety of functions, the most important of which are as a medium for plant growth, a foundation for buildings and a source and sink for water and pollutants (Bullock and Gregory, 1991). Soil is the ultimate and most important

sink for trace elements in the terrestrial environment. It is the end product of weathering. Water percolating through the soil particles causes dissolved material and colloidal particles to be carried from one layer to another. The attributes of the parent material that influence soil formation are the same as those that control rock weathering, i.e. texture, porosity, drainage and mineral composition. The significance of temperature and rainfall are of the utmost importance in the formation of soils. The biological factor in soil formation is mainly a function of vegetation plus the activity of micro-organisms in decomposing plant debris, which is in turn related to climate (Alloway, 1995). Topographic relief influences soil formation through its relationship with groundwater levels, drainage and erosion. The angle of the slope affects drainage and erosion. Erosion occurs at a faster rate on steep slopes, as there is a greater level of runoff and less percolation than on gentler ones (Oliver, 1973).

2.4.4 Chemical equilibria in surface environments

Heavy metal pollution can and does affect all environmental media, but its effects are most long lasting in soils because of the relatively strong absorption of many metals onto the humic and clay colloids in soils. For example, Cd has a half-life of 15-1100 years and Pb has a half-life of 740-5900 years (Alloway, 1999). Half-life is the time necessary to decrease the quantity of a substance to half the original amount (Merian, 1991). It is assumed that there is a dynamic equilibrium between the species in the soil solution and the solid phase (Davies,1994). The soil properties will display a major influence on the behaviour of contaminants within the soils. All soils contain humic material, which has a high but pH dependent cation exchange capacity (CEC) as well as a strong sorptive capacity for various contaminants including heavy metals. Soil organic matter can sequester metals by complexation, especially chelation, because of large numbers of functional groups on the macromolecules (Alloway, 1999).

The oxides of Fe, Al and Mn play an important role in the chemical behaviour of soils. Iron and Mn oxides co-precipitate and adsorb cations including Co, Cr, Cu, Mn, Mo, Ni, and Zn, and anions such as As from solution. Additionally, the varied chemistry and toxicity of various metal species (e.g. As) mean that total metal concentrations as have been mostly used in this study may not always give a true

representation of the chemically and biologically active concentrations in soils. The toxic effects of a metal are determined both by the chemical form and by the concentration. Within the soil profile, As, Cd, Cu, Pb and Zn are found concentrated in the surface horizons as a result of cycling through vegetation, atmospheric deposition and adsorption by the soil organic matter. Elements found concentrated in the lower surface horizons include Fe, Mg, and Zn, which tend to be associated with accumulations of clays and hydrous oxides. These factors will affect the analysis of the concentrations of metals in the study as the sampling was taken of top soils only and the depth and extent of the different soil horizons is unknown. Another point to consider is that recently polluted soils often have higher contents of metal pollutants in the topsoil from atmospheric inputs, as the pedogenic processes have not been operating long enough to effect the redistribution within the soil profile.

Metals in soils exist largely as cations although some elements such as As, P and Mo, exist as anions. CEC is the sum total of exchangeable cations that a soil can absorb. CEC of a soil is found to increase with a rise in pH. In this process, ions are exchanged between the soil solution and the (negatively) charged colloid surface (West, 1981). Anion exchange however involves the retention of anions on positively charged surface sites at pH values below 7 and through "ligand exchange" (a surface complex forms between an anion and a metal). Soil pH is a measurement of the concentration of H^+ ions in the soil solution. It is a major factor controlling the behaviour of ionic contaminants in soils (Table 2.3).

Soils under natural conditions may contain concentrations of certain metals at phytotoxic levels. For example saline soils possess sufficient levels of chloride salts of Na, Ca, Mg to depress the growth of sensitive plants (Thornton, 1983). Serpentine soils also contain elevated concentrations of certain elements (Alloway, 1995). Calcite ($CaCO_3$) is a major soil constituent in soils developed on limestones in humid areas. It buffers the soil to a pH value usually between 7-8.5 and also contributes to the sorptive properties of soils by chemisorption and precipitation of metal carbonates (Alloway, 1999).

Table 2.3 Relative mobilities of major and trace elements as a function of pH.

Relative mobilities	Acid	Neutral to alkaline
Very high	Cl, I, Br, S, B	Cl, I, Br, S B, Mo, V, U, Se, Re
High	Mo, V, U, Se, Ca, Mg, F, Sr, Ra, Zn, Cu, Co, Ni, Hg, Ag, Au	Ca, Na, Mg, F, Sr, Ra
Medium	As, Cd	As, Cd
Low	Si, P, K, Pb, Li, Rb, Ba, Be, Bi, Sb, Ge, Cs, Tl	Si, P,K, Pb, Li, Rb, Ba, Be, Bi, Sb, Ge, Cs, Tl
Very low to immobile	Al, Ti, Sn, Nb, Ta, Pt, Cr, Zr, Th	Al, Ti, Sn, Te, W, Nb, Ta, Pt, Cr, Sr, Th, Cu, Co, Ni, Hg, Ag, Au

Source: adapted from Plant and Raiswell, in Thornton (1983).

The pedogenic processes which occur in soils, result in the mobilisation and redistribution of trace elements within the soil profile. These processes exert a major influence on the uptake of elements by plants. As stated above, most trace elements exist mainly as cations in the soil solution, and their adsorption depends on the density of the negative charges on the surfaces of the soil colloids including clay, organic particles and hydrous oxides (Alloway, 1995). An interchange between cations on the surface of these active materials and the soil solution occurs by the process of cation exchange. Humic colloids have the greatest CEC; the CEC of hydrous oxides is the lowest with clay minerals being intermediates (Brady, 1999).

Specific adsorption involves the exchange of trace element cations and most anions with surface ligands to form partly covalent bonds with lattice ions (Alloway, 1991). It is strongly pH dependent and is related to the hydrolysis of trace metals. The hydrous oxides of Al, Mn and Fe are thought to be the main soil constituents involved in the specific adsorption reaction (Alloway, 1991). Co-precipitation is defined as the simultaneous precipitation of a chemical agent in conjunction with other elements by any mechanism and at any rate (Thornton, 1983). Organic complexation is a chelate complex formation between trace metals and organic matter in soils (Alloway, 1995). As chemical weathering takes place in soils, primary minerals dissolve and their chemical components subsequently can precipitate in secondary minerals and form complexes with inorganic and organic surfaces, for example Fe and Mn oxides and clay minerals (Thornton, 1983). Anthropogenic activities, such as agricultural treatment of the soil, mining and smelting as well as atmospheric deposition from

automobile emissions can have an effect on the distribution of trace elements in the soil profile (Alloway, 1995).

Soils are dynamic systems, transforming and evolving as environmental conditions change. The total content of an element is considered of little practical significance since only a small portion is available for plant uptake (Davies,1994). The physical and chemical form of the metal will determine metal mobility and thermodynamic stability in soils. The surface environment is an open system (Raiswell *et al.*, 1980) made up of different compartments, which are air, water, sediment, soil, and soil solution, dust and biological material. Transfer into different compartments is dependent on the speciation of the metal and the transport mechanisms. Solubility is a particularly important property as water is a significant medium of solvent, carrier and catalyst (Raiswell *et al.*, 1980). The partitioning of chemicals from the solid to fluid state is a significant factor for the availability of a metal (Rieuwerts *et al.*, 1998). Theoretically, elements attempt to reach chemical equilibrium, and computer-modelling packages such as GEOCHEM can help determine the speciation of elements. However, equilibrium is rarely achieved in natural open systems (Thornton, 1983; Crosby, 1998), particularly as the residence time for metals in urban compartments is short. Atmospheric particulates are rapidly deposited with a residence time of hours or days. Street and house dust have an intermediate residence time of days, weeks or months; urban soils have a longer residence time of up to thousands of years (Alloway and Ayres, 1997).

The different ways in which metals bind to soils and how this process is influenced by the different plant types, soil and environmental conditions is of great importance in the assessment of potential pollution (Alloway, 1995). Tessier (1979) states that metals in soils can be present in various physicochemical phases that act as sinks for that element in the environment. The form of a trace metal in soil has been identified as one of the most important properties in determining the solubility, mobility and availability of metals to humans and the wider environment. The phases as described by Tessier (1979) are:

1) Soluble: the metals are present as free ions, or as soluble complexes with inorganic or organic ligands in the soil solution.

2) Exchangeable: the metals are held by predominantly electrostatic forces in negatively charged sites on clays, other minerals or organic matter. Exchangeable cations are isotopically exchangeable and may also be displaced by the essential cations commonly present in the soil solution.

3) Specific adsorption: the metals are held at sites on which the trace elements are strongly bound by predominantly covalent or coordinate forces. Ions held in this way are taken up and released at a slower pace than exchangeable ions and are more easily displaced by other trace metals and hydro ions than by basic cations.

4) Occluded in oxides of iron, aluminium and manganese: these oxides are rarely pure; they usually contain cations from each other and probably trace metal cations as well. These oxides have been distinguished as "easily", "moderately", or "difficulty" reducible according to the reagents that dissolve them. The ease of the release occluded trace metal cations is thought to depend on the solubility of the oxides that contain them.

5) Organically bound: the metals are held in insoluble organic materials. This category includes trace metal cations in, or immobilised on living or recently dead cells, but consists mainly of cations complexed or chelated by organic materials, either recently synthesized or the resistant residues from microbial metabolism. This group includes both specific and non-specific sites.

6) Secondary minerals: this group includes carbonates, sulphates, phosphates hydroxides etc, but are often not specified. These precipitates may be newly formed compounds, they may contain more than one trace metal and often form mixed crystals or a mixture of crystals with the corresponding salts of major elements, usually calcium or iron.

7) Primary minerals: metals are held in a crystal lattice of primary, non-oxide minerals. This group includes sites of the crystal lattice within a mineral. They can be the lattice position of trace element mineral itself, but more often is a substitute lattice within the primary mineral of the major elements.

2.5 Urban soils

Bullock and Gregory (1991) define urban soil as "soil having a non-agricultural, man-made surface layer more than 50 cm thick, which has been produced by mixing, filling, or by contamination of the land surface in urban and suburban areas".

The chemistry of urban soils had initially, largely been neglected compared to their counterparts in rural environments (Thornton, 1993). The last decade has seen however, a rapid increase in the research carried out into soils in the urban environment. Urban geochemistry is concerned with the identification of metal sources in towns and cities and the degree to which they mask or change natural geochemical signatures in the surface environment (Kelly *et al.*, 1996). The urban environment is affected by a wide variety of anthropogenic activities; road networks, housing and metal processing, and manufacturing industries will tend to increase the heavy metal content of soils (Kelly *et al.*, 1996). In urban soils the effects of the geological parent material and pedogenic processes are overshadowed by the anthropogenic input and disruption from industrial and urban activity. It is the latter which exert the most influence on the distribution of trace metals. The history of an urban region can and usually does include a series of land use changes, including natural resource exploitation, industrial activities, post war housing, the addition of made ground and transportation of fill material (Thornton, 1993). When the effects of present day urbanisation are added to this, the resultant impact on local soils can be critical in terms of contamination with heavy metals from a variety of sources. Previous soil surveys have designated urban soils as "built-up" (Hollis, 1991 in Bullock and Gregory, 1991). Various soils types are found within urban areas, ranging from relatively undisturbed soils, similar in some respects to their rural counterparts (Hollis, cited in Bullock and Gregory, 1991), to man-made soils (Kelly, 1997), often referred to as "made ground".

2.5.1 Anthropogenic inputs of metals into soils

As previously stated, metals are present as natural components in all environmental media. It is the transfer of metals to the inhabited environment from industrial activities that has aroused the interest of scientists, stimulated the emotions of the

public and attracted the attention of politicians and regulatory agencies. Anthropogenic inputs of metals are varied and range from metal related industries to agriculture and waste disposal, in short, the everyday activities of man (Thornton, 1995). Table 2.4 below shows some of the sources of heavy metals found in the urban environment.

Anthropogenic emissions can be classed into point and diffuse sources. An example of a diffuse source is fly ash. Fly ash usually amounts to 70% of total ash residue produced in power plants. Chemical and physical characteristics of fly ash are key factors which determine the potential for metal pollution of soils that receive those wastes (Thornton, 1983). Table 2.5 shows the range of metal concentrations in fly ash and soils. Fly ash is deposited in landfill sites, but soils or dusts are often contaminated (on route) from fly ash sources. Hutton *et al.* (1988) reported a 90% reduction of volume in refuse after combustion with no significant increase in Cd or Pb in soils, dust or vegetation, which were adjacent to an incinerator. However, Mitchell *et al.* (1992) found heavy metal concentrations in fly ash from solid waste incinerators to be elevated when compared to values for UK soils. The median value for Pb in UK soils was reported as 40 mg/kg $^{-1}$, and 4337 mg/kg $^{-1}$ in municipal solid waste (MSW) fly ash. Cadmium has a soil median value of 1.21 mg/kg $^{-1}$ and an ash median value of 1372 mg/kg $^{-1}$. Similarly, the Cu values were 18.1 mg/kg^{-1} and 642 mg/kg^{-1} respectively.

Transport is a major source for pollution. Soils adjacent to roads show increased lead concentrations, the source being leaded petrol. Lead in soil is virtually immobile and such contamination is very long lasting (Thornton, 1995). The monitoring of element concentrations in road dust reflects the increase and successive decline of lead additives to petrol.

Wang *et al.* (1997) in a study between 1984 and 1996 in Birmingham, of road dust, house dust and garden soil, shows a decrease in Pb in road dust from 805 mg/kg to 494 mg/kg, house dust from 445 mg/kg to 232 mg/kg and garden soil from 405 mg/kg to 360 mg/kg. This is attributed to decreases in lead emissions from industrial processes and anti-knock petrol additions. The effects of vehicle emissions are prevalent. Particles from vehicle emissions make up a large component of lead in

urban dust, sediments and soils near to a main road (Yassoglou *et al.*, 1987; Nriagu, 1990; Thornton, 1995 and Sutherland, 2000).

Table 2.4 Sources of elements that may contaminate soils.

Source	Particular Elements
Primary sources	
Fertilisers (e.g. Phosphates)	Cd, Pb, As
Irrigation	Cd, Pb, Se
Lime	As, Pb
Manure	As, Se, Cu
Pesticides	Pb, As, Hg, Cu
Secondary sources	
Rubbish disposal *	Pb, Cd, As
Automobile aerosols *	Pb, Ba
Tyre Wear *	Cd
Refuse incinerators *	Pb, Cd, Hg
Coal combustion **	As, Se, Sb, Pb, Hg
Mining Areas	Pb, Cd, As, Hg
Smelters **	Pb, Cd, Sb, As, In, Hg
Paint (weathered) *	Pb, Cd, Ti
Marine	Sn
Long range aerosol	Pb, As, Cd,
Chloralkali cell	Hg, Cl

* = these sources can be found in Gibraltar. ** = these sources can be found in and around the industrial complex in neighbouring Spain (refer to section 3.7)

Source: Fergusson (1990), Alloway (1995). (* not part of data from Fergusson and Alloway).

The influence of a road is evident. Yassoglou *et al.* (1987) and Sutherland (2000) noted in topsoil samples that Pb concentration (0-5 cm) is inversely proportional to the distance from the road, with Pb concentrations falling to background values at around 50 m. The concentration of traffic and the intensity of the prevailing winds will affect the concentrations of Pb adjacent to the road and how they decrease with distance from the highway (Thornton, 1995). Another factor is the size of the particles released; particles greater than 9 microns travel up to 5 m from the road side, whereas particles smaller than 1 micron can go up to 100 m from the road side (Sutherland, 2000).

Similarly, enhanced levels of metals such as Pb, Zn, Cu, Cd, Ni, As, Al, and Se are reported in soils, which are in the vicinity of smelters (Thornton, 1983). Urban soils contain higher concentrations of metals than rural soils, in part as a result of close proximity to traffic and industrial activities. However, every day activities also lead

to increased metal concentrations in soils. Metals are present in domestic refuse in varying concentrations. This refuse is disposed of in landfills or municipal incinerators. Landfills are now carefully controlled but older landfill leachates still pose serious problems to soil and groundwater contamination. In incinerators where there is no separation of material at source, atmospheric dispersion of Cd, Pb and other metals has been recorded (Thornton, 1995).

Table 2.5 Range of some metal concentrations (mg/kg) in fly ash and soils.

Metal	Fly ash	Soils
As	2-6300	0.1-40
Al	1000-173 000	10 000-3000 000
Ca	1100-220 000	700-500 000
Cd	0.7-130	0.01-2
Cr	10-1000	5-1500
Cu	14-2800	2-250
Fe	10 000-290 000	2000 550 000
Mg	400-76 000	400-9000
Mn	58-3000	20-10 000
Ni	6-4300	2-750
Pb	3-5000	2-300
Zn	10-3500	1-900

Source: adapted from Thornton (1983)

2.5.2 Trace metals in the urban environment

The urban environment is affected by a wide variety of anthropogenic activities, which usually tend to increase metal concentrations in soils (Kelly *et al.*, 1996). Table 2.6 below illustrates the common uses of metals, which may in turn lead to soil contamination. The main input of metals in urban soils are from vehicle exhausts, industrial emissions, paint, bonfires, fossil fuel burning and the historic activity from factories, gas works and scrap metal yards (Thornton, 1995).

A great deal of attention is increasingly being focused on understanding the chemical nature of the urban environment. The knowledge gained from the behaviour of chemicals in rural soils may not always be applicable to the disturbed nature of urban

soils. The presence of rubble and concrete may well modify the chemical and physical processes operating in the rural environment (Thornton, 1993).

Table 2.6 Examples of common uses of selected metals.

Metals	Uses
Al	Engineering (aeroplane component) and packaging of foods and drinks
As	Insecticide, wood products, preservatives, ceramic and glass, lead and copper alloys
Cd	Metallurgical alloys, ceramics, solders, Ni-Cd batteries, corrosion-inhibiting coatings
Cr	Alloys particularly stainless steel, refractory bricks, tanning leather, pigments, wood preservatives, photography, leaded petrol and plating of car parts
Cu	Wire and cable, plumbing tube, roofing, brass and bronze alloys, electronics, disinfectants, ammunitions, dental alloys, coinage, printing inks and dyes, guttering
Pb	Electric storage batteries, roofing, guttering, electroplating, ammunition, petrol, rubber, paint pigments, pipe work, porcelain glazing, flashing, water distribution
Mn	Paint formulation, steel alloys, non-ferrous metal alloys
Mg	Used in Al alloys and ad additive to fertilisers and feed
Ni	Pickling, plating, steel and cutting tool alloys, medical prosthesis, Ni-Cd batteries, jewellery, electrical goods, household appliances and tableware, coinage
Zn	Brass, bronze and die-casting alloys, pulp and newsprint production, inorganic pigments, dye and glue manufacture, pharmaceuticals

Uses listed in blue can be found in Gibraltar.
Source: adapted from Alloway (1995) and Thornton (1995).

Metals such as Pb, Cd, Ni, Zn and Cu are used in small quantities in a wide variety of products (Scoullos *et al.*, 2001). Alexandrovskaya and Alexandrovskiy (2000) describes the top 20 m of unconsolidated material in Moscow as the "cultural layer", which provides an artefact recording historical and ecological events as well as archaeological features. The heterogeneity of the urban environment presents a challenge when approximating the source and dispersion of metals.

The manufacture of Pb rich components in batteries and paint products are important sources of Pb input into urban soils. Even though the Pb input from vehicle exhausts has declined considerably in the last 20 years, this is still an important source of Pb in soil due to long historical accumulation. Localised sources of Pb include ammunition, rifle ranges, paint chips, discarded batteries, primary and secondary smelters as well as dust from scrap yards, garages and breakers yards (Davies, 1994; West *et al.*, 1999; Thornton, 1993; 1995). Cadmium in urban soils comes from sources such as

electroplating, scrap yards, the manufacture of paints, pigments and dyes and the production and Cd cells (Alloway, 1995; West *et al.*, 1999; Thornton, 1993). Zinc originates from electroplating, the manufacture of electrical components and pigments for paint and dyes. It is also used in the chemical industry as stabilisers in plastics (Alloway, 1995; Kiekens, cited in Alloway, 1995; West *et al.*, 1999). One of the main sources of Cu in the urban environment is in the manufacture and uses of Cu wire, brass and bronze, galvanising and metal plating, production of high tension electricity cables, electrical components and batteries (West *et al.*, 1999). Nickel is used in manufacture of stainless steel, metal finishing, electroplating, galvanizing and Ni-steel alloys. It is also, used in vehicle components, aircraft and armaments as well as electronic components (Alloway, 1995; West *et al.*, 1999). Other sources of Ni include pharmaceuticals, catalyst components, Ni-Cd batteries and the combustion of diesel exhausts (McGrath, 1996). Arsenic is found in fine chemical works, glass manufacture, iron and steel production and coal combustion (Alloway, 1995). Chromium is used for electroplating in the leather tanning industry, in paints pigments and dyes in corrosion inhibitors and is found in components of motor vehicles, and break pads (McGrath, 1996; West *et al.*, 1999).

Kelly (1997) assessed the influence of geology and anthropogenic activity on the geochemistry of urban soils. He compared Richmond, a residential area of greater London with Wolverhampton, a city in the Midlands that has a long industrial history. Topsoils in Richmond displayed higher concentrations of Pb and other heavy metals in developed locations, in comparison to areas of parkland and open space. Analysis of soils in Wolverhampton showed concentrations of Pb, Cd, Zn and Fe to be higher in the vicinity of old industrial sites than in the agricultural land in the outskirts of the city (Thornton, 1998).

Trace metal contents in urban soil can vary significantly, but they have been found to portray a clear reflection of land use and industrial production (Birke and Rauch, 2000). For example, soil and dust samples are elevated in metal concentrations in areas of former or present industrial activity, roads with high traffic density and areas adjacent to incinerators and scrap yards (Gibson and Farmer, 1986; Yim and Nau, 1987; Ho and Tai, 1988; Chon *et al.*, 1995; Kelly *et al.*, 1996; Li *et al.*, 2001). The type of urban land use and industrial location geographically "controls" the

concentration and spatial distribution of metals in urban soils (Mielke, 1991; Birke and Rauch, 2000). However some trends have been identified. Studies carried out in London and Birmingham show the concentration of Pb to decrease exponentially with distance from the city centre (Davies *et al.*, 1987a). Studies carried out by Mielke (1991) in the cities of Baltimore, Minnesota, Minneapolis, St Paul and New Orleans, in the US, show that Pb in soils was found to be a function of city size; that is to say, higher values were found in the larger cities clustered in the centre of the town. This was attributed to higher density of roads and traffic.

As stated above, metal distribution in cities is frequently a function of geographic influence. In central London, urban dust was found to be elevated in Cu, Zn, Pb, Cd and Fe in contemporary and historic industrial areas along the Lee Valley and the River Thames in the east of the city, with minor industrial activity making a local influence (Schwar *et al.*, 1988). However, the Cd and Pb concentrations in the area surrounding a refuse incinerator stack in north London were not found to be elevated, which was attributed to the 100 m high stack dispersing emissions, within a greater radius. An elevated concentration of Cd inside the grounds of the incinerator was reported however, and this was attributed to the storage and transportation of fly ash (Hutton *et al.*, 1988). Farago *et al.* (1998) noted an increase in trace metal concentrations in surface soil and also in house dust close to a secondary lead smelter in Landskrona, Sweden. The pattern of metal dispersal was influenced by the prevailing wind. This meant that the concentrations of Pb in the soil fell to background values at 3.5 km from the stack. Rieuwerts (1996) detected an increase in the levels of Pb in areas near a metal mining and smelting area near the town of Pribram, in the Czech Republic. Total lead concentrations decreased with distance from the lead smelter.

The case studies discussed in this chapter all show that the spatial distribution of heavy metal concentrations in urban soils is influenced by a combination of factors including geology, industrial land use (past and present), transportation routes and urban regeneration. These factors must be taken into account in future planning development (Thornton, 1998). Increasingly, as a result of the increased and improved environmental regulations at an international level, (e.g. EU Directives) current research aims to make comparisons between locations. It must be stated however,

that such studies need to take into account the sampling strategy, depth of sample, particle size and method of chemical analysis and quality control. There is an obvious need for harmonisation in the aspects considered for soil sampling if reproducible and comparable soil samples are to be obtained throughout the European Union (as well as on a wider international scale) for soil quality evaluation (Theocharpoulos, 2001). Additionally, although total metal concentration provide the first assessment of trace metal distribution, and extent of contamination, a total metal concentration does not represent the true degree of the hazard and only allows a superficial comparison between cities (Gibson and Farmer, 1986).

2.5.3 Metal concentrations in outdoor and indoor dusts

Topsoils and street dusts in urban areas indicate heavy metal contamination from atmospheric deposition. Recent investigations have provided evidence of elevated metal concentrations in urban street dusts (Harrison *et al.*, 1989; Thornton, 1991). Heavy metals in dusts in the urban environment come from a variety of sources including traffic, vehicle emissions, industrial sources, building materials and even the weather, for example temperature and relative humidity can affect the chemistry of soils and dusts, thereby influencing the possible migration of elements between different environmental media. Additionally, rainfall can transport the contaminated dusts into the urban drainage system and consequently into sewage treatment works and rivers (Harrison *et al.*, 1989; Thornton, 1991). Cadmium, Cu, Pb and Zn are good indicators of pollution in dusts and soils because they are found in petrol, car components, oil lubricants, industrial and incinerator emissions (Alloway, 1995). Thornton (1991) states that the physical (and chemical) environment of cities is profoundly affected by almost every kind of human activity, from deliberate acts of construction, management or vandalism, to accidental or incidental pollution. The history of land use in urban areas is difficult to ascertain, for example major industrial sources from the last century may be masked by the presence of post world war II housing (Thornton, 1991).

High element values in street dusts as compared to roadside soils reflect the short-term contamination of dusts from sources such as vehicle exhaust emissions and component wearing of vehicles. As stated above, Cd, Cu, Pb and Zn appear in

gasoline, car components and oil lubricants (Li *et al.*, 2001). Zinc is used as a vulcanization agent in vehicle tyres (Alloway, 1995). Li *et al.* (2001) states that the higher wearing rate in a sub tropical environment may contribute to the high Zn concentrations found in street dusts.

Since the mid 1970s attention has focused on the possible health implications of long-term low-level exposure to heavy metals. The study of house dusts as an exposure pathway to children has been well documented. The concentration of trace metals in dust from urban homes can originate form both internal (within the home) and external (outside the home, e.g. garden) sources. Davies *et al.* (1987b) found the Pb concentration of house dust and garden soil in inner city properties from Birmingham, UK were correlated with the age of the property. House dusts in Hong Kong were also found to be higher in element concentrations taken in older buildings and neighbourhoods (Tong and Lam, 2000) whereas Cd, Cu Pb and Zn were elevated in soil from parks situated in older neighbourhoods in Hong Kong (Li *et al.*, 2001). In Ottawa, Canada house dusts were reported as having significantly higher concentrations of elements than street dust and garden soil. This is due to the low density of heavy industry causing internal contributions within the home to have a greater influence (Rasmussen *et al.*, 2001). In the UK house dusts were found to be higher in concentrations of heavy metals including Cu, Pb, and Zn than the associated soil and this was attributed to internal enrichment factors (Thornton, 1995).

The type of flooring and the frequency of when the floor was swept related to homes with lower metal concentration loadings. Additionally, factors such as if residents removed outside shoes at the entrance was also found to contribute to lower metal contents in the home (Farago *et al.*, 1999; Tong and Lam, 2000). Fergusson and Kim (1991) found that elements concentrations in house dust samples were influenced by the colours in the carpets, galvanised iron roofs and age of the properties. The proximity to busy roads increased Cu and Pb concentrations and house age, a fireplace and the colour of paint influenced Pb concentration in the house dust. Similarly, Tong and Lam (2000) found Cd, Cu, Pb and Zn to be higher in homes with yellow internal paint and Cu in homes with green internal paint.

2.6 Introduction to applied geochemical methods

Spatial information on the distribution of metals in the terrestrial environment on both a regional and a national scale has been compiled through geochemical mapping and the publication of geochemical atlases. Geochemical maps and atlases provide a useful time-dependent catalogue of baseline data showing the "natural distribution" of chemical elements, including metals relating to the composition of rocks and soils, and patterns of metal enhancement relating to mineralization, as well as anomalous patterns due to contamination. Such information is extremely useful when assessing the degree and extent of environmental pollution arising form anthropogenic activities. They also provide primary reconnaissance data indicating areas in which nutritional deficiencies are likely to be found in agricultural crops, livestock and wildlife (Thornton, 1993).

2.6.1 Geochemical mapping

Geochemical maps are based on systematic sampling and analysis of rocks, soils, as well as stream and lake sediments. Surface waters and/or vegetation were initially compiled for the purpose of mineral exploration (Hawkes and Webb, 1962). Geochemical mapping of metals in stream sediments and soils was widely used as a reliable tool for the detection of ore deposits in terrain with soil or vegetation cover (Hawkes and Webb, 1962; Plant *et al.*, 2001). The mobility, redistribution and leaching of metals during weathering processes, enables a pathfinder element, characteristic of an ore deposit, to be mapped. Samples taken from stream sediments reflect material entering the river from the entire catchments area (Hawkes and Webb, 1962; Webb and Howarth, 1979). Geochemical atlases for England, Wales and Scotland, based on the sampling of stream sediments, highlight several metalliferous provinces, the weathering of ore deposits are reflected by high concentration of trace metals in the stream sediment samples (Webb *et al.*, 1978; Institute of Geological Sciences 1978a, b; 1979; 1981; 1982). Professor John Webb at the Applied Geochemistry Research Group, Imperial College, developed the notion of multi-purpose geochemical surveys. His paper on "Geochemistry and Life" (Webb, 1964) pointed the way to extensive future studies in the development and application of geochemical maps to agriculture, pollution studies and human health (Thornton,

1993). In many natural systems, geological and geochemical features are continuous and therefore have a spatial correlation over short distances (Davies *et al.*, 1992).

Systematic mapping of element levels in soil or vegetation provides valuable information, which cannot always be obtained from normal geochemical maps. For example, published geological maps cannot be used as a basis for pinpointing localities in which problems occur relating to the relationships between an element such as Mo in rock, stream sediment and soil (Thornton, 1983). Similarly, the scale of the mapping, combined with the generalisation of the mapped formations without detail of internal changes in their lithology, poses additional problems to the geochemist (Howarth and Thornton, cited in Thornton, 1983). A geochemical database can be used to produce geochemical maps showing the distributions of elements. These maps are useful for mineral-resource assessments. They are also useful for identifying potential environmental hazards and specific health problems related to elevated concentrations of toxic elements, or inadequate concentrations of essential elements. A key component of multi-element maps is the ability to assess the distribution of elements on a regional scale and to define areas that require further investigation (Webb and Howarth, 1979).

The Wolfson Geochemical Atlas compiled at Imperial College, London indicated areas low in essential elements for crops and livestock and high in toxic metals that pose a threat to the health of plants, animals and humans (Howarth and Thornton, cited in Thornton, 1983). The town of Shipham, in Somerset was found to contain elevated levels of Zn, Pb and Cd in the area surrounding an old Zn mine. This area was identified through the Wolfson Atlas leading to a detailed report and environmental assessment of Cd (Alloway *et al.*, 1988). Further geochemical anomalies were identified by Howarth and Thornton, cited in Thornton (1983) through the use of regional geochemical maps. These areas included an area of elevated Pb and As in the old Derbyshire Pb mining areas and Sn-Cu-As from the mining provinces of South West England.

Geochemical backgrounds (concentrations of elements in natural materials that exclude human influence) and baselines (elemental concentrations, which may include human influence, measured at a specific time) can be determined using a

geochemical database. This type of information is essential for the decisions that have to be made about the environment (U.S. Geological Survey Technology Transfer Information Partnerships, 2000). Such databases constitute a baseline that provides a scientific basis by which to identify and assess global changes in the chemistry of the earth's surface. This is brought about by economic development, population growth and other causes, which could have detrimental impacts on the health of humans, animals, and vegetation (IUGS[1], 2000).

It is essential to have benchmark information on the chemical nature of the land at present and understand that the land is changing and may be rather different in 20 years time. If we fail to assess the present composition of the land on which we live, we cannot assess the impact of future events. We could be exposed to many different types of contamination, for example, another Chernobyl event (IUGS, 2000). An understanding of how such events could affect us, as well as having knowledge of the facts in order to question whether there is sufficient buffering capacity in the soil to absorb incoming contaminants without causing long-term damage, is of the utmost importance. The aim of a geochemical database is thus to provide environmental baseline data on the land surface environment. Such data have a range of environmental applications, some of which include: (IUGS, 2000):

- They identify areas where deficiencies or potentially toxic levels of chemical elements may be a risk to human health, to livestock or to crops;
- They provide quantitative information on natural levels of the chemical elements over different geological environments. These may be used to assess the effects of past, present and future human influence, particularly in terms of the critical loads that can be imposed on the land, without causing serious damage to its sustainability and productivity;
- They have an important contribution to make in land use planning issues.

The data can also be applied in mineral exploration, resource evaluation and the assessment of the impact of mineral exploitation, as well as in geological mapping and research into the fundamental processes of crustal evolution and ore formation (Thornton, 1983; 1993).

[1] International Union of Geological Sciences

The concept of multi-purpose geochemical surveys is now firmly accepted and their relevance to environmental issues plays an increasingly important role (Thornton, 1993). The uses of geochemical atlases to provide baseline geochemical data, and to focus attention on areas of appreciable metal pollution is another reason for the continuation of geochemical mapping at present and in the future. This would allow comparisons to be made between maps and would also provide valuable information to those concerned with the role of studies on environmental health and pollution (Thornton, 1993).

The growing demand in the past 20 years for more spatial data and better ways for researchers to analyse these data can only be accomplished through the use of computers. Stereo aerial photography and remotely sensed imagery have enabled large areas to be mapped with great accuracy. Before computer-mapping tools were available, the main "limitations" on paper maps were the loss of detail for classification of such data. This in turn reduced the volume of information, and the fact that the printed map is a static, qualitative document, making it extremely difficult to attempt quantitative spatial analysis within the units delineated on a thematic map (Howarth and Thornton, cited in Thornton, 1983). The use of computers for mapping and spatial analysis shows that there have been equivalent developments in automated data capture, data analyses and presentation in several broadly related fields. This has in turn resulted in the emergence of the general purpose GIS.

Most of the environmental problems being encountered have a spatial dimension. Geography concerns itself with the Earth's surface and its spatial parts (topography) in their entirety, in other words, the affiliation of phenomena with space. More importantly, geography is part of our everyday world; almost every decision we make is constrained or influenced or dictated by some fact of geography. Ambulances and fire engines are sent to their destinations via the fastest route. Similarly, central government grants are often awarded to local governments based on population, and diseases and contamination are studied by identifying areas of prevalence and rate of spread (ESRI, 1990).

Geographical Information Systems are designed as tools, which allow us to capture, manipulate, process and display spatial, or georeferenced data. They contain both geometry data (coordinates and topological information) and attribute data (information describing properties of spatial objects such as points, lines and polygons) (Fedra, 1994). GIS is basically a "toolbox" of spatial processing functions that is used for data manipulation. Many computer programs (e.g., Stata, SAS, SPSS, Minitab), or drafting packages (e.g. AutoCad) can handle simple geographic or spatial data. Why, then, are they not usually thought of as a GIS? The reason is that a GIS integrates *spatial* and other types of information, it provides a consistent analysis framework for geographically referenced data and provides new and insightful ways of *manipulating* and displaying data. It also allows viewing and *analyses of data* based on geographical proximity and relationships It combines primary (field data) with secondary data (maps, tables, other sources), (refer to chapter 4, sampling and analytical procedure).

A GIS database similar to the one that will be created for this project will include: (ESRI, 1990)

1. A data input subsystem, which allows the collection and/or processing of spatial data obtained from maps, remote sensors, etc;

2. A data storage and retrieval subsystem, designed to organise the spatial data in a manner, which allows the data to be quickly retrieved by the user. It also permits it to be used for ensuing analysis as well as allowing quick and accurate updates and corrections to be made on the spatial database;

3. A data manipulation and analysis subsystem, which performs a wide number of functions. Some of these functions are changing the form of the data through user-defined aggregation rules, or producing estimates of parameters and constraints for various space-time optimisation or simulation models;

4. A data reporting subsystem which allows the user to display part or all of the original database as well as manipulated data, together with the output from spatial models in tabular or map form;

5. A subsystem responsible for the graphical user interface, which enables the user to interact with the programming language within the GIS environment.

GIS systems were developed in part because of the need to understand the spatial and temporal patterns of resources, as also to give an insight into the spatial and temporal processes governing their availability (ESRI, 1990). One of the major strengths afforded by GIS lies in the *spatial data handling* and *storage capabilities* such systems provide. This, combined with the ability to transform the original spatial data held, enables answers to be given to a number of different questions, so allowing researchers to develop environmental impact scenarios. GIS maps provide graphical representations of the acquired data; they allow interactive work with the user to achieve the required analysis, consequently permitting the examination of a range of various alternatives in a project, thereby producing the best possible information. The GIS database allows spatial operations as well as statistical analysis to be made on the dataset whilst delivering the results in an "easy to use" graphical user interface.

GIS is a useful tool for the formulation and implementation of sustainable development strategies in particular those which are land and resource related, such as policy implementation for use of heavy metals in the environment. By testing different development scenarios and land use parameters, planners and government officials can use GIS sustainable land development models as a decision support system for sustainable land use management in areas in the world that are under great pressure of rapid urban growth whilst simultaneously experiencing land shortages. The model will allow the identification of areas where future urban development should take place. Planners can use this as a guide in developing strategic plans to meet the objectives of sustainable development.

2.6.2 Geochemical baseline

The term "geochemical background" became an important reference with increasing environmental awareness and with the rising number of contaminant investigations into various environmental media. The background range was defined by Hawkes and Webb (1962) as the "normal abundance of an element in barren earth". There are

two types of background concentrations: natural (NBC) and anthropogenic (ABC) (Matschullat *et al.*, 2000). Natural geochemical background data are generally defined as element concentrations in natural media without human influence, in other words, a pristine environment (Kabata-Pendias *et al.*, 1992; Brooks *et al.*, 1995). Due to long-range atmospheric transport and persistence of contaminants, truly pristine soils no longer exist in most settings. This makes it almost impossible to establish true NBC levels of elements in soils (Chen *et al.*, 1999). Using baseline concentrations as a reference to determine clean soils has been proposed, which represent elemental concentrations specific for a *given region* and *time period*, but do not always represent true background concentrations (Salminen and Tarvainen, 1997). Geochemical baseline concentration is a term which expresses an *expected range* (not a single value) of element concentrations around a mean in a normal sample medium. It is not generally a true background concentration and defined as 95% of the expected range of background concentrations (Kabata-Pendias *et al.*, 1992; Chen *et al.*, 1999; Dudka *et al.*, 1995). Increasingly, the term "ambient background" is being used within the European Union (EU). It is basically defined as the current background concentrations.

There is a practical relevance in defining the threshold between concentrations of a chemical element that occurs naturally in environmental media as compared with concentrations of the same analyte present as a result of anthropogenic activities (Matschullat *et al.*, 2000). A literature search for the term geochemical background yields an almost innumerable amount of citations. Some of the most prominent ones include Hawkes and Webb (1962); Kabata-Pendias *et al.* (1992); Plant *et al.* (2001); Mattschulat *et al.* (2000) Chen *et al.* (1999) Brooks *et al.* (1995); Dudka *et al.* (1995); Adriano (2001); Hayek and Buzas (1997); Swan and Sandilands (1995); Ferguson (1990); Chirenje *et al.* (2001); Salminen and Tarvainen (1997) and Zillioux (2001). This shows the apparent need and demand for the term. A closer inspection of the literature, however, also highlights that the term does not appear to have a clear definition and similarly no agreement on its use (refer to Chapter 1 for definitions to be used in this work).

Geochemical baselines are of great importance in the formation and application of environmental legislation, which sets down limits for heavy metals in contaminated

land as defined by environmental authorities. Regional geochemical maps indicate that natural background concentrations vary widely due to differences in basic geology. Additionally, several different backgrounds can be characterized depending on the sampled constituent of the overburden, grain size, analytical method etc. The task of defining or calculating the background value for an element is not just a scientific problem; for a landowner whose land is declared contaminated the financial implications can be paramount (Salminen and Tarvainen, 1997). In the secondary environment, the geochemical background changes regionally with (as mentioned above) basic geology and locally with the type and genesis of the overburden. While geological baselines in regions of sedimentary rock may remain the same over extensive areas; in shield areas the variations may be large. Similarly, the analytical method selected, together with the material and grain size analysed will have a major influence on the average background values obtained (Salminen and Tarvainen, 1997).

The term "geochemical baseline" was officially introduced in 1993 in the context of the International Geochemical Mapping Programme (IGCP) 360 project, Global Geochemical Baselines, after considerable discussion during the preceding five years of the IGCP 259 project International Geochemical Mapping (Plant *et al.*, 2001). The original intention of the IGCP 259 project had been to prepare a geochemical map of the globe, but the unreasonableness of this task quickly became apparent (Salminen and Tarvainen, 1997). While the last 30 years of geochemical data collection have provided a wealth of valuable geochemical data, these data cannot be easily compiled for use in assessing the extent of the environmental problems on a European or global level because the datasets have been collected for different surveys using different sampling, analytical and data interpretation methods. This is because there are currently no internationally agreed standards for geochemical surveys. It is hoped that, if such standards were to be achieved and implemented, this would minimise if not eradicate many of the problems associated with assessing contamination of areas on large international scales (Plant *et al.*, 2001).

Data on geochemical baselines are urgently needed in Europe because environmental authorities are defining limits for levels of contaminants in soils used for different purposes in most European countries (Salminen and Tarvainen, 1997). Natural

concentrations of elements vary noticeably between geologically disparate areas as well as in the various constituents of overburden. State authorities are not always aware of these considerable natural variations, which must be taken into account when defining action limits based on environmental regulations, as there are already examples of action limits that are lower than natural concentrations. Existing geochemical data in Europe were not (until very recently) in the form that can be readily used for this purpose (Plant *et al.*, 2001), so it has not been possible to on the basis of existing geochemical data, to define a European Geochemical Baseline even for a single element. This appears to be changing, with the work being carried out by the Forum of European Geological Surveys (FOREGS) programme. This programme was initiated with the aim to produce high quality geochemical baseline data for Europe (Salminen and Tarvainen, 1997).

Due to this increasing influence of geochemical baseline mapping on environmental legislation, there is much debate as to the validity of baseline geochemical mapping on larger (international) scales. The main arguments presented include firstly the spatial heterogeneity found within very small distances in urban areas, and indeed rural areas (due to the presence of mineral deposits and natural geochemical anomalies) and secondly the temporal variability of element input from anthropogenic sources to the natural environment. It would however, be unreasonable to establish separate action limits for contaminated land in every type of overburden and for every analytical method. It is important that the potential variability in geochemical baseline data be taken into consideration when they are used in political decision-making and environmental regulation (Salminen and Tarvainen, 1997). It has been thereby suggested that if the current datasets could be normalised against a standard reference dataset then they could be used to assess and highlight the extent of the problems related to geochemistry mentioned throughout this chapter (Plant *et al.*, 2001).

Hawkes and Webb (1962) emphasize the need to calculate separate background ranges for different study areas. Matschullat *et al.* (2000) define the geochemical or natural background *range* as a characterisation and quantification of an element that has no anthropogenic contamination. The use of single values for a geochemical background is neither useful for the characterisation of a geogenic background nor for

the determination of an anthropogenic contamination. This is because single values do not give information about the natural deviation of element concentrations in natural environmental media. Subsequently, a differentiated interpretation of results is impossible. It would be possible though, to define upper and lower limits for calculated baseline data with a defined statistical reliability (Matschullat *et al.*, 2000).

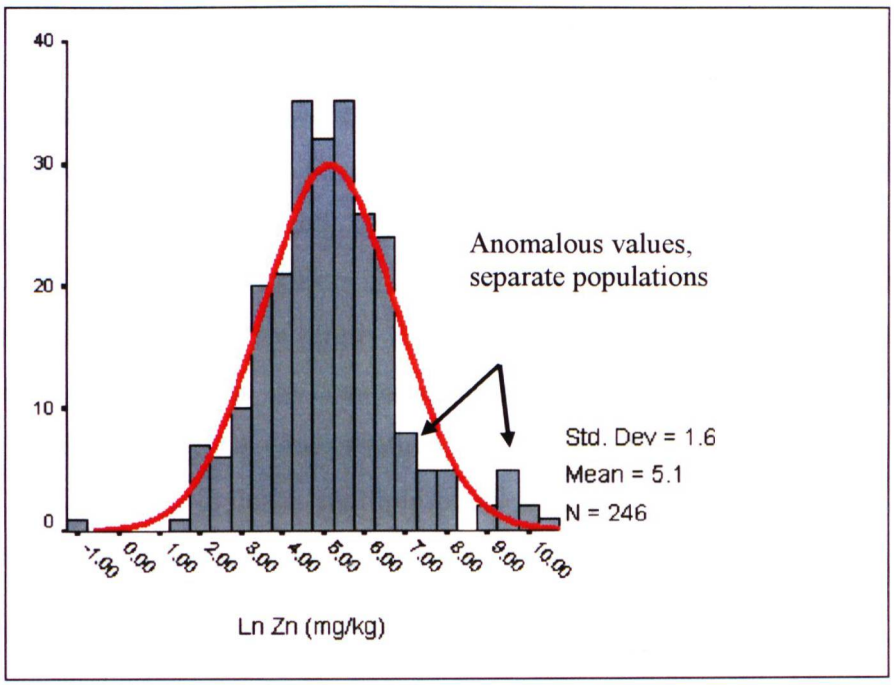

Figure 2.2 Zn concentrations in surface soils from Gibraltar

The first step before any values are calculated should be an assessment into the number of populations present with the particular geochemical dataset. This is because homogenous populations are rare in geochemical data within an urban environment. There will most likely be at least two populations present. One being an ambient background population and the other, a population representing a pollution source such as emissions from motor vehicles, a scrap yard, an incinerator or other types of industry such as gas works or even newspaper printing works.

A series of methods to calculate the background and anomalous samples is given in a review by Matschullat *et al.* (2000). Plotting the data on a histogram can show which values are anomalous to the data set. An example of the methodology is shown in

Figure 2.2 for Zn concentrations in the surface soils of Gibraltar. This procedure is effective when the two populations are separate but when they overlap, as commonly occurs in urban environments, difficulties arise in distinguishing between which levels represent a contamination source and which ones indicate threshold values between background (or baseline) and anomalous values (Brooks, 1995). Geochemical data are typically positively skewed with a portion of the samples exceeding the upper baseline range or "threshold" value.

Using 2 times the standard deviation follows Tchebychev's theorem, which insures that at least 75% of the data lie within 2 standard deviations from the mean, a probability of 1 in 4 samples will occur above or below the threshold (Hayek and Buzas, 1997). Another way to view if different populations exist within the dataset is through cumulative probability plots. A change in gradient indicates the "threshold-level" above which samples are considered anomalous (Figure 2.3, is an example of this methodology using Zn concentrations for surface soils in Gibraltar). Several changes in the trend indicate multiple-populations. A multiple of the standard deviation about the mean is a common method of defining a background range.

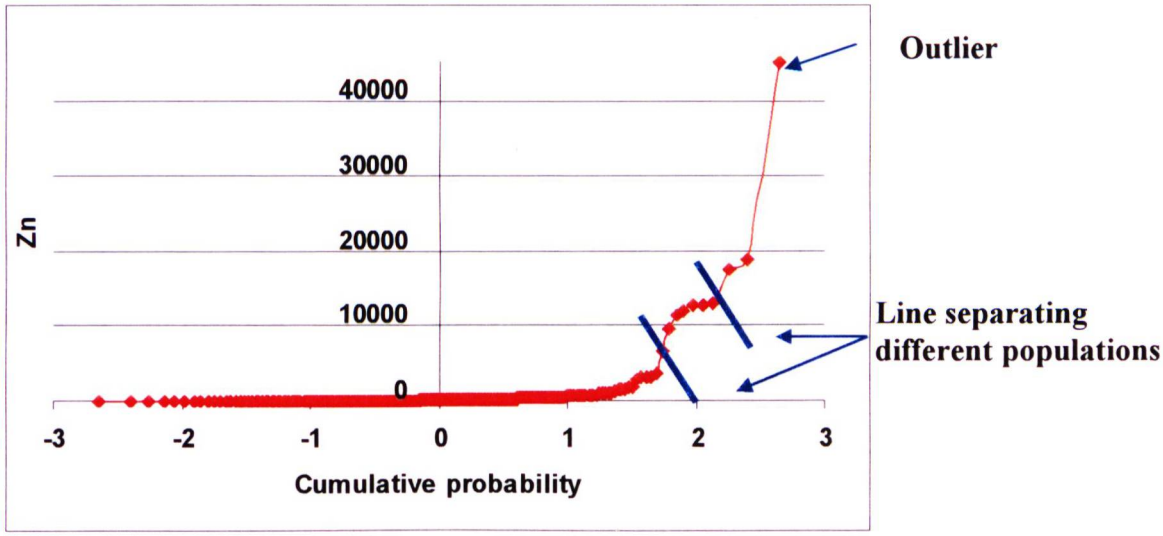

Figure 2.3 Cumulative probability plot of Zn concentrations in soils from Gibraltar.

The procedure can be iterated, omitting outliers individually until the remaining data set falls within 2 standard deviations (SDs) of the mean. Alternatively, a statistical test can be used to test the hypothesis that the maximum value is not significantly different from the mean. Typically, a t-test is used at 5% significance. Once outliers

are removed, a t test can be carried out to check most of the data fall within 2 SDs of the mean.

When calculating the baseline ranges, based on a log normal distribution theory, (Dudka *et al.*, 1995), the expected range can be expressed as ± 2 standard deviations (Dudka *et al.*, 1995). Baseline concentrations are calculated using [2]$GM*GSD^2$ and GM/GSD^2 (Dudka *et al.*, 1995; Chen *et al.*, 2001). Two SDs include 95% of the area under the distribution under a normal frequency curve. Thus a baseline value for a contaminant may represent the upper limit of the normal range of concentration. It is appropriate to use the standard deviation as a function to describe the variability within the dataset as it reflects the deviation around the average value. Background ranges between the 20^{th} and 80^{th} percentile values are used by Plant and Raiswell, cited in Thornton (1983) for stream sediments in northern Scotland. A baseline range for soils in the Sudbury Plain, Ontario Canada uses the method outlined above by Dudka *et al.* (1995) of the $GM*GSD^2$ and GM/GSD^2 to calculate the upper and lower baseline range from a regional soil database. When formulating regulatory or guideline values it is necessary to accurately determine the ambient background levels, considering spatial heterogeneity so that unrealistically low values can be avoided.

2.7 Regulation of metals in the environment

Throughout Europe (and on a global level) public concern about the environment is growing. In response, national governments and the EU are attempting to develop policies, legislation and infrastructure, such as the European Environment Agency (EEA) (Salminen and Tarvainen, 1987) with the hope to be able to provide better management and solutions to the environmental problems being encountered today. However, an awareness of the potential harmfulness of metals for man and the environment has existed almost as long as man's ability to exploit the wealth they represent (Thornton, 1993). Modern environmental law, however, began to emerge as late as the 1970s and it was driven largely by public concern following the publication of Rachel Carson's book Silent Spring (1964). Through this book,

[2] GM stands for Geometric Mean
GSD stands for Geometric Standard Deviation.

millions were made aware for the first time, of the impacts of substances such as lead, mercury and arsenic on ecosystems. Calls for legislation soon followed, leading to a plethora of laws in countries worldwide dictating the appropriate use and disposal of the substances (Thornton, 1995).

The prime objective of environmental law is to prevent or reduce the harmful impacts of metals upon human beings and the environment (Scoullos *et al.*, 2001). Most laws operate to control either the processes which discharge metals to the environment, or the finished products containing metals, both before and after they enter the environment (Thornton, 1995). The basis of control may vary so that standards may be formulated in terms of performance or technology. They may be set in a site-specific basis or across a particular industry. They may also be supplemented by environmental quality objectives which set certain standards to be met in the relevant environmental medium (Thornton, 1993).

2.7.1. The European Unions approach to pollution control

Due to EU and other international and national policies as well as considerable improvements in available technologies, heavy metal emissions from industrial *point sources* have been reduced considerably over the past few decades. Emissions from defuse sources however, e.g. traffic and combustion processes have either remained stable or increased (Scoullos *et al.*, 2001). The EU has been, and still is, a major producer and consumer of heavy metals. A major part of the production of heavy metals and their compounds and products is taking place in EU member states. Several of them are also actively involved in the import and export of metal concentrates and, to some extent, of wastes such as used batteries. All these activities, contribute to different degrees of heavy metal emissions and subsequent contamination (Scoullos *et al.*, 2001). Other activities which contribute indirectly to the emissions and deposition of heavy metals within the environment include exploitation of the very high quantities of fossil fuels and of other mineral resources.

The EU has adopted five major action programmes and passed well over 200 pieces of legislation relating to the environment since 1973 (Makuch, 2000). These range from the use of marketing and use of chemicals right through the life cycle of a

product through to waste disposal (Thornton, 1995; Makuch, 2000). The most common form of legislation within the EU is the "directive", which member states have to implement via national measures such as statutes. Usually, EU legislation in regards to the environment takes the form of a framework directive which sets up a broad system of control. European legislation tends to be media-specific so that controls operate to regulate discharges into air, water and to land (Makuch, 2000). A framework directive on dangerous substances was adopted in 1976 setting out two lists of substances for which pollution was to be either eliminated or reduced. List I substances included were selected on the basis of their toxicity, persistence and bioaccumulation. They include Hg and Cd compounds. List II substances include Pb, Zn and Cu which are perceived to be not as dangerous (Thornton, 1995).

2.7.2 The UK's approach to soil management and contaminated land

In the UK, there are three main areas for dealing with contaminated land and its management. These include the condition of the soils and their management. Secondly is the classification of brownfield sites and the definition of this term, and lastly is the legal definition of contaminated land and its subsequent effects on land use management. Each is discussed below.

Soil is highlighted as a neglected aspect of the environment in the latest report by the Royal Commission on Environmental Pollution (DEFRA[3], 2001). The Royal Commission considers soil to be a neglected topic where "Environmental policies have largely taken soil for granted" and it recognises a growing need for "soil pollution to be given the same priority as pollution of air and water" (DEFRA Draft Soil Strategy, 2001). The Department for Environment, Food and Rural Affairs have published a Draft Soil Strategy for England following a report from the Royal Commission on Environmental Pollution, "*Sustainable Use of Soil*" (DEFRA Draft Soil Strategy, 2001). The report emphasises the pressures on soils in the UK as a result of:

- The great intensification of agriculture during this century

[3] DEFRA – Department for the Environment, Food and Rural Affairs

- Continuing demand for land for building, particularly in areas with fertile soils
- Extraction of peat and minerals
- Increasing amounts of sewage sludge (for which disposal at sea was banned after 1998)
- Large quantities of other wastes spread onto land or buried in the ground
- Contamination from industry
- Pollutants reaching soils from the atmosphere.

The report sets out the role of soils and identifies three key objectives. Soils fulfil a wide range of inter-related functions, which have been categorised into six groups, and are summarised as (DEFRA Draft Soil Strategy, 2001):

1. **Environmental interaction** - Soils act as a link between the atmosphere, geology, water resources and land use, filtering substances from water and regulating the flow from rainfall to water courses and vegetation. Soils receive deposits from the atmosphere and regulate the flow of water from rainfall to watercourses, aquifers, vegetation and the atmosphere.

2. **Food and fibre production** - Soils are the growing medium for crops and timber and act as the basis for livestock production.

3. **Providing a platform** - Soils form the foundation for buildings, infrastructure and the landscape.

4. **Support of ecological habitat and biodiversity** - Soils supply the nutrients, water and structure for vegetation, micro biota and the terrestrial ecosystems. It is also a store for seeds and soil dwelling organisms.

5. **Providing raw material** - Soils provides a direct source of minerals and resources, such as peat and topsoil and acts as a reservoir for water.

6. **Protection of cultural heritage** - Soil protects artefacts of historical and cultural interest and provides data on environmental change.

(Paragraph 1.2, Chapter 2; The Overall Strategy, Draft Soil Strategy for England A Consultation Paper, DEFRA, 2001).

The Royal Commission (DEFRA Draft Soil Strategy, 2001) sets out five principles to form the basis of soil protection policy. Firstly, soils must be conserved as an essential part of life-support systems. Secondly, soils should be given the same priority in environmental protection as air or water. The third point concerns the fact that an integrated approach to environmental management must include management of land. The fourth point states that contaminated sites should, wherever practicable, be recovered for beneficial use. The final principle states that further contamination of soils should be avoided. The Soil Strategy identifies three key objectives, they are to manage the extent of soil as a resource, to manage the diversity of soil and to maintain and improve the quality of soil for current and future social, environmental and economic needs (DEFRA Draft Soil Strategy, 2001). Metal contamination reduces the quality of soil by reducing the function of soil. Urban soils are affected by emissions from transport and industry, and by direct discharges and dispersed sources (DEFRA Draft Soil Strategy, 2001).

Brownfield land is a term used to describe urban land, which has a history of industrial use, but which still has some potential for re-development. The National Brownfield Sites Project (Alker *et al.*, 2000a, b) has set up a database of brownfield sites in England and Wales. It defines brownfield sites as;

"a brownfield site is any land or premises which has previously been used or developed and is not currently fully in use, although it may be *partially occupied* or *utilised*. It may also be *vacant, derelict or contaminated*. Therefore a brownfield site is not necessarily available for immediate use without intervention."

Under the Planning Policy Guidance PPG3 Housing (2000) (DEFRA Draft Soil Strategy, 2001) five individual components which may constitute brownfield land have been identified as follows:

- Previously developed land which is now vacant;
- Vacant buildings;
- Derelict land and buildings;
- Other previously developed land or buildings, currently in use, allocated for
- Development in the adopted plan or having planning permission for housing;
- Other previously developed land or buildings where it is known there is potential for redevelopment.

Vacant indicates land where previous activity has finished, *derelict* land is in some way affected by previous use and is incapable of further use without treatment. In order for the land to be c*ontaminated* there has to be evidence of previous or current contaminants on the site. *Partially occupied or utilised* requires some of the land to be in some form of "productive" use and *intervention action* refers to remediation, regeneration, infrastructure, and planning (Alker *et al.*, 2000a).

Despite the many definitions available on brownfield sites, some definitions identify brownfield land as contaminated or potentially contaminated. For land to be classified as contaminated, harm to the receptor must not only be significant, but there must also be a significant possibility of the significant harm occurring (EPA[4] 1990, in DEFRA, 2000). Determination of site status should be through a risk assessment, at its heart a consideration of source-pathway-target relationships. Risk assessment (RA) can be defined as a scientific evaluation of the likelihood and uncertainty of environmental hazards being present in a product, system, or plan (USEPA, 1997; Wang *et al.*, 1997). The Environmental Protection Act (EPA) (1990) Part IIa states that whilst a risk assessment may indicate that on the balance of probabilities the assessed area of land appears not to be contaminated, it is still possible that the land is contaminated (refer to appendix A).

Part IIa of the Environmental Protection Act (1990) was inserted into that Act by section 57 of the Environment Act 1995. It provides a new regulatory regime for the identification and remediation of contaminated land. In addition to the requirements

[4] EPA – Environmental Protection Act

contained in the primary legislation, operation of the regime is subject to regulations and statutory guidance (DEFRA, 2002e).

The government's objectives with respect to contaminated land underlie the "sustainable for use" approach to the remediation of contaminated land. This approach consists of 3 elements:

1. Ensuring that the land is suitable for its current use – i.e. remediating the land
2. Ensuring that the land is made suitable for any new use, as official permission is given for that new use – i.e. assessing the potential risks from contamination, on the basis of the proposed future use and circumstances, before official permission is given for the development, and where necessary remediating the land before the new use commences; and
3. Limiting requirements for remediation work necessary to prevent unacceptable risks to human health and the environment in relation to the current use or officially permitted future use of the land - i.e. recognising that risks from contaminated land can be satisfactorily assessed only in the context of specific uses of the land, and that any attempt to guess what might be needed at some time in the future for other uses, e.g. as a school site, is likely to result in risking the distortion of social, economic and environmental priorities or unnecessary work (wasting resources)[5] (DETR, 2000).

The "suitable for use" approach provides the best means of reconciling the governments various environmental, social and economic needs in relation to contaminated land. Contaminated land requires well-thought-out and cost-effective measures to contain, control or eliminate the risks. Under the new Contaminated Land Regime, specific duties are placed on local authorities to identify land falling within the definition and where they do, require remediation in line with the "sustainable for use" approach. The assessing of liabilities is based on the "polluter pays principle" (DEFRA, 2001a).

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[5] (DETR – Contaminated Land: Implementation of Part IIA of the environmental Protection Act 1990 (September 1999)
DETR – Department of the Environment, Transport and the Regions

2.7.3 Assessment of existing environmental controls over metals

Despite the existence of a large body of environmental legislation at both the national and EU levels, it is now generally acknowledged that the legislation has not led to the prevention of environmental deterioration (Kramer, 1992; Thornton, 1995). Some of the difficulties experienced by environmental agencies lie in the efforts to provide the legal controls with a scientific basis through standards. This is because existing institutional and administrative mechanisms do not easily incorporate scientific principles into legislation. European legislation has been particularly criticised in this respect, and an attempt is being made to tackle this problem through expert working groups and greater consultation at an earlier stage in the legislative drafting (Thornton, 1995). The basis upon which the standards have been set is always plagued with problems relating to scientific ambiguity which are not always well documented or understood by future users. Thus, authorities are not always clear about the limitations of the standards or the circumstances in which they should be applied (Thornton, 1995). For example standards exist at the European level regarding sewage sludge discharges to soil, but not regarding discharges from any other industrial activities, so different approaches are used by member states, which differ again from those used in different countries outside the EU. Additionally, the legal status of these values and the purposes for which they are used also vary from country to country. In the Netherlands and the USA, the relevant standards are mandatory. In the Netherlands they are used to define both when a site is contaminated and the level of clean up which must be carried out (target and intervention values). Soil guideline values (table 2.7) are commonly used during the redevelopment of former industrial or brownfield sites and are based on potential hazards to human health with people as the receptors. The United Kingdom Interdepartmental Committee for the Redevelopment of Contaminated Land (ICRCL) was set up in 1976 to consider the problems associated with the development of contaminated sites.

Table 2.7 Summary of soil guideline values (mg/kg)

Metal	Dutch Values[1]		ICRCL Trigger[2]		DEFRA/EA Soil Guideline Values[3]		
	Target	Intervention	Domestic gardens, allotments and areas where plants are grown	Parks, playing fields and open spaces	Residential plant uptake	Residential no plant uptake	Industrial and commercial land
As	29	55			20	20	500
Cd	0.8	12	3	15	(pH <6) 1 (pH 6-7) 2 (pH >7) 8	30	1,400
Cu	36	190	130	-	-	-	-
Ni	35	210	70	-	50	75	5,000
Zn	140	720	300	-	-	-	-
Pb	85	530	500	2,000	450	450	750

References: 1.Zeroenvironment (2001), 2. ICRCL (1987), 3. DEFRA and Environment Agency (2002)

The ICRCL values were continually under review with some having as many as eight editions in only twelve years. They were, and still are, very useful documents, and have formed the mainstay of UK contaminated land guidance over two decades. One difficulty has always been the quantification of contaminants in soils and the concentration at which the chemical forms a risk to known targets. This is no less a difficult question now as it was twenty years ago. To assist in the risk assessment process the committee developed *tentative* trigger concentrations for a range of inorganic contaminants (DEFRA, 2002a-e). These contaminants were chosen as those most likely to form a risk from seven identified hazards. The trigger values define three possible concentration zones (Environmental Agency, 2000):

1. Below the "threshold" value, the site can be regarded as uncontaminated.
2. Above the "action" value, the presence of the contaminant has to be regarded as undesirable or even unacceptable, so some kind of remedial action is unavoidable.
3. Between the two values, there may be a need to consider the contamination and take action where circumstances demand it. The decision to do so should be based on "informed judgment".

On the 14th March 2002, the Department for Environment, Food and Rural Affairs (DEFRA) and the Environment Agency, United Kingdom, published a series of reports that provided a scientifically based framework for the assessment of risks to human health from land contamination. DEFRA have now formally withdrawn the guidance on the health effects of contaminated land given in ICRCL Guidance Note 59/83 (2nd edition). The source information is still available from DEFRA on request to aid understanding of historical decisions on the remediation of contaminated sites but it should not be used in the assessment of new sites. Any decisions regarding guideline values for potentially contaminated sites are based on the DEFRA and the Environment Agency Contaminated Land Exposure Assessment (DEFRA/EA 2002a-e) Soil Guideline Values (SGV). The CLEA model derives Soil Guideline Values by comparing the calculated intake with the total daily intake (TDI) or Index Dose. If element concentrations in soils are below these guideline values, the site is considered safe, if the concentrations are above the guideline values, the site may be deemed unsafe and further investigation is required. Thus the DEFRA/EA guidelines provide an objective basis for decision-making based on an assessment of risk to human health. The DEFRA/EA values are to be used by Local Authorities in the UK to support Part IIA of the Environmental Protection Act 1990 (DEFRA/EA 2002a-e). The main objective of this legislation is "...to provide an improved system for the identification and remediation of land where contamination is causing an unacceptable risk to human health or the wider environment assessed in the context of the current use and circumstances of the land" (DEFRA, 2000a).

In a densely populated country such as the Netherlands, protection and where necessary, improvement of the quality of soil is a crucial aspect of the environmental policy. In the Netherlands the government sought to improve contaminated land so it would be suitable for any potential use. This lead to the development of guideline values for a range of fifty-seven contaminants known as the "ABC values". These were consequently refined to form the "Target and Intervention Values" for sixty-seven contaminants. The interpretation of the values is as follows (Zero Environment Ltd, 2001):

1. The *target value* is the baseline concentration below which compounds and/or elements are known or assumed not to affect the natural properties of the soil.

2. The *intervention value* is the maximum tolerable concentration above which remediation is required. This occurs if one or more compounds are present in concentrations equal to or higher than the intervention value of more than 25 m^3 of soil or 1000 m^3 of ground water.
3. The *middle value* – (target value + intervention value) *x* 0.5. This is regarded as a threshold value for further investigation.

In addition to using soil guideline values for the assessment of sites, a pollution index (PI) is sometimes used when mapping such information. Plotting the PI spatially provides an indication of overall contamination in the decision making process. The pollution index calculates the concentration of metal in soil against the soil guideline value. Chon *et al.* (1995) define it as:

$$PI = \Sigma(M_{soil}/SGV)/N$$

Where the PI is calculated from the concentration of the element in the soil M_{soil}, the soil guideline value (SGV), and N represent the number of samples. A soil with a PI >1 exceeds the guideline values and a PI < 1 would be regarded as unpolluted. The PI is dependent on the soil guideline values used and gives an average value.

2.8 Chapter conclusions

Soils are critical environments in terrestrial ecosystems where rock, air and water interface. The element contents of soils are obtained from various sources which range from the underlying parent material through to anthropogenic activities, i.e. pollution. Soils are subject to short-term fluctuations, such as variations in moisture status, pH and redox conditions whilst simultaneously undergoing gradual modifications in response to changes in management and environmental factors. Additionally, soils can show marked spatial variability in physical and chemical properties at both the macro- and micro-scales (Alloway, 1995). In the past few decades, the natural input of particular elements to soils due to pedogenesis has been exceeded by anthropogenic input. It is thereby necessary to understand the extent, association and environmental availability of the elements that are harmful to the health of the flora, fauna and people.

In the past few decades, public awareness concerning environmental degradation has grown. In response to this, heavy metals have been the focus of much attention because of their peculiar pollutant characteristics (Facchinelli *et al.*, 2001):

1. They do not generally decay with time;
2. They can be necessary to flora and fauna at certain concentrations, but also toxic when exceeding specific thresholds;
3. They are always present at some concentration of non-anthropogenic origin as their initial input to soils is governed by the weathering of parent rocks and pedogenesis;
4. They often occur as cations, which strongly interact with the soil matrix; consequently heavy metals in soils, even at high concentrations can be present in inert and non-harmful forms, but they can become mobile as a result of changing environmental conditions or by saturation beyond the buffering capacity of the soil. This situation has been referred to as a "chemical time bomb"

Geochemical baseline maps are used for identifying the natural distribution and potential environmental hazards and specific health problems related to elevated concentrations of toxic elements, or inadequate concentrations of essential elements. A key component of multi-element maps is the ability to assess the distribution of elements on a regional scale and to define areas that require further investigation. Baseline mapping of geochemical datasets requires a different interpretation when applied to urban environments as anthropogenic factors outweigh lithogenic ones for certain elements. Sources and distribution become more important than parent material and soil forming processes when assessing metal concentration in soil in an urban setting.

Geographical Information Systems are useful tools for the presentation of multi-layered data sets including metal distributions in soils, sediments, rocks and dusts. Such techniques aid in the formulation and implementation of sustainable development strategies, especially for those which are land and resource related. Remediation of contaminated land is expensive and planning is one of the most

effective ways of minimizing costs. The value of geochemical maps is evident here. When the distribution of metals in contaminated areas is known, land use management, for example, the development of new motorways, railways, office complexes and industrial sites, can be planned accordingly in order to contain the contamination, thereby leaving uncontaminated areas for residential and ecological land use planning. GIS projects are being developed as decision support systems. The use of GIS allows strategic planning, development control and pre-application assessment. It assists in the modelling of urban regeneration based on the "suitable-for-use" approach adopted by various EU governments by offering various options to assist government departments in the integration of legislation.

Environmental law, in particular legislation which aims to manage and control the impact of metals is currently in a state of flux. Traditional methods of regulation do not appear to have been entirely effective, and consideration is being made to develop new instruments. For example a major point of criticism has been the absence of sound scientific principles guiding their use (Thornton, 1995). Regulators are now turning to risk assessment based principles in an attempt to reinforce "command and control" mechanisms as more effective methods of environmental protection. In order to contribute to sustainable development in the long term, risk assessment (RA) needs further work as follows:

- Examination and application of lessons from RA
- Improvement in current quantitative assessment methods
- Application of uncertainty analysis to make uncertainties explicit
- Integration of scientific RA and public perception to make cost-effective policy and regulatory response.

Land contamination, if not dealt with adequately, can pose a serious threat to health and/or the environment. Current and future pollution is generally tackled through legislative means, but the legacy of past contamination is generally not fully addressed. Additionally, uncertainties about remediation requirements and liability for them can cause blight, deterring development of land which in turn affects urban regeneration. One of the main principles for environmental policies is that decisions

or actions that could have an adverse effect on the environment should be based on the best possible information and analysis of risks.

The challenge is to integrate scientific tools of analysis with environmental policy making and management processes.

CHAPTER 3

Gibraltar

This Chapter discusses the different aspects of Gibraltar, which either directly or indirectly are believed to have some bearing on the investigation.

3.1 General History

"The Rock of Gibraltar is arguably one of the most "fought over" places in Europe" (Rose, 1998, p87). It has been subjected to fifteen major sieges since the year 1309. The Moors first seized it in AD 711, to be later captured by the Spaniards in 1462, and subsequently by an Anglo-Dutch operation in 1704. It was later ceded to the British in 1713 through the Treaty of Utrecht. Gibraltar joined the European Union as a European territory in 1973 under Article 227 (4) of the Treaty of Rome (Treaty of Rome, 1960). This means that its external affairs are the responsibility of the Member State. The British provided the bulk of Gibraltar's economy for nearly 300 years. However, the contributions of the Ministry of Defence (MOD) to this economy are now around 5% or less (Rose, 1998).

The Moors established the town in AD 1160. The main development of the town occurred under the British occupation, particularly after 1900 when land reclamation began in order to expand the town. The town was developed on the gentler western slope and onto the flat ground on the west and south. The majority of the reclamation on the western side of Gibraltar was for residential and commercial development, and on the west side of the Rock, for the extension of the harbour and port area. Land has recently been reclaimed on the east side thereby joining the beaches known as Eastern Beach and Catalan Bay, with a view to building an additional Marina to those already in existence in Gibraltar. This reclamation site was also being used as a landfill site for the bottom ash of the incineration process until this ceased in 2000. The demand for land is a result of the population density of Gibraltar. The population is c.33,000. There are some 23,000 Gibraltarians, 6,000 British expatriates and 4,000 Moroccans, although these figures are subject to daily fluctuation due to migration across the

frontier into neighbouring Spain and seasonally with the influence of tourism (c. 4,000,000 tourists visit the Rock every year).

Gibraltar is located on one of the most important tanker routes of the world. The Straits of Gibraltar is classed as possibly the busiest maritime traffic thoroughfare in the world with the Port of Gibraltar being developed into one of the main bunkering facilities in the region.

3.2 The Natural Environment

The Rock has been thrust outwards as a result of plate tectonics some 20 million years ago by as much as 100 kms from the Alboran Region. The thrusting, faulting and partial overturning at the boundary of the European and African plates resulted in the creation of the historically renowned "Rock of Gibraltar" (Rose and Rosenbaum, 1991). Africa and Gibraltar were once joined forming a chain of mountains, which separated the Mediterranean Sea from the Atlantic Ocean. The present shape of the Rock is the result of the denudation processes acting on the Rock over the past 20 million years. The Rock of Gibraltar was raised above sea level through the influence of plate tectonics. Effects of climatic changes during this period are evident by the sediments (extensive scree breccias formed during cold climates and reddened sands and soils formed during warm climates) found on the Rock (Palao, 1982). Gibraltar is on the plate boundary between Europe and Africa. No major earthquakes have been recorded there recently although in the past 90 years, earthquakes of intensity (Modified Mercalli Scale) 4 - 7 have been experienced (Rose, 1998).

Gibraltar, like other southern parts of Europe and the Mediterranean basin, is situated in the middle latitudes. This regional part of the Mediterranean is surrounded by mountain ranges with notable foothills often reaching the coastline. The most relevant here are the Atlas Mountains of North Africa and the Penibetic and Iberic Systems in Spain. The topography makes up the area as a closed basin isolated from other regions through valleys and the narrow straits (Romero *et al.*, 1998).

Gibraltar is comprised of a narrow peninsula (part of the Iberian Peninsula) running outwards from the south-west coast of Spain (Plates 3.1 and 3.2). Gibraltar is

connected to Spain by a low sandy isthmus. Physiographically, Gibraltar can be divided into three parts, the isthmus, the main ridge and the southern plateaux (Rose and Rosenbaum, 1991) (Plate 3.1):

1) The Isthmus. To the north, there is a runway, 1,700 m long, built horizontally from east to west. Beyond this can be found the small air terminal, the meteorological office and the frontier, which connects the Rock of Gibraltar to Spain. This section is an isthmus, 800 m wide, and at most 3 to 4 m above sea level.

2) The Main Ridge. The rock face on the eastern section comprises of a steep cliff. The eastern side slopes very abruptly down to the sea. Scree breccias and wind-blown sands moderate the angle of the slope at the lower parts of this side, although the limestone cliffs above are nearly vertical. A large portion of the upper part of these slopes have in the past been covered with corrugated iron sheets to form rain-water catchments which have recently been dismantled as they were no longer in use. The bases of these slopes have been subject to years of rock falls of large boulders displaced by rain. Most of the beaches are located on the eastern side. There are 3 main ones in this area which are used by the local population. Some smaller coves can also be found in this region.

On the western side, the Rock consists of less steep and gradual slopes. The lower area of the slope is covered by sands and this is where the city and central business district are situated. On the lower section of this slope, housing estates and other buildings sprawl both up the Rock and westwards from this area. During the past decade large amounts of sea have been reclaimed in an attempt to help solve the serious housing problem. The "top of the Rock" (upper section of the western slope) is largely covered by woodland. This area has been designated as a nature reserve, and a large portion of the main tourist attractions is situated in this location. There are a few disused farms, but the majority of the buildings cater for the tourist industry and some for MOD services. Half way down the western slope, there is a north-south trending cliff-line, possibly a relic from a time when relative sea level was significantly higher than present (Rose and Rosenbaum, 1991).

2) The Southern Plateaux. The southern and western sides have more housing estates, although the residential areas are much less dense and the buildings less congested than in the city. This area extends to the most southern point of Gibraltar and is called the Southern Plateaux. It consists of rock platforms, which then meet the sea at the bottom of a vertical steep cliff. The higher of the two platforms is called Windmill Hill (a gently sloping plateaux generally between 130-190 metres above sea level), and the lower is called Europa Flats (30-40 metres above sea level). These are wave-cut platforms and mark previous sea levels clearly, they constitute the only naturally existing land which extends out from the actual Rock.

3.2.1 Climate

The Rock of Gibraltar, although governed by the general Mediterranean climate of warm dry summers and cool wet winters has its own distinct microclimate, which does display an influence on the daily lives of the local population (Mesilio, 1999). The microclimate is the result of the huge topographical variations within Gibraltar as well as in the surrounding Bay area. Temperature and relative humidity levels vary in relation to the different wind directions within different areas of Gibraltar. The amount of variations experienced within a given region of Gibraltar is related to factors such as the location of this site, as also to the relief and urban topography within the area.

The mean annual temperature for Gibraltar is approximately 18.2 °C. The mean yearly minimum temperature is approximately 14°C and the mean yearly maximum temperature is c. 27°C (Gibraltar Met Office, 2003). Mean annual rainfall is around 768 mm. The prevailing winds are easterly and westerly, followed by the less prevalent south-westerly and occasional northerly. Each wind brings with it its own distinct climatic features, for example the easterly wind results in very warm but very humid conditions, an important factor which may affect the soil geochemistry of certain areas. The "Levanter" is a local weather condition, which occurs when moist easterly winds are pushed up the eastern slope and condense at the top, forming a cloud of variable thickness, extent and duration (Linares, 1994).

3.3 The Geology of Gibraltar

3.3.1 Geology

"An understanding of the geological structure of Gibraltar is essential as a basis to understanding both its major physical features and some of the constraints upon its urban development" (Rose and Rosenbaum, 1991).

This section relies on the review of Gibraltarian geology by Rose and Rosenbaum (1991).

Studies conducted since the early 1900's and which are still continuing have revealed that the Rock of Gibraltar is not a monotonous limestone sequence as previously believed (Rose and Hardman, 1995). Gibraltar is composed of several different sedimentary rocks. Although the main type is fossiliferous limestones c. 200 million years old, there are also ancient mudstones and sandstones (Figure 3.4 (a and b)), which indicate deposition and accumulation as sediments in a shallow, tropical sea. The relatively common occurrence of algal laminations found throughout the Gibraltar limestone is again evidence that the sea in which the sediments accumulated was warm and quite shallow (Rose and Rosenbaum, 1991).

Table 3.1 Limestone units mapped within the Gibraltar Limestone Formation

Limestone Units	Description
Bleak Member	Dark grey bituminous dolomite, often well bedded with some poorly defined algal laminations
Europa Member	Pale, white-grey crystalline dolomite with poorly defined bedding
Keightley Member	Well-bedded and including light coloured algal boundstones, dark bituminous beds, and coarsely crystalline and microcrystalline beds of limestone and dolomite
Buffadero Member	Light or medium grey fine-grained limestone, dolomatic at base, with a sparse fauna of gastropods and occasional brachiopods

Source: tabulated from descriptions by Rose and Rosenbaum (1991).

Shales and wind-blown dune-bedded sands are found on the Rock. The Gibraltar limestone is formed from the mineral calcite ($CaCO_3$), with dolomite or dolostone, composed in significant proportions of the mineral dolomite ($CaMg(CO_3)_2$) (Rose and

Hardman, 1995). The bedrock of Gibraltar (which lies beneath extensive Quaternary deposits) can be described in terms of two main rock types, limestone and shales. Rose and Rosenbaum (1991) divided the Gibraltar limestone into four members defined by gross lithology and weathering characteristics. Table 3.1 lists the different divisions.

Fossils have not been observed in the Bleak and Europa Members. Rose and Rosenbaum (1991) state that they have been destroyed during dolomitization, when the original calcium carbonate of the sediments and shells was changed to calcium magnesium carbonate (dolomite) by the introduction of magnesium-rich fluids from either magnesium-rich components of the rock or from the shales below. Two types of shales have been mapped in Gibraltar (Table 3.2).

Table 3.2 Shale formations mapped in Gibraltar

Shale formations	Description
Little Bay Shale	Found on the south-west coast. Consists of >15 mof red and green fissile clastic mudstones with thin beds of fine sandstone and pebble conglomerate, together with thicker beds of dark grey dolomite
Catalan Bay Shales	Found along the base of the north face and along the east coast. The rocks are medium-bedded grey cherty carbonates alternating with thinner beds of reddish-grey fissile clastic mudstones, originally overlain by thinly-bedded cherts

Source: tabulated from descriptions by Rose and Rosenbaum (1991).

The two most extensive Quaternary wind-blown sands found on the Rock are the Catalan Bay sands and the Alameda or Red Sands (Table 3.3). Rose and Rosenbaum (1991) state that the Rock of Gibraltar is defined as a Klippe, an eroded remnant of a thrust sheet which is fractured by a dominant north west – south east (NW-SE) series of faults and positioned as a result of the Cenozoic two continents collision. Quaternary sediments are found in the caves piercing the bedrock.

Table 3.3 Sands mapped in Gibraltar

Quaternary wind blown sands	Description
Catalan Bay sands	Comprised of 70% quartz with subordinate lithic fragments of schist and speleothem, and shell fragments and benthic foraminifera
Alameda or Red Sands	Underlie most of the town area and like the Catalan Bay sands are comprised mainly of quartz, but contain some lithic sandstone fragments, which the latter sands do not possess. The grains are more rounded than the Catalan Bay sands and the red colour seems to represent well-developed pedogenesis

Source: tabulated from descriptions by Rose and Rosenbaum (1991).

3.3.2 Vegetation and soils

The history of the vegetation in Gibraltar is rather atypical of the region. The history of sieges and fortification of the Rock meant that on several occasions, it was left "entirely barren" (Cortes, 1994). Subsequent re-growth was a combination of natural succession and man induced planting of vegetation. Currently, the atypical geological and climatological circumstances of the Rock give rise to conditions favouring the growth of certain species of plants, which are distinctive to Gibraltar and/or North Africa, not found anywhere else in Europe. Around 600 species of flowering plants can be found on the Rock (Linares, 1994); this richness arises from the variety of habitats: limestone cliffs, rocky shoreline, sandy shoreline, and consolidated sand-dunes, maquis, garrigue and steppe which are found in Gibraltar. As a result of the underlying geology, the natural soils in Gibraltar are largely alkaline although isolated and scattered pockets of more acidic soil can be found (Linares, 1994). The pH data gathered in this work are in agreement with this statement. Soil depth is minimal in most places, not exceeding 30 cm. Soils vary in texture from orange coloured clayey textured soils, to dark brown sandy soils with large quantities of organic matter, to very sandy soils.

The majority of garden soils are imported from the province of Cadiz in Spain (different gardening companies will import from different locations) because it is close to Gibraltar and presumed to be "more in line" with the flora, which grows in this region. The imported soil has been described by Cortes *et al.* (2004) as generally clayey in texture during winter months and very sandy during the summer months. A

good proportion of organic matter is incorporated with this soil to improve the texture. Gibraltar is said to contain little natural soil except for the Red Sands in the Alameda Gardens and that in the Upper Rock Nature Reserve. The Upper Rock has few places where soil depth is of any significance (more than 30 cm) and in these places it is the result of many years of accumulation of leaf litter, blown sand and allied materials. The soils are deposited between stones and crevices and the soil is alkaline, with a pH of 7-8. Imported garden soils range from pH 5-7.

3.4 Geology across the Bay of Gibraltar

In the town of La Linea, immediately across the border with Spain, the sandstones are coarse and poorly sorted dating from the Tertiary in Age. On travelling around the Bay towards Algeciras and Punta Carnero, white limestones from the Early Cretaceous, and polygenetic limestone breccias from the Late Jurassic age are found. Additionally, mudstones, thinly bedded sandstones and traces of siliceous clay can also be found (Rose and Rosenbaum, 1991).

3.5 Water Supply

Restrictions on water supply have been a long standing problem for the inhabitants of Gibraltar. The water supply in Gibraltar has been obtained from four main sources, rainwater, groundwater, by importation from the UK and seawater desalination (Rose, 2000). There has always been a naval/military water supply on the Rock that is separate from that of the civilian population. The history of the civilian water supply is discussed below. The government water catchments were 243 000 m^2, on the east side of the Rock. Timber piles 150 mm x 38 mm x 1.52 m long were driven through the sand for their full length and a timber framing of 76 x 64 mm purlins and 76 x 50 mm rafters were nailed on to them. This framing was then covered with 2.44 x 0.91 m corrugated iron sheets secured by means of drive screws round their edges (Rose, 2000). Rainwater flowed from the sheets into reservoirs inside the rock, via tunnels (figure 3.1). These catchments have contributed a declining percentage to the total potable water supply due to increasing maintenance costs. On a cost per m^3 basis, maintenance costs made the corrugated iron catchments the most expensive source of potable water supply in Gibraltar and so their use was discontinued in October 1993" (Rose, 1998).

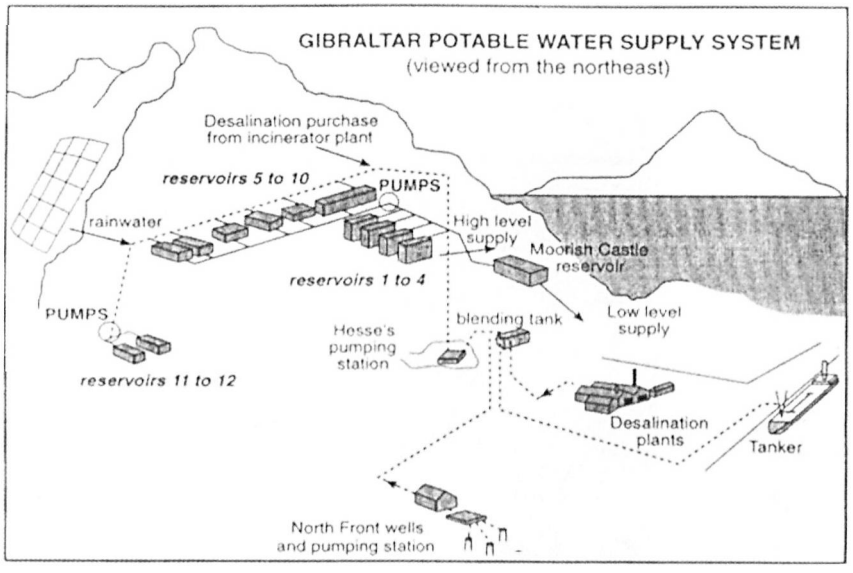
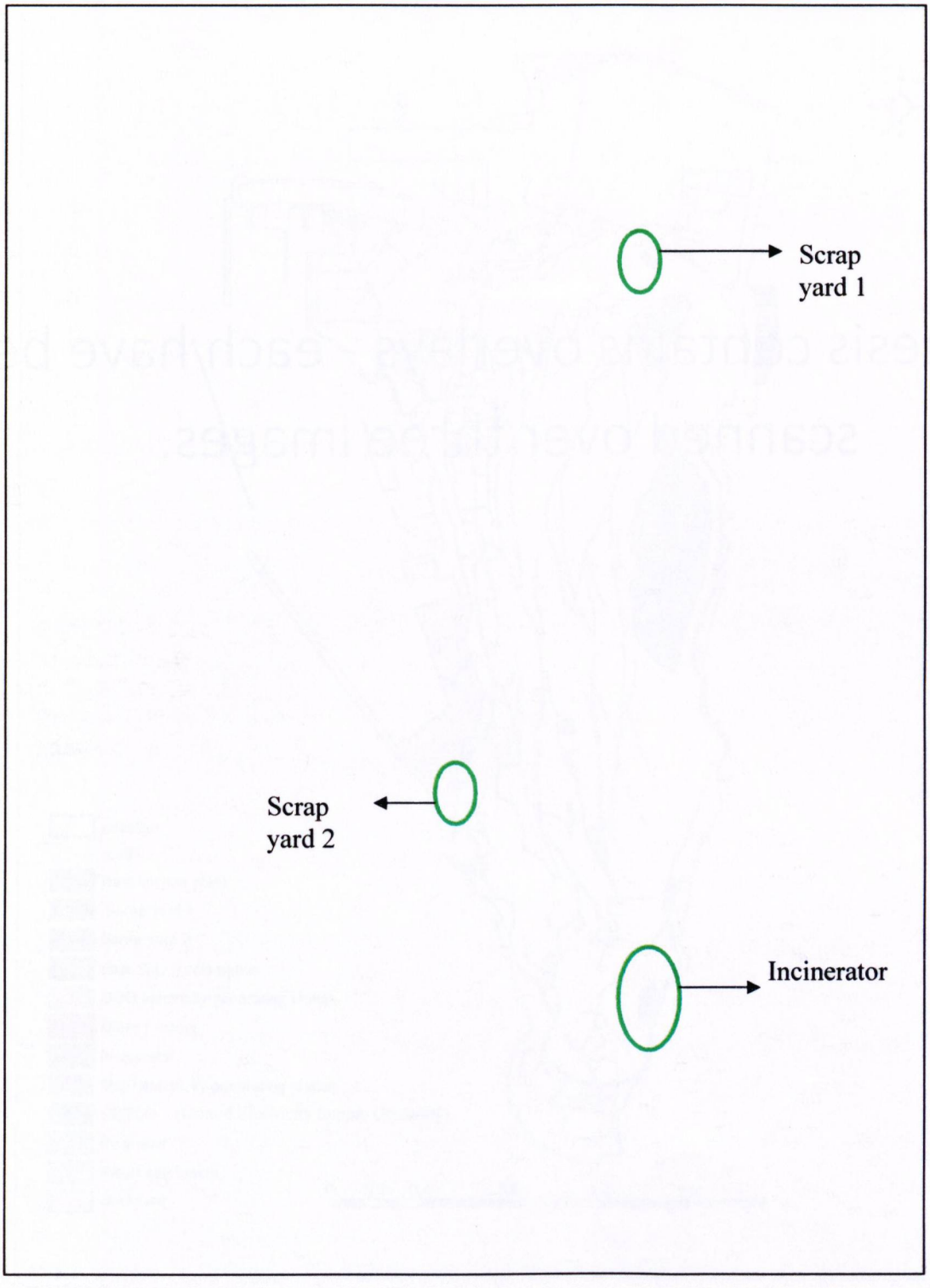


Figure 3.1 Gibraltar's potable water supply system.
Source: redrawn by Rose (2000).

The many faults and joints found on the Gibraltar limestone make it permeable to groundwater. Groundwater was discharged through springs, which ran along the western part of the north face and to the east and south east of the current town area. Wright *et al.* (1994) identified an aquifer within the bedrock of the Rock, as a thin lens of fresh water overlying seawater. Similarly, two aquifers were identified in 1933 in the Quaternary sands by the airport, namely, a top unconfined aquifer of fresh water and a lower confined aquifer with brackish water.

Recharge rates for the bedrock aquifer were estimated by Wright *et al.* (1994) to be around 400,000 m^3 per annum. The demand for fresh water supply in Gibraltar is round 1,000,000 m^3 per annum. Approximately 10% of Gibraltar's potable fresh water supply comes from 19 wells, which go into the top "airport" aquifer. The main bulk of the potable fresh water supply (90%) comes from the desalination plant. The water comes from two multi-stage flash distillation and two reverse-osmosis plants (Rose, 1998). Seawater is pumped and distributed to houses for flushing toilets, street cleaning, and is also used for fire fighting and for any other uses where fresh water is not needed.


Scrap
yard 1
Scrap
yard 2
Incinerator

3.6 The Anthropogenic Environment

3.6.1 Incinerator

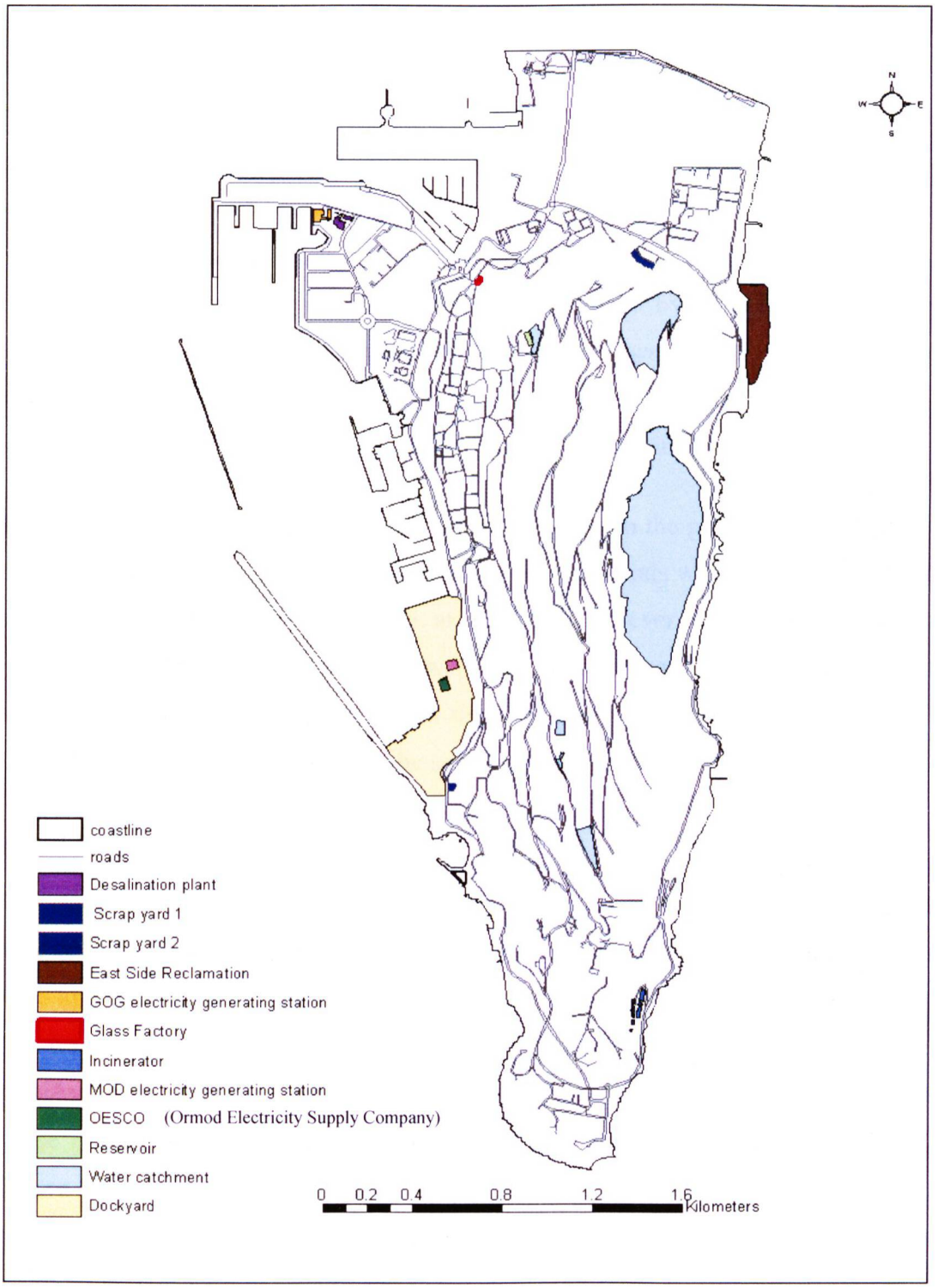


Figure 3.2 Industrial locations in Gibraltar.

The incinerator located in the south east of Gibraltar (figure 3.2) is the third constructed in Gibraltar, and is no longer in operation. It was in operation

3.6 The Anthropogenic Environment

3.6.1 Incinerator

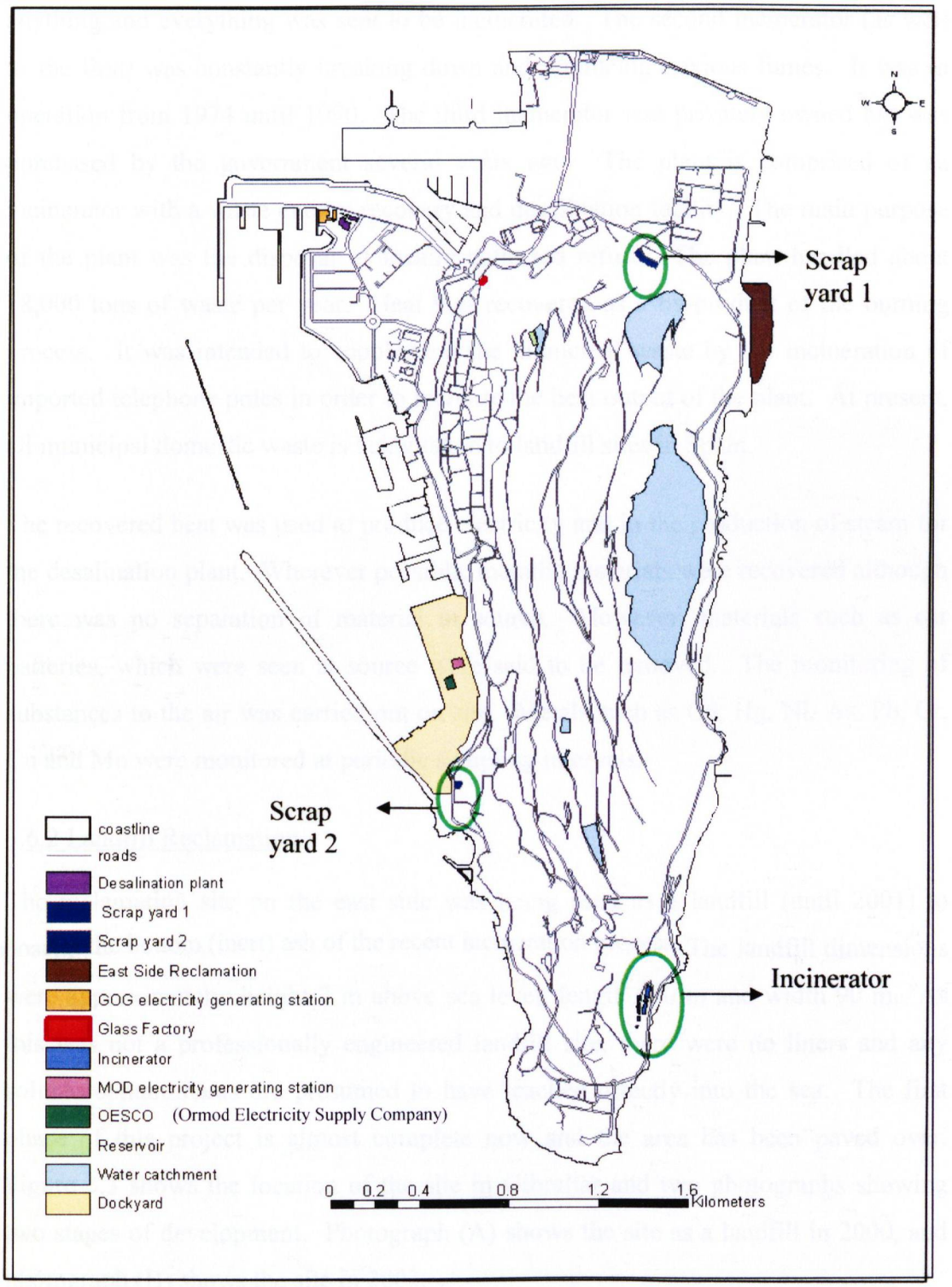


Figure 3.2 Industrial locations in Gibraltar.

The incinerator located in the south east of Gibraltar (figure 3.2) is the third constructed in Gibraltar, and is no longer in operation. It was in operation

from 1992 until April 2000, when it was closed down because the emissions were exceeding air quality standards. The first two have been described as environmentally unfriendly in the sense that there was no separation of material at source, similarly anything and everything was sent to be incinerated. The second incinerator (as well as the first) was constantly breaking down and producing noxious fumes. It was in operation from 1974 until 1990. The third incinerator was privately owned but was purchased by the government several years ago. The plant is comprised of an incinerator with a waste energy recovery and desalination facility. The main purpose of the plant was the disposal of locally collected refuse. The plant handled about 18,000 tons of waste per year. Heat was recovered as a by-product of the burning process. It was intended to supplement the municipal waste by the incineration of imported telephone poles in order to increase the heat output of the plant. At present, all municipal domestic waste is being taken to landfill sites in Spain.

The recovered heat was used to produce electricity and in the production of steam for the desalination plant. Wherever possible, metallic materials were recovered although there was no separation of material at source. However, materials such as car batteries, which were seen at source were said to be removed. The monitoring of substances to the air was carried out on site. Metals such as Cd, Hg, Ni, As, Pb, Cr, Cu and Mn were monitored at periodic sampling intervals.

3.6.2 Landfill Reclamation

The reclamation site on the east side was being used as a landfill (until 2001) to dispose of the bottom (inert) ash of the recent incineration process. The landfill dimensions were approximately: height 7 m above sea level, length 600 m and width 90 m. As this was not a professionally engineered landfill site, there were no liners and any soluble contaminants are presumed to have leached directly into the sea. The first phase of this project is almost complete now and the area has been paved over. Figure 3.3 shows the location of the site in Gibraltar and two photographs showing two stages of development. Photograph (A) shows the site as a landfill in 2000, and photograph (B) shows the site in 2003.

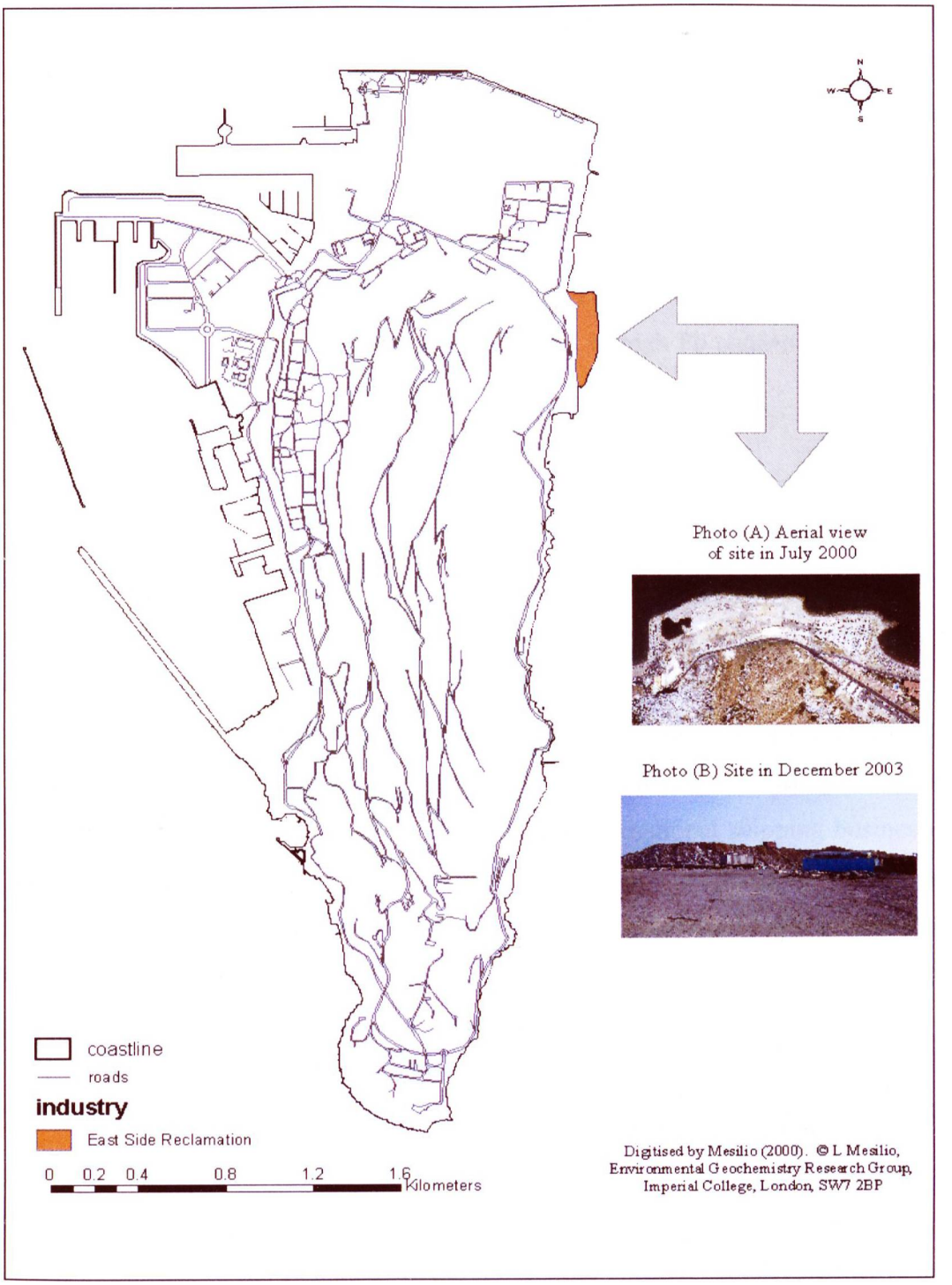


Figure 3.3 East side reclamation site in Gibraltar.

3.6.3 Ministry of Defence (MOD)

The rifle ranges used by the MOD are a potential source of lead contamination. In the 300 years of British occupation of Gibraltar, the MOD has never remediated land, that is to say, they have never disposed of or picked up any materials, ranging from

scrap metal to canons which are no longer in use (Carter, personal communication). However, in September 2003 the MOD Defence Estates commissioned a detailed investigation into the impact of MOD activities in Gibraltar on groundwater quality - to contribute to a wide reaching strategic Land Quality Assessment of MOD facilities in Gibraltar (Rose, personal communication).

Gibraltar has several rifle ranges, ranging from MOD sites to those belonging to the local Gibraltar Rifle Association. These could result in high Pb concentrations in the soils.

3.6.4 The Dockyard

Gibraltar's position has always been a key location for maritime activity. For centuries it was the most strategically important naval harbour in the western Mediterranean. Today this location, together with the accumulated maritime skills of its workforce, is being used to turn it into the region's premier shipping centre. In order to do this, public and private facilities are being improved while the government ensures that a modern legislative framework allows international shipping businesses to thrive. In changing with the times, Gibraltar provides a wide portfolio of maritime services that meet the needs of today's industry. These range from ship registration to ship repair as well as the provision of supplies and spares for ships. Gibraltar also caters for all aspects of leisure cruising and yachting activities.

Gibraltar's impressive harbour is one of its major assets. Today, its position on one of the world's busiest shipping lanes allows the commercial port to act as an important service centre for the international merchant fleet and also to offer the cruise industry an exceptional destination and hubbing port (web reference 4). In 1999, 2.67 million tonnes of bunkers were delivered to over 3200 vessels (web reference 4). Gibraltar also has a very busy cruise terminal, where in 1999, 173 cruise ships docked (web reference 4).

Within the dockyard area itself general underwater repairs are undertaken including underwater welding, cutting and patching, underwater hull cleaning and propeller polishing and the disposal of sludge and slops from the ships. The nature of these

sludges and slops, and the method of disposal were not stated in the information provided by the port services. There are also dry docks where ship repairs and maintenance are carried out. Potential sources of pollution occur from the removal of old lead bearing paint from the hulls of ships using sand blasting and also, the application of anti-fouling paints and slimicides.

Each year over 80,000 ships pass through the Straits of Gibraltar making the bay a central point for ships seeking bunkers or provisions. The bunker market is very competitive and Gibraltar now ranks among the world's leading bunker ports. In 1996 around 1.7 million tonnes of bunker fuel was supplied. This has led to some oil spillages. Between 1998 and 2004, sixteen spills have occurred, two of them occurred on the Spanish side of the Bay of Gibraltar. All spills, including the Spanish, totalled to 4,750 litres of oil into the marine environment. There is also a ship-repair facility, which is run by Cammell Laird. The yard, originally a Royal Naval Dockyard, was built in the 1890s to repair ships in the Home and Mediterranean Fleets of the Royal Navy. It is equipped with three dry docks, the largest able to accommodate the bigger ships which are able to transit the Panama Canal.

3.6.5 Electricity Generation

There are currently three generating stations on the Rock. One belongs to the MOD and is on MOD property. The second belongs to the Ormrod Electricity Supply Company (OESCO), a private company, which is contracted to the government, and the third is situated in the North Mole area of Gibraltar and is government owned. This station has been running on distillate fuels since 1990. Rimula oil has been used since 1999, which is a straight mineral oil, as opposed to the Shell Argina S30 oil which was previously used which contained certain additives. The additive oils are used on engines running on heavy fuels whereas the mineral oils are used with low contamination fuels. Calcium, Mg and Zn are elements included in the additive packs, although they are usually in the form of hydroxides or phosphates. This is said to be the reason for the relatively high concentrations of these elements found in the lubricating oils used (Aguilera, personal communication).

3.6.6 Scrap yard

There are currently two scrap yards in Gibraltar (figure 3.2) and both are owned by the company, Metalrock. All types of metal scrap are kept at these locations where they are periodically compressed and subsequently sent abroad for disposal and/or recycling.

3.6.7 Former industrial activity - Gas works plant (location not shown on Figure 3.2)

The following information was obtained from Barton (personal communication) an engineer who worked at the plant. The information was obtained from memory, some 50 years after the gas works plant closed and may contain errors but on the whole is considered to be of potential use to the possible effects of previous anthropogenic activity on element concentrations in soils. The City Council of Gibraltar operated the manufacture and distribution of gas. The plant was situated in the area known as Rosia, below what is now known as Vineyards estate and closed down in the 1950s. The manufacture of gas was abstracted from coal by a distillation process from diesel oils. The coal was imported from the UK via ship, unloaded at the harbour and transported to the gasworks site where it was stored at a higher level behind the abstraction plant. Once the gas was abstracted, the resulting material was clinker and ash in which the majority is believed to have been disposed of via dumping at the foreshore. The gas was then distributed in cast iron pipes, buried under the surface of roads throughout Gibraltar. No monitoring of possible organic or inorganic contamination as a result of the manufacture and distribution of gas is believed to have occurred.

3.6.8 Tourism

The number of tourist arrivals via motor vehicles in Gibraltar in 1999 was 1,242,452 and the number of coaches was 11,987. These figures, when added to the high number of existing vehicles owned by the local population (at least 1 car per family and 1 or 2 motorcycles per family). This large number of vehicles in a small area would be expected to result in a Pb rich environment as leaded fuel is still in use in Gibraltar. The Pb content of unleaded fuels is c. 0.003 g/l and 0.15 g/l for leaded fuel (Lugnani, Personal communication).

The Rock has enormous tourist potential. As well as having cheap shopping facilities, it also has an interesting military history. Colonial, Spanish and Moorish styles of architecture can be seen throughout Gibraltar. There is also an abundance of rare birds and plant species. Wrecking- diving (artificial reefs made out of sunken ships) sites are available and when out at sea vast schools of dolphins can be seen skimming The Straits. Much of Gibraltar's potential has been under-exploited; therefore the government identified four priority areas for action: (Burns, 2000)

1. The Cruise Liners market
2. The day visitors
3. The tourists on short breaks
4. The people on business conferences.

Success in the industry is shown by figures such as 4,000 000 visitors via land alone in 2002. A large number of the visitors to the Rock cross the land frontier on a single entry basis in order to fill up their vehicle tanks with petrol which is cheaper in Gibraltar than in Spain. Once at the petrol stations, they also contribute to the economy by purchasing the odd product, for example, tobacco, spirits and groceries.

Among the government's short-term aims, there are plans to increase the number of hotel beds, of which there are 12,000 at present. The availability of rooms is a strong limiting factor when trying to develop tourism and thereby keep visitors on the Rock. Lack of accommodation deters companies from considering Gibraltar as a venue for business conferencing.

It is also proposed to use Gibraltar as a base for "2 continents - 3 country" experience rather than just for a day trip. Airlines can fly only to the United Kingdom because Spain voted Gibraltar out of all air liberalisation packages since they joined the EU. There are also other considerations that must be taken into account which deter airlines from using Gibraltar as a route. These are that the Gibraltar airport is more expensive to land on as opposed to Malaga or other neighbouring airports in Spain because the landing strip is on MOD property and the MOD landing charges are very high. In the past, the Government entered into negotiations with the MOD to take over the running of the runway in some manner these failed possibly because the

maintenance costs for the runway were too high. Nevertheless, the air terminal is under private management.

An interesting factor to be taken into account is that in Gibraltar, road traffic as well as pedestrians travel across the runway. If there is an increase in air traffic to Gibraltar, this will create a problem of congestion simply because vehicular and pedestrian movement would practically come to a halt. Possible solutions could be either underground tunnels beneath the airstrip, or roads which could go around the airstrip, either to the east or to the west of it. Both these solutions would however be costly. Traditionally there has been a lack of statistics from tourists as to what they find enjoyable and/or interesting about Gibraltar. The government is now starting to gather information through a visitor information patrol who are responsible for the collating of data as to the reasons why visitors have chosen to see Gibraltar. Some data were available in the past, but it was sporadic and small, now much larger samples are being obtained.

A point to take note of is the possible effects of increasing tourism on the natural ecosystems in Gibraltar and how this would in turn affect issues related to sustainable development.

3.6.9 Banking and Insurance

Gibraltar is very well placed to serve the expatriate market, which resides along the Spanish East Coast. As a safety net, the business of servicing the Costa del Sol's wealthy non-Spanish population could hardly be improved upon. Lawyers in Gibraltar are also kept busy catering for the legal requirements of property owners who possess or acquire their properties via a Gibraltar registered company. A vast majority of non-resident companies on the Rock are completely innocuous and have very little activity because they are merely a device for getting round legislation, such as Portuguese inheritance laws and property transfer taxes (Burns, 2000). In the UK, the report of the Chancellor of the Exchequer on the "Offshore Business Independent Territories", Gibraltar was singled out as the example to follow.

3.7 Industry across the Bay of Gibraltar

An industrial complex can be found in neighbouring Spain. The main industries of concern regarding possible contamination into air, water and soils in this area include:

1. Acerinox - a steel and aluminium metal smelting plant
2. An electricity generating station
3. Celupal - a paper processing plant
4. A coal processing plant
5. Cepsa oil refinery.

Plate 3.2 and figure 3.5 show the locations of the industrial and military locations in the bay.

3.8 Waste Disposal

Waste products from Gibraltar which could not be incinerated for whatever reasons were originally dumped at sea. From 1845 a rubbish dump was marked out at the area known as "Four Posts" on the isthmus. This area has since then been built over for the airfield and associated buildings. Until recently, unserviceable motor cars and other large items of non-combustible waste were jettisoned from an area known as the Europa Flats at a car chute on the east coast. Tunnel spoil and some building wastes have been used for land reclamation from the sea, but there are currently no landfill sites for waste disposal as such. Incineration has long been used for disposal of combustible waste. The Gibraltar Ornithological and Natural History Society (GONHS) (personal communication) stated that the incinerator "does not work well (it often breaks down), emits fumes and questionable fluids and toxic fly ash that no one knows how to dispose of". Some of this waste has been locked away into the many tunnels inside the Rock. The adjacent disused "Europa Advance Quarry" was being used for temporary storage of waste, pending incineration. Gibraltar government engineers are more sanguine in their perception than GONHS, whose views are disputed (Rose, 1998).

3.9 Future Prospects and Economic Strategy

The Rock of Gibraltar has a promising future ahead as the government and various business enterprises plan to exploit fully the vast potential the Rock has to offer. Part of this future is as a financial centre delivering tax efficient investment services

throughout the Euro-zone. Gibraltar is no longer being viewed as has been the general consensus in the past by the outside world, as a repair dockyard for Royal Navy vessels on their passage through the Mediterranean, or as meagre refuelling stopover location.

An agreement between the UK and Spain, which took place in 2002, meant that the Gibraltar government can finally introduce EU directives (Burns,2000). One of the key outcomes of this agreement is the acknowledgement of Gibraltar's financial regulators as being the capable authorities to implement them, thereby allowing Gibraltar to develop its own economic strategy. The government of Gibraltar states that this agreement has justified its claim that it is a mainstream territory, which fully complies with all matters related to the financial sector with supervision standards that are second to none (Burns, 2000).

The UK government's opinion on Gibraltar is that it is now a benchmark for financial regulation in other UK dependent territories (Burns, 2000). The present chief minister of Gibraltar, Mr Peter Caruana, states that his government (centre-right) has encouraged sustainable and diversified prosperity driven by three main pillars in the shape of financial services, tourism and shipping (Burns, 2000). Whilst the MOD now has a diminished presence on the Rock, a new "player" in Gibraltar's sphere of business activities, electronic gaming, appears to be a possible fourth economic pillar. Gibraltar has changed substantially and has developed an indisputable attitude of self-assurance. Gibraltar has almost full employment and increasing developments on reclaimed land appears to be solving the constant housing shortage. This inhibited the general development of Gibraltar for a long period of time.

Gibraltar's population at around 33,000 is less than half that of the neighbouring Spanish town of La Linea, and the land area of Gibraltar is a quarter of the area of San Roque, its main neighbouring municipality. Despite this however, there is no doubt that its very strong national identity and pride drives an intense debate over Gibraltar's right to self-determination. The two tasks identified by Mr Caruana for Gibraltar are as follows: one is to adjust to the several initiatives, backed by bodies such as the International Monetary Fund and the Organisation of Economic Co-operation and Development. These bodies seek to function in offshore banking

centres and diminish what are known as "damaging" tax systems that deform international capital flows. The other is to modernise the relationship between Gibraltar and the UK. Gibraltar considers it to be in its best interest to maintain British sovereignty but to end the colonial status of the Rock. Models for this new constitutional arrangement include those of the Isle of Man and the Channel Islands. The ending of the colonial status of the Rock remains however a complex issue. Under the Treaty of Utrecht (1713) the only formal title to Gibraltar by the UK is that of a crown colony and under the terms of this treaty, Gibraltar would have to revert to Spain if it were to cease being a colony. The future political situation of Gibraltar and its effect on sustainable development can however, only be speculated.

3.10 Chapter Conclusions

Gibraltar is situated in latitude 36°7'N longitude 05°21 and stands out steeply and suddenly, from the adjoining low-lying Spanish Territory to which it is connected by a sandy isthmus about one mile long and half a mile wide. Five miles across the Bay of Gibraltar to the West lies the Spanish port of Algeciras and 20 miles across the Strait to the south of Africa.

The Rock runs from north to south for a length of 5.2 kms. Although there has been a land increase due to reclamation, the use of square miles as a measurement of area does not reflect this difference or increase. Its highest point is 424 m above sea level. The top of the Rock is a sharp, knife-ridge extending for about a mile and a half from the north escarpment, which is virtually inaccessible, and then sloping gradually to the south for about a mile, to terminate at the southern extremity, Europa Point, in perpendicular cliffs about a hundred feet high. The upper length of the eastern face is inaccessible and the steep upper half of the western slopes is uninhabited and has been designated a nature reserve.

Gibraltar's sub-tropical climate supports over 600 varieties of plants and trees. In the spring and autumn the Rock is a staging post for millions of migrating birds. There are no permanent natural water supplies in Gibraltar, main sources used to be the water catchments on the rock face, which collected rainwater and supplied the reservoirs hollowed out inside the Rock, and wells on the sandy plain to the north.

The main supply is currently provided by AquaGib Ltd through an efficient number of distillers, distilling sea-water located at the North Mole.

Vegetation in Gibraltar is rich and varied on the western upper slopes and in the Alameda Gardens. The Gibraltar limestone is formed from the mineral calcite ($CaCO_3$), with dolomite or dolostone, composed in significant proportions of the mineral dolomite ($CaMg(CO_3)_2$) (Rose and Hardman, 1995). The bedrock of Gibraltar (which lies beneath extensive Quaternary deposits) can be described in terms of two main rock types, limestone and shales.

The population concentrates mainly of the western side of the Rock resulting in the densely populated town area and in the slightly more spacious residential estates which have been developed to the north of the town. More recently the large harbour reclamation (over 30,000 sq metres) has permitted further land to be developed for large scale housing projects. On the east side of the Rock is Catalan Bay, a small village, with some 350 inhabitants.

The natural features of Gibraltar preclude all possibility of agriculture and major industrial production. Gibraltar is however admirably suited and situated for the development of a flourishing tourist trade as well as a financial centre delivering tax efficient investment services throughout the Euro-zone.

Plate 3.1 Gibraltar and the Bay

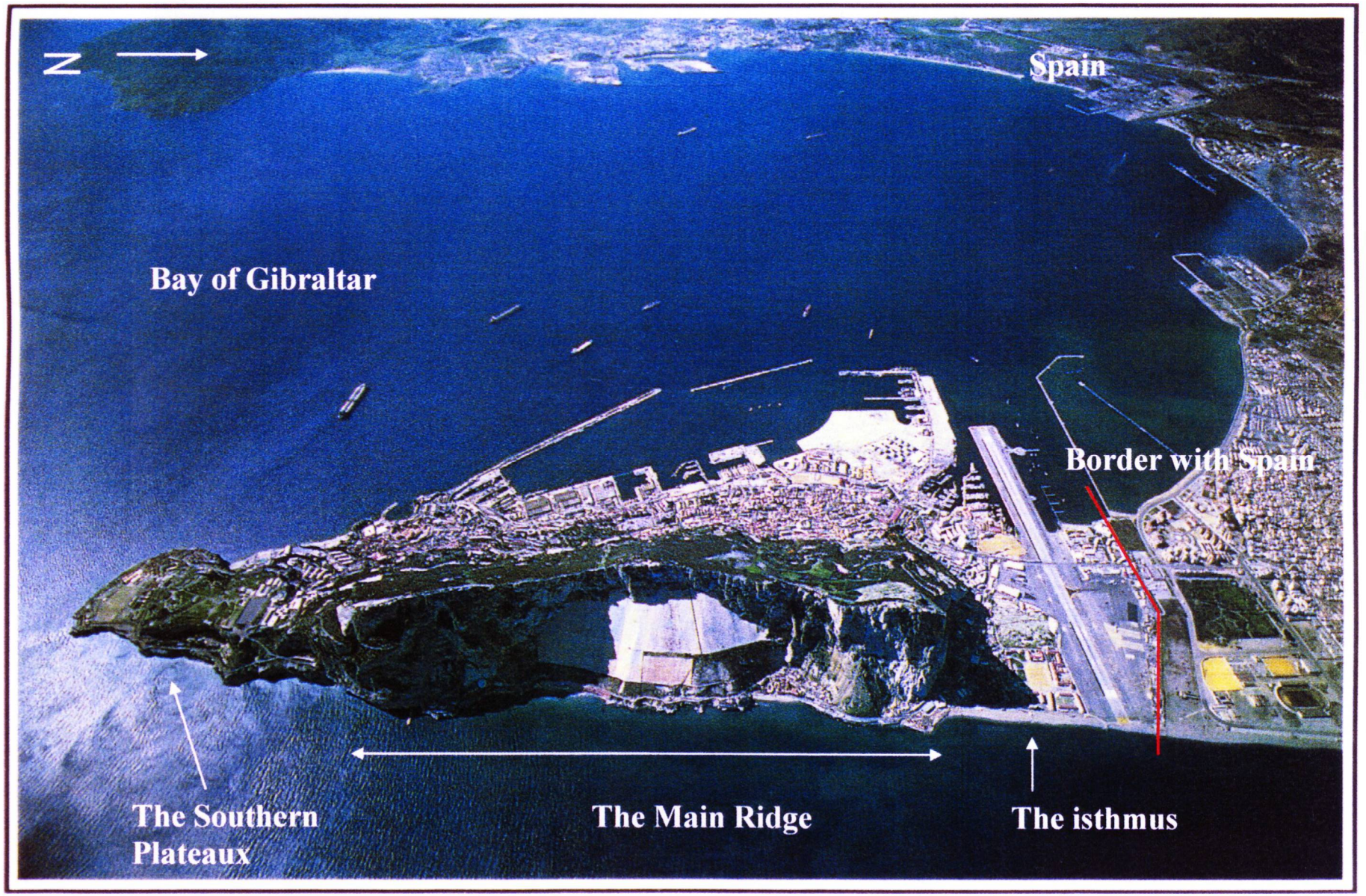


Plate 3.2 Gibraltar

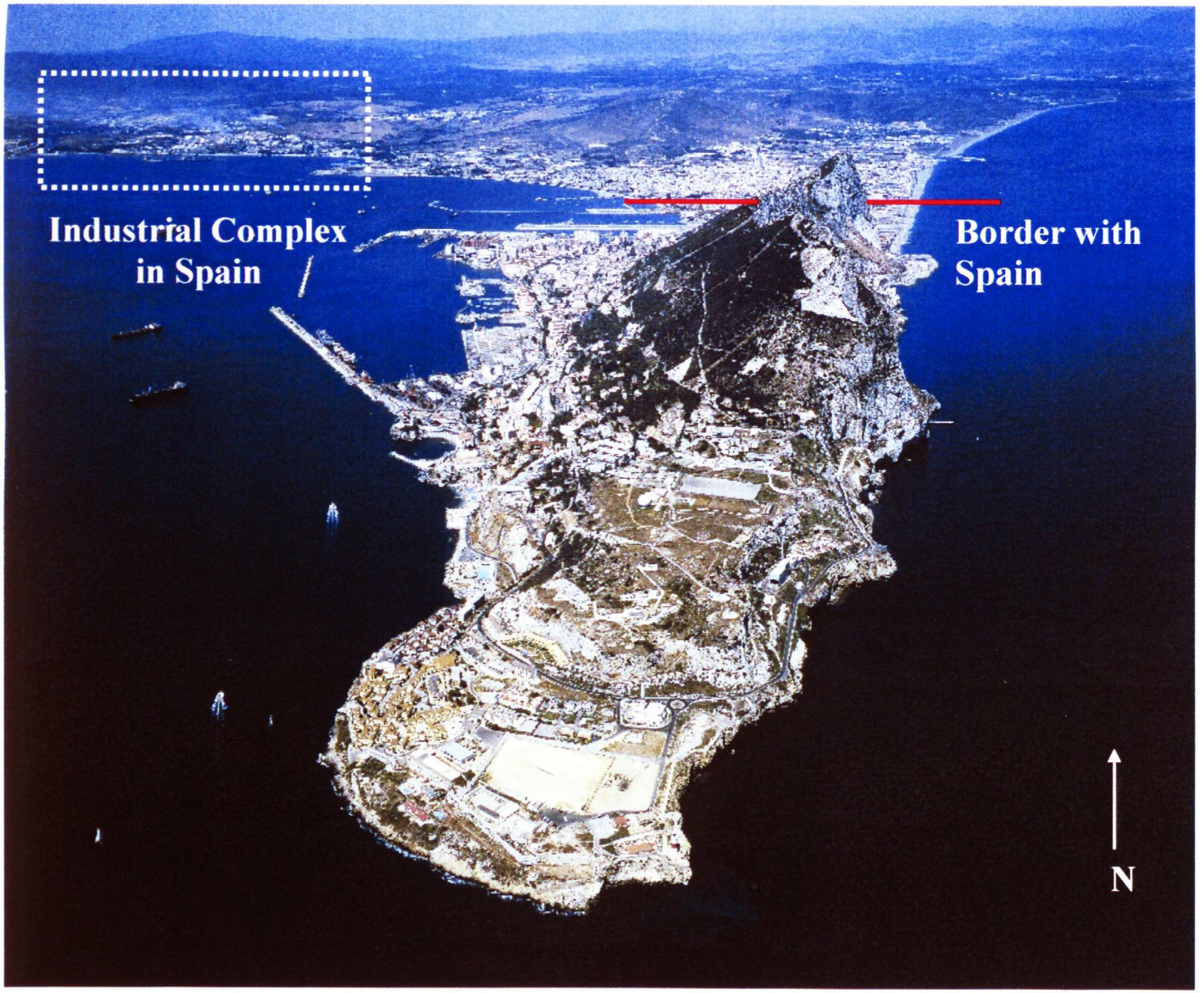


Figure 3.4 (a) Map of Pre-Quaternary Geology of Gibraltar (Rose and Rosenbaum, 1991)

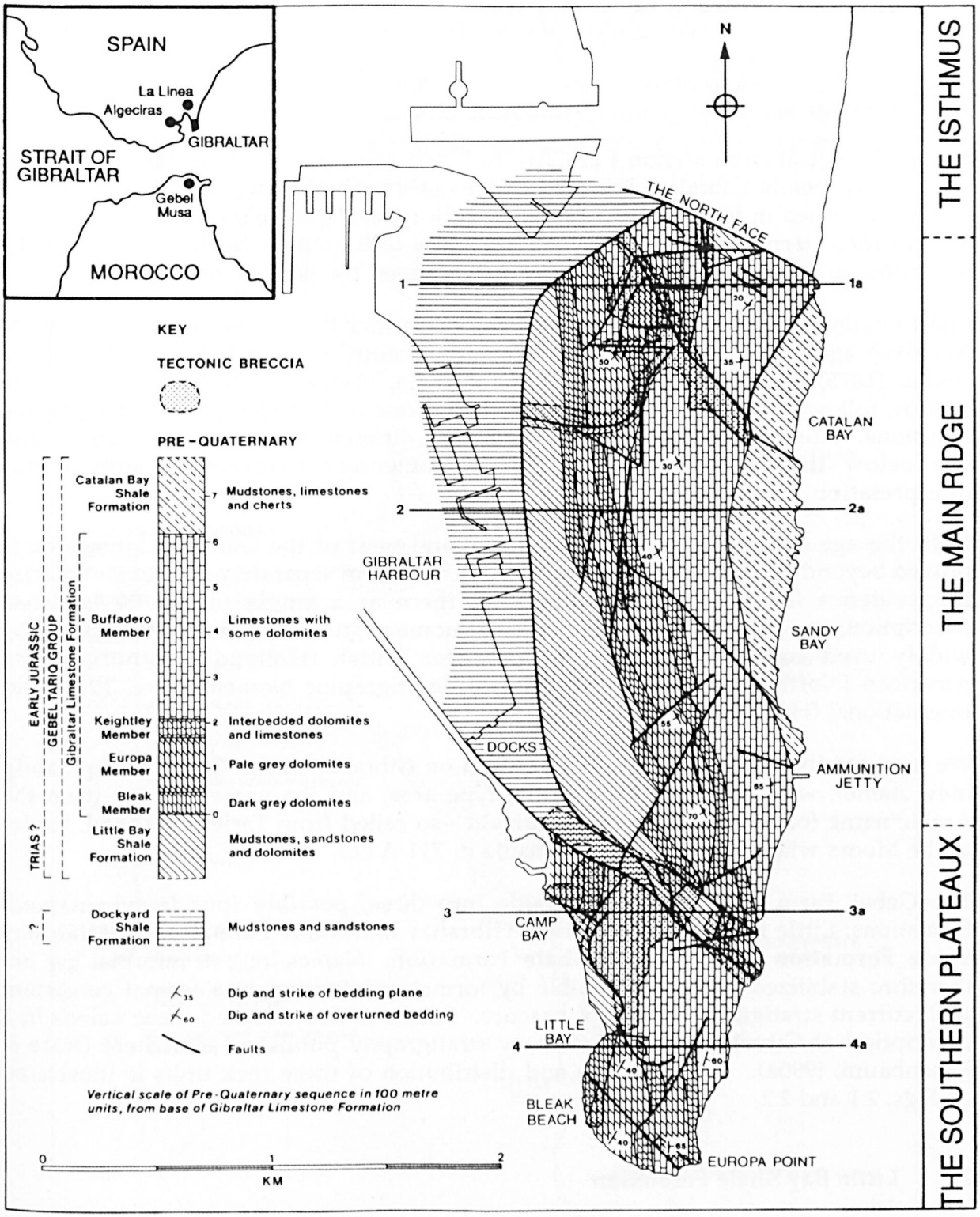


Figure 3.4 (b) Map of most widespread Quaternary sediments on Gibraltar (Rose and Rosenbaum, 1990b)

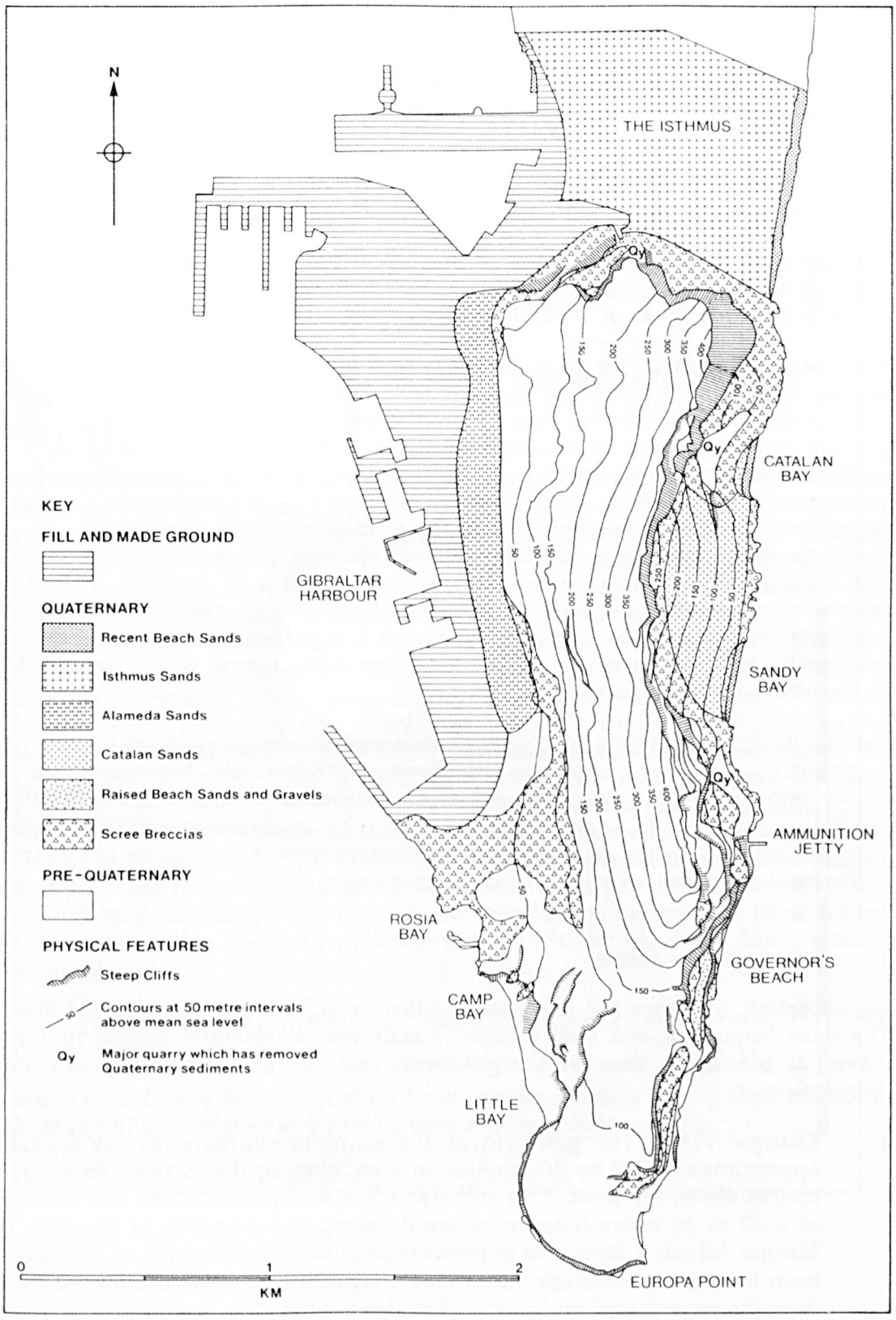
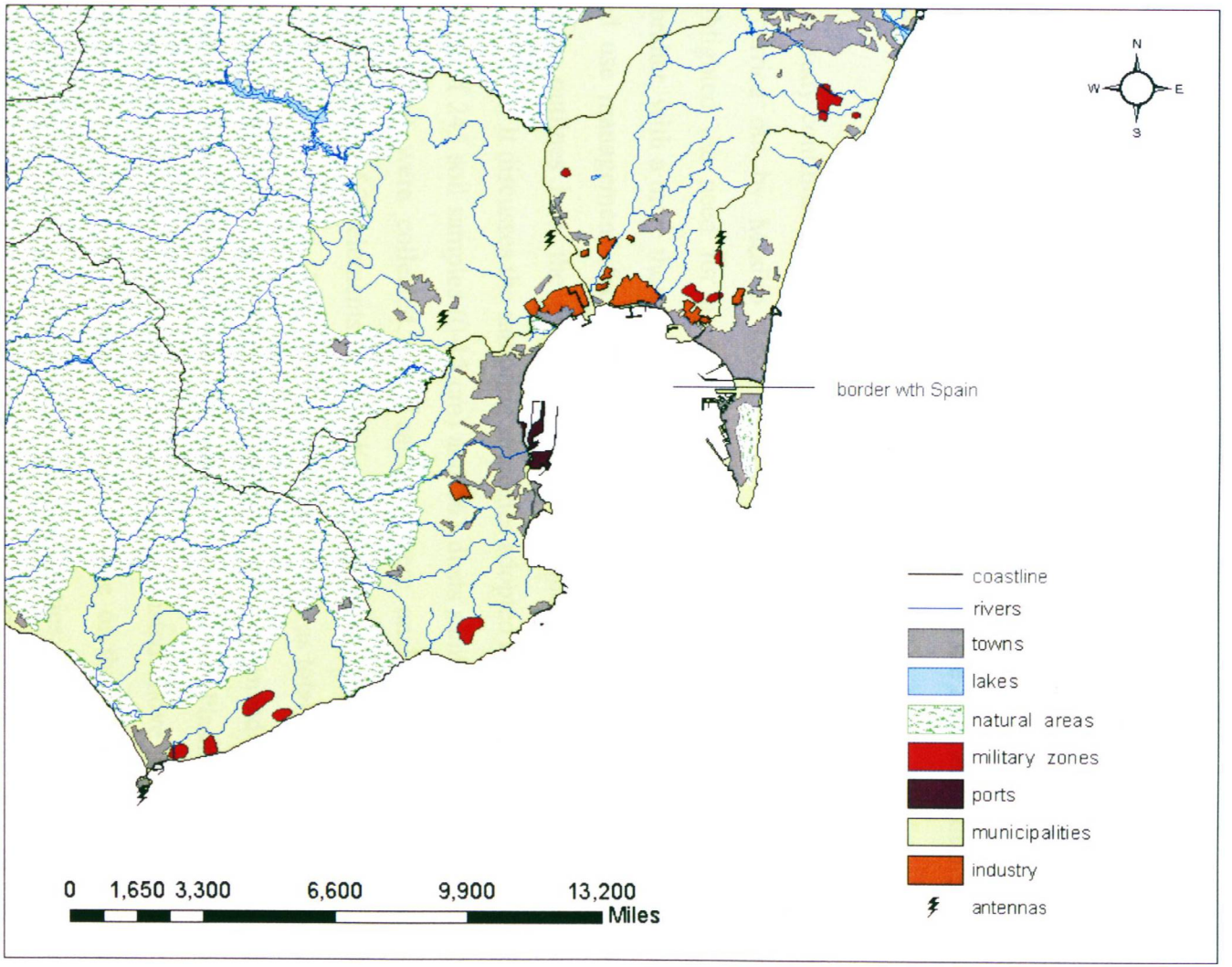


Figure 3.5 Schematic representation of industrial locations in Bay of Gibraltar
Source: modified from Digital Map of Andalucia : Junta De Andalucia (1999).



CHAPTER 4

Sampling and analytical procedure

4.1 Introduction

In order to obtain quantitative data on element concentrations in different environmental media (soil, air, water, dusts, flora and fauna), measurements of these variables must firstly be made. Sampling and analysis are the means through which such measurements are made.

This study continues from a reconnaissance soil survey of Gibraltar (refer to chapter 1) carried out by Mesilio (2000). The results from the initial reconnaissance highlighted the need for a more detailed baseline survey of soils and dusts in Gibraltar, with a more thorough statistical and spatial analysis. This will assist future land use management if compliance with EU directives is to be achieved. This chapter outlines how the practical side of the investigation was approached and carried out. It discusses the sampling strategies adopted and the analytical work done. A total of 245 soil samples (0-15 cm) and 163 dusts samples (80 house dusts and 83 street dusts) were collected. All samples were analysed for "total" elemental concentrations of 26 elements (Li, Na, K, Be, Mg, Ca, Sr, Ba, Al, La, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb, P, S, As), as well as total organic carbon content and pH. The "total" elemental concentrations were determined by ashing in a nitric perchloric acid mixture followed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analysis. The 26 elements listed above represent the multi-element range available from the ICP-AES. One of the limitations of ICP-AES analysis is the inability to distinguish different species of the same elements. This then means that a) the more soluble and potentially bioavailable fractions of elements are not identified by this method and b) organic compounds of an element are not included, and there is a risk that potential contamination may not be detected. Testing for organic compounds would have involved further laboratory analysis. Financial as well as time-related restrictions meant that this was not possible.

Selected samples were then chosen for sequential chemical extractions in order to assess solubility and potential bioavailability of these samples. Table 6.1 summarises the different media sampled in this research.

4.2 Sampling Strategy

4.2.1 Sediment and soil sampling

The purpose of a sampling strategy is to try and obtain measurements with low bias and high precision[1], the reason for this being to be able to check compliance with environmental quality standards (EQS), test the hypotheses and understand spatial and/or temporal patterns. A carefully developed sampling strategy is a crucial part of any geochemical investigation. If the sampling strategy is poorly designed or too sparse, it may not be a true representation of the entire site and it increases the likelihood of contaminated areas being missed. Equally, over sampling is costly, impracticable and can still be ineffective. An efficient sampling strategy should be stratified with each stratum having one sample location. It should also be systematic and unaligned (Ramsey, 1997; Shaw, 2000).

The sampling strategy in itself constitutes a source of error, both systematic and random. These errors cannot be avoided entirely, but steps must be taken to reduce them to a level where they do not significantly influence the scientific outcome (Ramsey, 1997). The most basic aim of any sampling strategy should be to provide measurements that accurately reflect the true mean value of an environmental variable. Other aims usually are to determine spatial and temporal distributions of the variable. With these objectives in mind a basic sampling check list should be based on the following (Ramsey, 1997; Shaw, 2000):

1) Define the objectives of the survey.
2) Formulate hypotheses or define appropriate EQS.
3) Determine the media to be sampled.
4) Define the sampling "population" of interest and the "sample units" which make up this population (e.g. in a contaminated land survey define the boundaries of the

[1] Definitions provided in section 2.2.1

area of interest and the area over which individual samples will be taken – e.g. from a 1 m^2 quadrat).

5) Determine the variables to be measured and the analytical techniques required
6) Determine the type of sampling strategy (random, systematic, judgmental and stratified).
7) Implement a method of quality control to determine:
    - how the quality of the sampling can be estimated
    - what levels of sampling errors are acceptable
    - what scheme of sample identification is to be used (as part of a quality assurance scheme for monitoring sample progress)
8) Carry out a pilot study if possible or a desk-based background survey - *prior knowledge* of values and distributions of variables can be gained from:
    - a pilot study
    - a review of site/case history
    - access to existing data bases
    - interrogation or elicitation of "experts"

There is no universal protocol which meets the requirements of every analytical investigation. It is therefore crucial that the sampling checklist outlined above be used as a guide and that established methods are adapted if necessary to meet conditions encountered in the field. A number of problems exist when sampling in urban areas which are linked with the built up environment. Adhering to a pre-defined sampling strategy in Gibraltar can often be difficult due to restrained access to private property or MOD areas, and the lack of suitable sampling sites in heavily developed areas close to city centres (Kelly *et al.*, 1996). A number of uncertainties also exists regarding the history of land use at particular sites, and the actual origin of the topsoil which has been sampled. These factors emphasise the importance of measuring sampling quality (Kelly *et al.*, 1996).

4.2.2 Sampling strategy adopted in Gibraltar

Gibraltar has an area of 6.5km^2. The nature of the topography in Gibraltar means that a grid pattern can be applied only on the Southern Plateaux area (plates 3.1 and 3.2). This is due to a number of factors including slope, vegetation cover, density, and land

use. Additionally large areas of Gibraltar have been paved over and as stated in Chapter 3; continuous areas where soil depth is greater than 30 cm are limited.

The sampling strategy was initially based on a desktop study of Gibraltar. This involved a thorough review of the site history of military and civilian areas from Dennis (1990) and Hughes (1995) and a review of the geology by Rose and Rosenbaum (1991). Any potentially contaminative uses (past and present) of the land were investigated. This was done by reading the existing literature and interviewing people within various government departments. Also interviewed were members of the public such as academics, historians and people who worked in certain types of industry such as the old Gasworks Plant. A review of the geology was obtained from the literature, including, most importantly, the work of Rose and Rosenbaum (1991). A site reconnaissance was also conducted to identify any site hazards such as derelict buildings or naturally unsafe areas, such as, cliffs. This information was used to form an initial working hypothesis and to aid the sampling strategy which was adopted.

Other sources of information used in this investigation included written and verbal historical accounts of industrial, waste disposal and MOD activities. Additionally the local environment agency and members of the Gibraltar Ornithological and Natural History Society (GONHS) have proven essential, not only formulating a sampling strategy, but also in aiding the interpretation of the analyses.

Soil samples for the reconnaissance soil geochemical survey (Mesilio, 2001) were taken from as wide a range of exposed sites as possible, either bare soil or vegetated, in order to provide the optimum geographical distribution (Mesilio, 2001). Further sampling continued as much as possible in a pre-determined judgemental fashion. This entailed further surface and sub-surface (>20cm depth) soil sampling (aimed at increasing the sample density across Gibraltar as conducted during the reconnaissance survey), house and street dust sampling and limited rock sampling. The amount of land occupied by the MOD, combined with the limiting factors mentioned above, such as the nature of urban regeneration and sprawl, meant that on occasions, planning a sampling strategy for certain areas was extremely difficult.

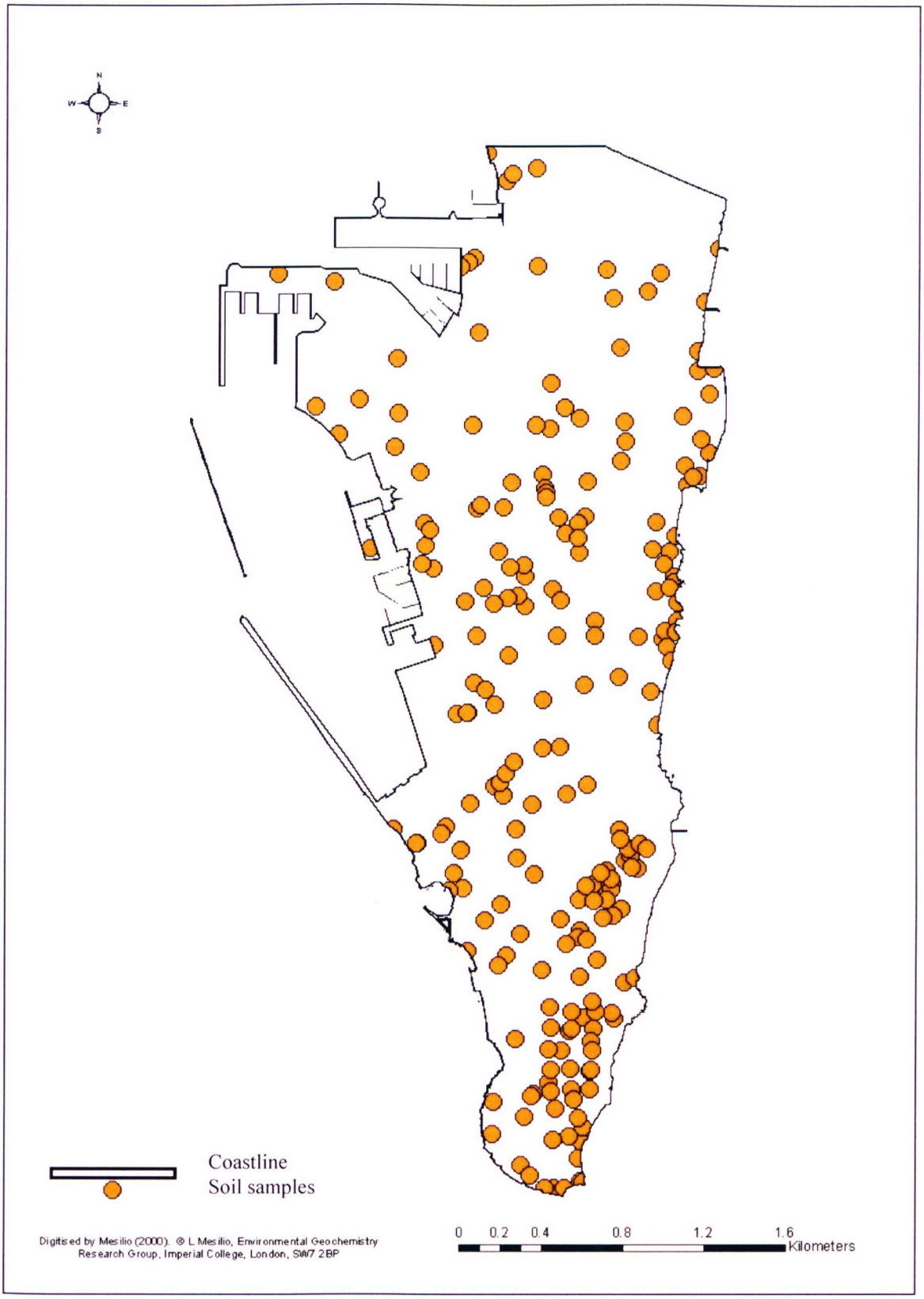


Figure 4.1 Soil sample locations in Gibraltar (n=246)

Sampling took place over a five week period, and usually at the discretion of the owner or occupier of the areas in question. Figure 4.1 shows the soil sampling

locations in Gibraltar. Every tenth sample was taken in duplicate; the duplicate sample was located 1 m to the right of the original sample.

The overall sampling strategy was based as closely as possible on the European Soil Sampling Guidelines (ESSG) as described by Theocharopoulos (2001). There is an obvious need for harmonisation in the aspects considered for soil sampling if reproducible and comparable soil samples are to be obtained throughout the European Union for soil quality evaluation (Theocharopoulos, 2001).

General	Pollution	Monitoring	Background	Fertilisation
yes	yes	yes	yes	no

Sampling scale	Risk precaution	Sampling plan	Sampling protocol	Pre-analysis
no	yes	yes	yes	yes

Pedology	Land use	History	Geology	Pre-screening	Site related
yes	yes	yes	yes	no	yes

Detailed description of sample	Single or composite	Sampling only from	Mass/volume related sample	Sample amount
Yes	Yes composite	Yes where possible	Yes both	Yes >0.25

Figure 4.2 Schematic representation of ESSG

A schematic representation of the soil sampling guidelines as outlined by Theocharopoulos (2001) is shown in Figure 4.2. The boxes that are answered "yes" illustrate the sampling protocols which were applied to Gibraltar.

In this investigation the sampling area is the whole of Gibraltar. The sampling sites are different areas within Gibraltar which are under investigation. With each sampling site there will be a given number of sampling units, depending on whether a random or grid pattern was used. Any division of the sampling unit will be for data mapping purposes and for the statistical evaluation of the results. These will be described as sampling sub-units. The sampling sites in Gibraltar were defined according to pedology, land use, history, geology and site related criteria. The size of the sampling units varied by site and sampling pattern used, for example a grid pattern was used on an area known as Windmill Hill Flats and sampling units were every 100 m.

A stainless steel Dutch style auger with a 3 cm bore was used to collect the soil samples. Where the sample texture was not appropriate for an auger, a stainless steel trowel was used. Each sample consisted of four augers full of soil taken to a depth of 15 cms at a notional 1 m^2 area. Where possible the sample amount was >0.25 kg. A detailed description of each sample was taken including grid coordinates, soil depth, colour and texture. Factors such as proximity to roads and/or the sea were also considered during sample collection. An overall site description was taken including the topography which included the types of flora and fauna present. An example of the field notes is found in Appendix B.

4.2.3 Dust Sampling

4.2.3.1 Street dusts

Street dusts often contain a range of elevated metal concentrations from both direct deposition of vehicle-derived metals and from relocation of metals deposited on the road surface (Harrison *et al.*, 1981). A total of 82 samples were collected, the majority being roadside dust. Figure 4.3 shows the distribution of street dust in Gibraltar.

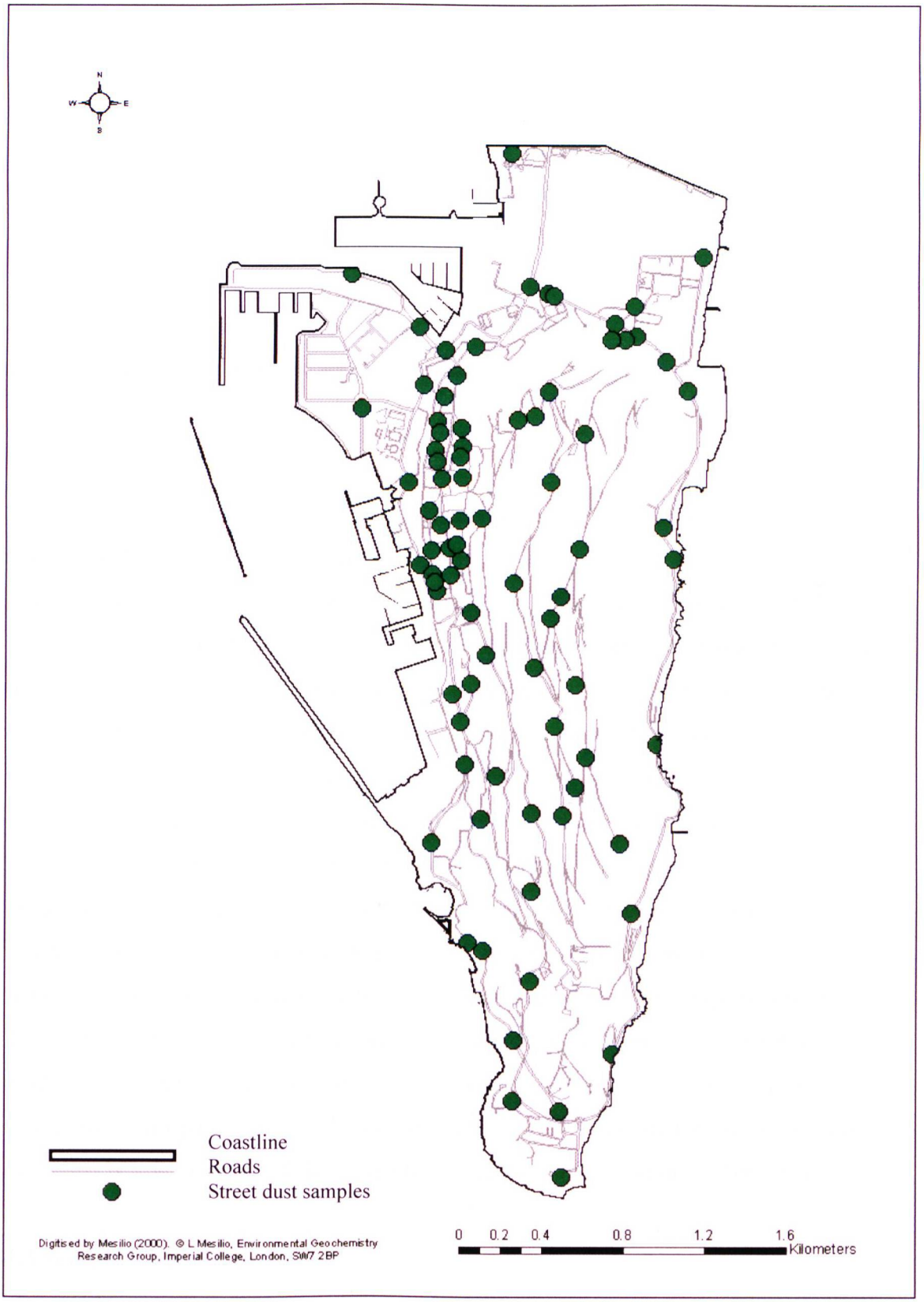


Figure 4.3 Street dust sample locations in Gibraltar (n=83)

A map of the road network was used to select the roads to be sampled. The sampling distribution was aimed at producing a systematic spread across Gibraltar. The samples

were collected using a plastic dustpan and brush. The sides of major and minor roads were swept gently to collect the sample. Playground and park dusts were also collected.

The sample was then sieved to remove any material >2 mm and placed in a paper sample bag. The roads in Gibraltar are cleaned every morning and therefore arrangements had to be made with the cleaning company to allow the collection of samples before the roads were swept. The samples then underwent the same treatment as the sediments for acid digestion.

4.2.3.2 House dusts

The study of house dusts as an exposure pathway to children has been well documented. Eighty households participated in this study. Once again the households chosen were aimed at producing an optimum spread across Gibraltar based on the existing land use. Each participating household completed an extensive questionnaire (a copy sample sheet is provided in Appendix B) which was designed to document the house age, heating sources, distance from the road, and history of redecoration, number of adults, children and pets, as well as other factors which would be relevant to the study. Due to the hot climate experienced in Gibraltar, very few households have carpets, so methodologies used in the UK do not apply. Areas of flooring were swept and on occasions dust was removed from shelving. Care was taken to avoid areas immediately below windows sills which could have broken paint flakes. In households which did have carpets, vacuum cleaner samples were taken. The method of sample collection was documented at each home and an effort was made to keep the general methodology as consistent as possible. The samples were then placed into paper bags and were subjected to the same analytical methodology discussed below. Figure 4.4 shows the house dust sample locations in Gibraltar.

4.3 Sample Preparation

All soil and dust samples were air dried for 3 days at 30°C, then disaggregated using a pestle and mortar and passed through a 2 mm mesh sieve. Any remaining material >2 mm was discarded. Each sample was then divided into two, one portion for pH analysis and LOI (2 mm), and the other for the total metal concentration by acid

digestion. The latter portion of the sample was milled in an agate Tema swing mill until a fine powdered particle size was achieved (180 μm). Thirty millilitres of sample were weighted out at a time and placed in the Tema pot and then in the Tema swing mill (model TS100A). The samples were ground at a speed of 710 min^{-1} for 3 minutes. The Tema pot was cleaned with deionised water (DIW) and acetone after each sample to ensure no cross contamination occurred. Total metal concentrations and sequential chemical extractions were carried out on this fraction. Precautions were taken through the laboratory work to ensure that cross contamination of the samples did not occur for example the instruments used were washed after each sample.

4.4 Chemical Analysis

The "total" elemental concentrations of 26 Elements (Li, Na, K, Be, Mg, Ca, Sr, Ba, Al, La, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb, P, S, As) were determined by nitric/perchloric acid digestion as described by Thompson and Walsh (1988), (detailed methodology used is given in appendix C) followed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analysis on an ARL 3508B machine at Imperial College, London. Analytical quality control was performed using field and analytical duplicates and reference materials. Two house reference materials (HRM1 and HRM2) and two certified reference materials, (NIST SRM 2709 and NIST SRM 2711) were used. This is one of the more common techniques used for trace metal determination in bulk samples (Thornton, 1995). All chemicals used were of Analar© grade and deionised water. All pipettes, test tubes and containers were washed and soaked in Decon© detergent for up to 24 hours, then rinsed in DIW and soaked in 2% nitric acid for up to 48 hours and finally rinsed again in DIW.

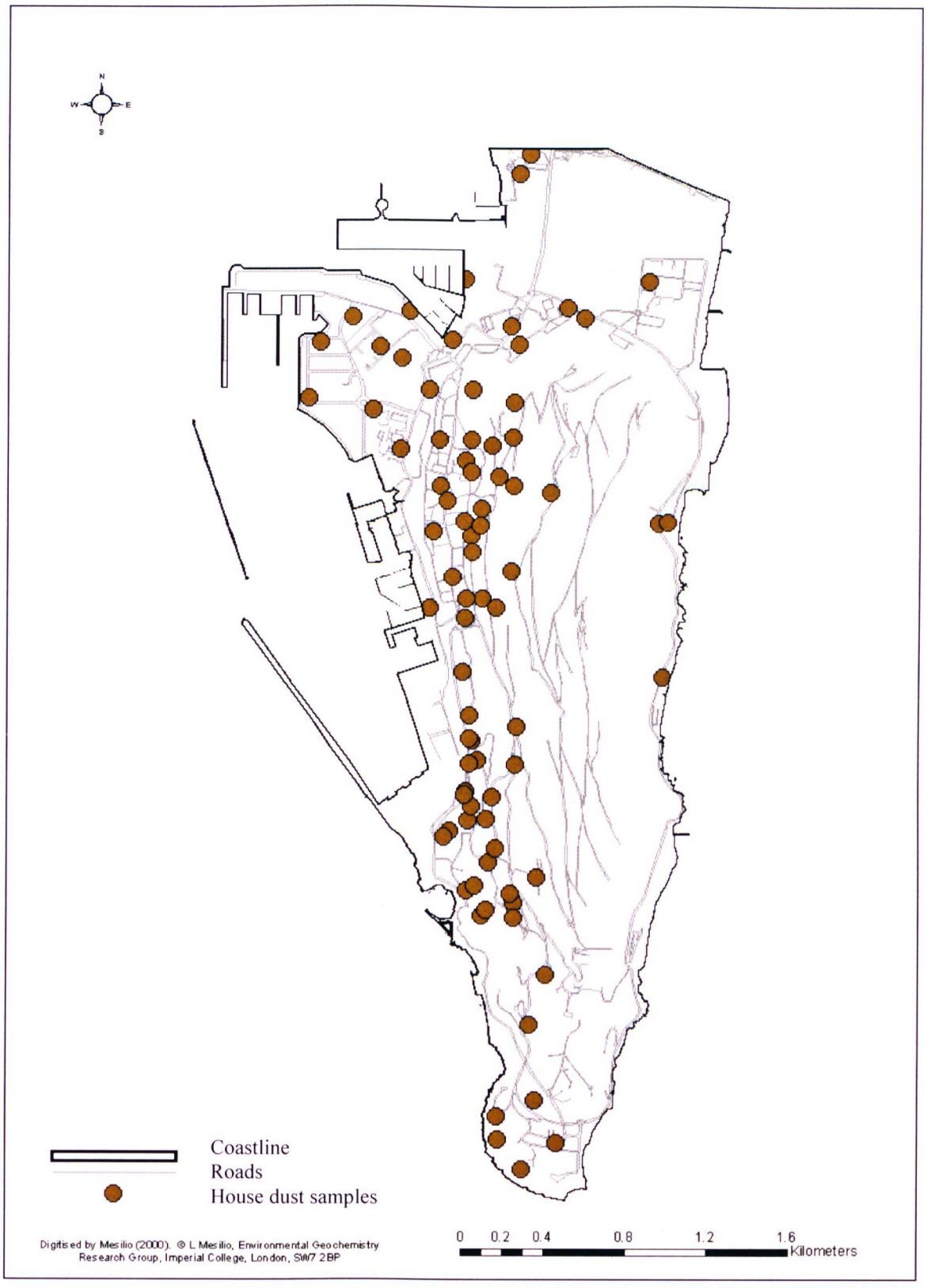


Figure 4.4 House dust sample locations in Gibraltar (n=80)

4.4.1 Sequential Extraction

Three batches of sequential extractions were conducted in this investigation, two on soils and one on street dusts. Each batch obtained 36 samples including 10% duplicates and reference materials. Sequential extraction techniques were used to examine the partitioning of the elements among the various geochemical phases of the soils on the basis of their chemical reactivity. This method aims to provide detailed information concerning the source, mode of occurrence, biological and physiochemical availability, mobilization and uptake of trace elements in soils (Tessier *et al.*, 1979). There are opportunities to clarify the phases that become soluble under progressively aggressive solutions by mineralogical techniques. Tessier's five step sequential extraction has been modified and applied to soil samples by Li (1993) (table 4.1).

Table 4.1 Tessier's five step sequential extraction. (Modified by Li, 1993)

Step in sequential extraction procedure	Description
Step 1 Soluble and Exchangeable Phase	Represents metals that are taken into solution by a weak electrolyte solution of magnesium chloride under neutral pH conditions
Step 2 Carbonate Phase	Dissolves metals in the carbonate phase and those specifically adsorbed onto carbonate compounds lattice
Step 3 Bound to Mn-Fe oxide fraction	Dissolves the iron, manganese and aluminium oxides and hydroxides under reducing conditions. These are common secondary amorphous minerals in soils and trace metals which are incorporated as impurities in the lattice or adsorbed onto the surface
Step 4 Bound to organic/sulphide fraction	The organic matter is oxidised. Metals are bound to organic chelate complexes directly by bonds with carbon or indirectly through N, S or O atoms. Hydrogen peroxide is used to release the metals.
Step 5 Residual fraction	Dissolves the remaining primary rock forming minerals, ore minerals and organic matter.

The samples analysed by this method were chosen to reflect processes in the urban and natural environment. For example, samples were pre-selected for this experiment according to site location criteria and "total" concentrations obtained for the heavy metals from the ICP-AES analysis. Samples were chosen from sites which were known to have either no history of industrial land use or specific industrial land use, either at present or previously. Similarly, samples, which displayed elevated concentrations (refer to definitions provided in chapter 1) or concentrations which were classed as outlying values when the data were plotted in histograms and box plots (i.e. samples more than 2 SD's from the mean) were selected for this analysis.

A detailed methodology is given in appendix C. Although it is understood that the phases applicable to soils and sediments are unlikely to be found as such in dust samples, a series of sequential extractions can give valuable information concerning the extractability, and thus mobility, of metals in the dusts.

4.4.2 Quality control for elements analysed by the sequential extraction method

The precision of elements analysed from five sequential solutions was calculated from two randomly selected duplicate pairs. An estimate of the coefficient of variation has been calculated and the median value, as a percentage, is given in Table D5 (Appendix D). This value provides an approximate estimate of the overall precision (Section 4.8.4) (Gill and Ramsey, 1997). A value exceeding 10% suggests that the data may not be taken from a normal distribution. Results for Ag and Mo are not included for soils or street dusts. The reason being that the samples had values below the instrumental detection limit for most if not all of the five steps. The Cd data has been included but needs to be assessed with caution due to (a lesser extent) the reasons described for the Ag and Mo data. In Step 1 all the elements analysed (excluding S and P in soils) in soils and street dusts exceed 10%. Li, K, Be, Sr, La, Ti, V, Mn, Co, Ni, Cu and Pb all exceed 10% in step 2 for soils and dusts. Li, K, Be, Cu, Sr, Al, La, Ti, Cr, Fe (Fe in soils only), Co, Cu, P, S and As exceed 10% in step 3 in soils and street dusts. Mg and Na are omitted from the sequential extraction analysis as step 1 and step 2 reagents containing large amounts of Mg and Na, therefore the solution and subsequent steps are saturated in these elements. Li, Na, K, Be, Sr, Al, La, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb and As exceed 10% in step 4 for

soils and street dusts and in step 5 Li, Na, K, Be, Ca, Sr, Ba, La, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn and As exceed the 10% coefficient of variance model in both soils and street dusts. From these, Ca, Ba, Ti, Cr, Mn, Fe, Cu, Co, Ni and Zn were below 20% for soils.

Many of the elements exceeding the 10% estimate of the coefficient of variation of the data in the analysis may be due to the measurements being close to or below the detection limit of the method (Gill and Ramsey, 1997). This was particularly evident in the street dust samples. Additionally, one of the samples chosen generally had low concentrations in most if not all of the steps for most elements. The precision for the sequential extraction is not satisfactory for soils or street dusts. This may also be due, in part to the heterogeneous nature of the samples, as well as the fact that only two duplicates pairs were used in the analysis of the model. This said however, the coefficients of variation have been given, in order to provide a rough estimate of the precision of the results. This then means that the sequential extraction data must be analysed with caution. Error in the sequential extraction procedure occurs due to the lengthy experimental procedure that requires digestion in open tubes. Hot H_2O_2 in step 4 reacts vigorously with organics, which may cause a loss of material from the test tubes during this stage. Material may also be lost during the washing stages after each step. In conclusion, it appears that this method of sequential extraction is not suitable for Li, Na, K, Be, Cu, Sr, La, Ti, Cu and As in Gibraltar soils and street dusts and the reproducibility of the elements in the steps listed above should be taken into account in the interpretation of their geochemistry. Further analysis of the precision with a higher number of duplicate pairs, and including samples with concentrations above the IDL in most if not all steps of the procedure would be needed before the precision of this method can be fully verified.

To measure the bias of the sequential chemical extraction the recovery has been calculated using reference materials. The sum of the concentrations from the five steps was compared with the certified value from reference materials. The recovery rates are reported as a percentage of the certified value and displayed in Figure D4, Appendix D. A comparison between the recoveries of elements from the five-step sequential extraction procedure in this study has been made with the results reported by Li *et al.* (1995a). The percentage recovery for elements in NIST SRM 2711 was

calculated from the data reported in Li *et al.* (1995a) and most elements range between 80-100%, with P at 70%. Recovery rates were generally higher in the Li study (1995a and b), than in this study (soils). The percentage recovery for the elements in this study was also generally between 80–100% for most elements with Co having a recovery of only 55%, K of 79% and Zn of 78%. The interpretation of the Co data for sequential extraction therefore needs to be assessed with caution. The recovery was below 100% for all the elements in this study with Cd, Mn, Sr, Ti and V having a recovery above 90% in this study. A recovery rate exceeding 80% has been indicated as an acceptable accuracy for the sequential extraction method (Li *et al.*, 1995a and b).

4.4.3 Limitations of the sequential extraction method

Limitations have been encountered with various sequential extraction methodologies and have been reported by several authors (Fergusson and Kim, 1991; Li *et al.*, 1995a; Rubio and Ure, 1993; Tessier *et al.*, 1979 and Rauret, 1998). Examples of such limitations include incomplete dissolution of the targeted phase, which results in subsequent re-precipitation during the method (Fergusson and Kim, 1991; Li *et al.*, 1995a). Also the loss of material is almost unavoidable when washing the sample and also whilst decanting the solution after each step. This then leads to a total recovery of less than 100% (Rubio and Ure, 1993). The percentage recovery is calculated by dividing the sum of the 5 sequential extractions by the independent total concentration.

4.5 ICP-AES Analysis

ICP-AES is an established and mature analytical technique in geochemistry (Gill, 1997). The advantages of using ICP-AES include good precision, low detection limits as well as low interference effects. Additionally it has good reliability, a fast analysis time and flexibility for adaptation to different methods of sample introduction (Thompson and Walsh, 1988). It can also carry out multi-element analysis. Its limitations however lie in sample dissolution problems and in its inability to distinguish between different species of the same element. Samples are introduced into the unit by a nebuliser and converted into an aerosol by a cross flow

of argon gas. The aerosol enters the spectrometer where the sample is converted into atomic or ionic form. The spectrometer energises the atom to emit photons of energy which are separated into spectral lines that are specific to a particular element (Walsh, 1997).

Limitations of this instrument include the detection of trace metals below a concentration of 1 mg/kg; inert gasses, oxygen, nitrogen and carbon cannot be measured (Walsh, 1997). The detection limits of the instrument for certain elements such as Cd is known to be problematic. Additionally, limitations of the nitric-perchloric attack used must also be noted. These include incomplete dissolution of certain minerals high in quartz as well as elements such as Cr.

4.6 Loss on Ignition (LOI)

Approximately 2 g of <2 mm air dried soil was weighed into previously weighed ceramic crucibles. The crucibles were placed into an oven at 105°C for 12 hours, removed and left to cool for a number of minutes. They were then placed into a desiccator for 45 minutes. Samples were reweighed for the estimation of the moisture content. The samples were subsequently placed back into the oven at 450 °C for 24 hours. They were allowed to cool and then placed into the desiccator for an hour and reweighed for the estimation of organic matter. This is done by the following equation:

$$\text{LOI \%} = \left(\frac{A-B}{A}\right) \times 100$$

A = mass of oven dried soil (105°C)

B = mass of ignited soil (450°C)

4.7 pH analysis

This was carried out using a 2.5:1 ratio of distilled water to sample weight. This is the methodology used at the laboratory within the Department of Geochemistry at Imperial College. Four grams of each sample were weighed out in a top-pan balance and placed into polystyrene test tubes. 10 ml of DIW were added to each tube which

were then capped and shaken by hand for a few seconds. The samples were then placed in a mechanical shaker for 30 minutes. Once this was done the samples were centrifuged at 2000 rpm for 5 minutes. The pH test was conducted using Hanna Instruments 8521. The instrument was calibrated using pH 4, 7 and 10 buffer solutions. A glass-calomel electrode probe was placed in each sample and left for up to 2 minutes to allow an accurate reading to be taken. The accuracy of the instrument was further checked after every 10 samples with the buffer solutions.

4.8 Sampling and Analytical Quality Control (AQC)

A sampling and analytical quality control scheme is an essential part of the production of analytical data (Thompson *et al.*, 2002) and therefore essential in any geochemical or environmental investigation. Measurement uncertainty is an important concept in analytical science. It refers to uncertainty arising from chemical analysis and also to that arising from the sampling procedure. Thompson *et al.* (2002) define uncertainty as "the interval around the result of a measurement that contains the true value with high probability". In the case of environmental and geochemical investigations, primary sampling can be the main source of uncertainty and may dominate analytical sources such as instrumental determination or the sub-sampling of test materials within the laboratory (Ramsey, 1997). The inclusion of the sampling step into the quality control scheme becomes particularly important when deciding acceptable levels of uncertainty arising from the chemical analysis. If the sampling uncertainty is too large, then a point is reached where reduction in uncertainty from chemical analysis makes a negligible impact and is thereby not cost effective (Ramsey, 1997).

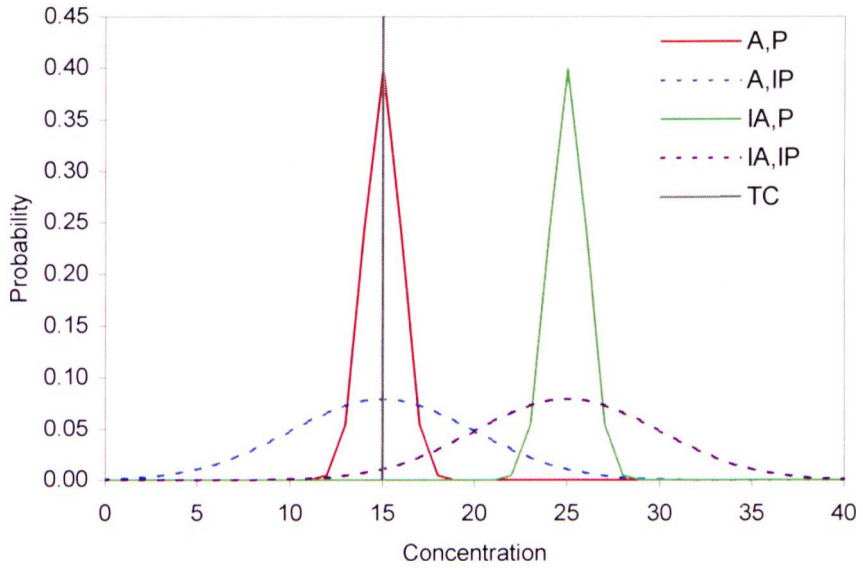
4.8.1 Interpretation and Data Quality

Before the data can be interpreted, the quality of the data needs to be assessed in terms of its validity. This is done through the internal Quality Testing (QUTE), which is carried out together with the analytical runs on the ICP-AES. Two house reference materials (HRM 1 and HRM2) and two certified reference materials were used in this research, (NIST SRM 2709 and NIST SRM 2711). The use of reference materials, which have a known composition, is necessary in order to identify any errors through the analytical run. The data show that the percentage bias is lower in the HRMs than

for the NIST SRM materials. General accepted bias values lie within ±10%. Where samples have values exceeding this threshold (whether they be reference materials or samples obtained in the field) indicates that some of the values obtained are just above the detection limit of the instrumentation. An example of this occurred with values for Cd and therefore resulted in a large bias.

4.8.2 Uncertainty in Environmental Measurements

The true value of an analyte concentration is always unknown, but when estimated as the "accepted reference value" it acts as a reference point for the estimation of uncertainty, error, accuracy and bias. All measurements are characterised by some degree of error. A key factor in interpreting measurements is uncertainty.



Key: A = accurate, IA = inaccurate, P = precise, IP = imprecise, TC = true concentration

Source: modified after Shaw (2000), unpublished lecture notes.

Figure 4.5 Graphical representation of the types of errors found in environmental datasets.

There are two components to uncertainty, accuracy and precision. Accuracy is "the closeness of the agreement between a test result and the accepted reference value" (Ramsey, 1997). Bias is described as "the difference between the expectation of the result and an accepted reference value" (Ramsey, 1998; ISO, 1993). Precision is "the

closeness of agreement between independent test results obtained under prescribed conditions" (Ramsey, 1997). Refer to figure 4.5.

It is the closeness of agreement between results obtained by repeating an analytical procedure several times under the same conditions (Gill and Ramsey, 1997). Stating that an analysis is precise, is simply a qualitative statement about the random error associated with the analysis, not about how close the result is to the true value (Gill and Ramsey, 1997). High precision thus means small random error. Basically, it can be expressed as the reproducibility and repeatability of your results, based on the same conditions and under no special circumstances under which the measurements are replicated. How precise an analysis is can therefore be quantified in terms of the standard deviation obtained from replicate measurements: the smaller the standard deviation, the more precise the analysis. For any normal distribution there is a 95% probability of an individual reading lying within $\pm 2\sigma$ of the mean value (Gill and Ramsey, 1997).

4.8.3 Accuracy

Accuracy can be described as the extent to which the mean concentration obtained in the analysis approaches the accepted value (Thompson, 1983). Analytical bias (section 4.3.4) for reference materials analysed during total metal digestion is illustrated in Tables D1 to D4 in Appendix D. The null hypothesis is assumed. The null and alternative hypotheses are defined below:

H_0 = mean of duplicate reference materials equals the accepted value

$H_1 \neq$ mean of duplicate reference material does not equal the accepted value.

If the calculated test statistic (t-calc) is lower than the test statistic (t-tab), calculated from the t-distribution at 5% ($P<0.05$), then the H_0 is accepted.

The certified reference material NIST SRM 2709 has a low to medium concentration of trace metals whereas NIST SRM 2711 has a high concentration of trace metals. Major elements have a low bias in NIST SRM 2709 (Coles, personal communication). At low concentrations Cd (0.38 mg/kg) displays an unacceptable bias, but the precision of the duplicates is acceptable (<10%). The bias is thereby accepted to be

acceptable and the deduction is made that the measurement of Cd at values ≤0.38 mg/kg is not reliable. Bias for major elements is unacceptable in the reference material NIST SRM 2711 as the ICP-AES parameters are optimised for the detection of trace metals (Coles, personal communication).

The reference materials with low metal concentrations show Ag, and Cd to have a significant difference from the certified values and the hypothesis (stating that there is no significant difference between the values) is thereby rejected. The test of analytical bias shows that for concentrations below 3 mg/kg for Ag and 2.5 mg/kg Cd there is a high bias; the accuracy is therefore unacceptable for low concentrations of Ag and Cd. A significant negative bias in some analytical runs suggests a loss of material or incomplete digestion during analysis. Complete nebulisation in the ICP-AES may not have been achieved and adsorption of materials onto the glassware can reduce the material available for analysis (Coles, personal communication).

4.8.4 Precision

In each analytical batch, 10% of the samples were analysed in duplicate and were randomly included in the batch. Each duplicate was independently taken through the analytical procedure. Each duplicate analysis pair (as seen in table 4.2) was used to calculate a mean and an absolute difference ($X_1 - X_2$). The bottom row of the table shows the difference of each duplicate pair as a percentage of the mean. A value < 10% is accepted as good precision.

Table 4.2 Thirteen duplicate determinations of Pb (mg/kg^{1}) in soils in Gibraltar with estimates of precision. (Modified from Gill and Ramsey, in Gill, 1997)

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	Median
X1	97	1087	490	1725	851	480	302	465	110	1031	933	1766	2068	
X2	108	1220	472	1553	913	468	294	441	103	967	871	1734	2356	
Mean	102	1154	481	1639	882	234	298	453	107	999	902	1750	2212	
X_1-X_2	11	132	19	172	62	12	9	24	7	65	62	32	288	
[X_1-X_2]%	11	11	4	10	7	5	3	5	7	6	7	2	13	7

Twice the median value of the percentages (14) gives an estimate of the precision of the method with 95% confidence. A median value above 10 indicates the random error incorporated into the sample measurement is less than 10%. The mean value and the

absolute difference for each pair of duplicate results were then plotted on a control chart (Thompson and Howarth, 1976). This was done for each element in the analytical run. Figure 4.6 shows a control chart for Pb, where the distribution of the data does not follow the model, but is above 10% which fits in with the calculated value of 14% (twice the median value). If the distribution of the data on the control chart are such that half of the points fall below the 50% line, then a precision of 10% has been achieved at a 95% confidence limit. For some elements, 2 (or more) points lie above the 99% line, representing 22% of the population as opposed to the 1% predicted by the model. This suggests the data may not be taken from a strictly normal distribution (Gill and Ramsey, in Gill, 1997).

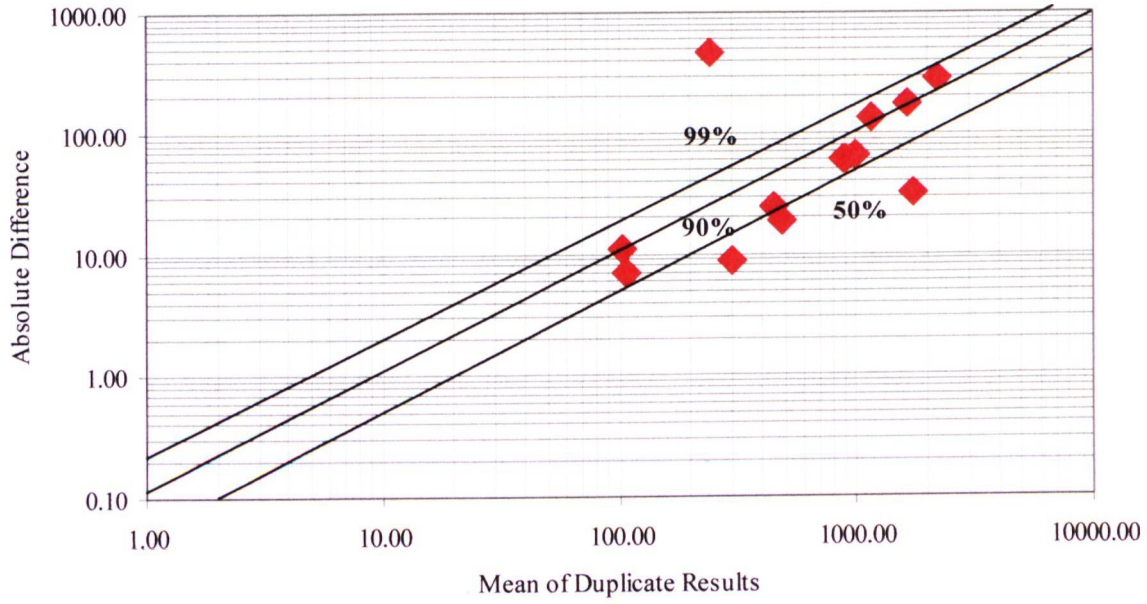


Figure 4.6 Control Chart for Pb concentrations in soils from Gibraltar
Source: adapted from charts used by Thompson and Howarth (1976).

Individual duplicate pairs may exceed 10%, in the majority of cases however, this occurs when a large amount of concentrations for that particular element fall close to the instrumental detection limit (IDL). The analytical error for most elements analysed are within the acceptable 10%. Cadmium, Ag, and As are outside the 10% model, due to low detection limits and low concentrations of these elements in the sample. Precision generally is better at higher concentrations.

4.8.5 Bias

The main method for the estimation of bias is by analysing a certified reference material with known concentrations for the elements in question several times. Bias is calculated using the following equation:

$$\text{Bias} = (\bar{x} - x_c)$$

Where $\bar{x}$ is the mean of the values obtained from the analyses of the certified reference material and x_c is the certified concentration for the element in question.

The relative standard deviation (RSD) of the sample duplicates was used to ascertain the precision. A low RSD value indicates a high level of precision. It was calculated using the following formula:

Relative Standard Deviation = (σ/mean) x 100

4.8.6 Estimation of uncertainty due to sampling and analysis

Robust Analysis of variance (ANOVA) has been used to estimate sampling and analytical errors. Robust ANOVA differs from classical ANOVA in that it accommodates outlying values rather than rejecting them (Ramsey, 1993). Estimates of the mean ($\bar{x}$) and standard deviation (s) are made by an iterative process whereby any data that exceed a certain distance from the mean are assigned a new value equal to that distance. The distance is a product of a constant (c) and the standard deviation, c being selected to suit the expected proportion of outliers. A value of c=1.5 is regarded as optimal.

Classical methods are used to obtain estimates of $\bar{x}$ and σ. These values are then used to adjust values which fall outside the range of $x \pm cs$ to be equal to $x+cs$ or $x-cs$. The modified mean and standard deviation estimates ($\bar{x}_2$ and s_2) are then calculated form the modified population. Iteration continues until the calculated values of $\bar{x}$ and s converge, at which point they are called he robust estimates (Ramsey, 1993).

Table 4.3 **Assessment of the relative importance of sampling and analytical precision compared with geochemical variability for topsoil samples in Gibraltar.**

Element	Geochemical %	Sampling %	Analytical %
Li	99.64	0.08	0.29
Na	97.39	2.28	0.33
K	99.55	0.24	0.22
Be	98.90	0.78	0.33
Mg	97.82	1.99	0.19
Ca	91.44	8.29	0.28
Sr	94.50	5.06	0.44
Ba	99.33	0.53	0.14
Al	99.45	0.44	0.11
La	92.75	5.01	2.24
Ti	95.77	1.74	2.50
V	99.09	0.58	0.34
Cr	90.68	4.38	**4.95**
Mn	99.28	0.16	0.56
Fe	98.87	0.78	0.35
Co	97.50	1.94	0.56
Ni	94.79	5.02	0.19
Cu	99.71	0.25	0.04
Ag	**46.57**	**14.52**	**38.91**
Zn	97.78	2.19	0.03
Cd	81.68	<0.01	**18.32**
Pb	99.57	0.40	0.03
p	99.62	0.16	0.22
s	98.80	0.80	0.41
As	96.08	2.60	1.32

Values in bold indicate the elements with measurements which fall below the criteria suggested for accurate interpretation of results.

Sampling and analytical variance are often collectively known as technical variance. The technical variance should not exceed more than 20% of the total variance with the analytical variance contributing no more than 4% of the total variance (Ramsey, 1993). A consensus of opinion believes that it is necessary for geochemical variance to account for at least 80% of the total variance to allow for a confident interpretation of the spatial distribution of the geochemistry (Ramsey, 1993).

Table 4.3 shows the results of the robust ANOVA applied to soils in Gibraltar. Chromium display an analytical variance slightly above the recommended value of 4%. Cadmium has a large analytical variance, and this is attributed to the low concentration range for this element in soils in Gibraltar, whereby over 50% of the samples have concentrations within or below the ADL. Silver is the element where all three values fall below the criteria suggested for an accurate interpretation of the results. The reasons for this are considered to be the same as have been suggested for Cd. This then means that the Ag and Cd, and to a lesser extent Cr data need to be assessed with a degree of caution.

4.9 Data screening

In the multi-element analysis of soils and dusts, the data produced usually deal with elements occurring in very different units. In geochemistry, the chemical elements are divided into *major elements*, which are measured in % or tens of a %; *minor elements* which are measured in 1% amounts; and *trace elements* which are measured in milligrams per kilogram (mg/kg or ppm) or even parts per billion (ppb) (Reimann *et al.*, 2002). Geochemical and environmental datasets are often characterized by a high number of samples with values below detection limit and are therefore not characterized by a representative measured value. The precision of the measurements thereby changes with element concentrations, as values are less precise at very low and very high concentrations. Additionally, this may become a problem in multivariate techniques where all variables are considered simultaneously, as the variables with the greatest variance will have the greatest influence on the outcome (Reimann *et al.*, 2002). The raw data from the laboratory analyses therefore require preparation before they are subjected to statistical techniques for data evaluation purposes. Possible solutions include logarithmic transformation and/or standardisation.

4.10 Samples below Instrumental Detection Limit (IDL)

Elements that have sample concentrations below the IDL (Cd and Ag are common examples of this) are replaced by the analytical detection limit (ADL) to allow the use of these samples in further statistical analysis. This method allows for a conventional estimate of the minimum value. The ADL is calculated as 3 times the instrumental detection limit (Coles, personal communication). This method allows a conservative estimate of the minimum value; however the analytical bias for Cd suggests that concentrations below 2 mg/kg should be treated with caution. If there are a high number of values (>25%) below detection, then there is no chance that these data will approach a normal or lognormal distribution; then it is recommended that the variable be removed from analysis (Reimann *et al.*, 2002).

4.11 Normality

The distribution of the data are of the utmost importance and should be assessed before any further statistical analyses are carried out. The reason for this is that multivariate statistics and indeed most classical statistical tests are based on the assumption of a normal distribution. Geochemical and environmental measurements tend to show SPATIAL DEPENDENCE. It is now well known among environmental scientists that spatially dependent data are not, in general, normally distributed, and several scientific papers and books have been written to address this problem (Hawkes and Webb, 1962; McGrath and Loveland, 1992; Reimann *et al.*, 2002).

There are several tests that one can use when testing for a normal distribution. The easiest method is to plot a histogram and check for the typical bell shaped curve. Another method to test for a normal distribution in the data is by using probability plots (P-P). They plot the cumulative proportions of a variable against those of any number of test distributions. Probability plots are generally used to determine whether the distribution of a variable matches a given distribution. If the observed data cluster around the line, then a normal distribution is observed. Section 6.2.1 shows

probability plots for both untransformed and log transformed data. These graphical tools give a good first impression of the data distribution. However, in order to demonstrate that the data deviate significantly from a normal distribution, a more formal statistical test should be applied (Reimann and Filzmoser, 1999).

The Kolmogorov-Smirnov (KS) statistical test was applied to both untransformed and log transformed data to measure if the distribution of metal concentrations in dusts is normal. This test compares an independent identically distributed sample from an unknown univariate distribution with a reference sample with a known distribution (Reimann and Filzmoser, 1999). If $p<0.05$ the null hypothesis of a normal distribution is rejected. As can be seen from table 6.3, 6.12 and 6.14, once the data underwent logarithmic transformation, the null hypothesis was accepted.

In this work, statistical analyses have been conducted on the log-transformed data. Standardisation to zero and unit variance of the raw data were not done because the distributions were strongly skewed. Log transformation should be first carried out before a decision on standardisation is taken. Log transformation is widely used to approach considerably more homogenous ranges.

4.12 Outliers

Regional geochemical datasets usually contain outliers (Reimann and Filzmoser, 2002). Outliers are defined as data with anomalously high values. Outliers often present a dilemma in data analyses. These values should not be ignored and should be analysed as they contain important information about data quality and unexpected behaviour in the region of interest (Reimann and Filzmoser, 1999). The outliers may originate from another population separate to the main body of data and may therefore be indicative of a pollution source.

Univariate and multivariate statistical analysis can present biased results when outliers are kept in the dataset. Korre (1997) states four reasons for the presence of an outlier:

- Incorrect data
- Failure to specify missing values codes in computer control language so that missing value indicators are read as real data

- The outlier is not a member of the population intended for sampling and should be deleted
- The case is from the intended population but the distribution of variance has more extreme values than a normal distribution.

Screening of univariate outliers is relatively simple through graphical methods such as the use of the cumulative frequency plot mentioned above. Multivariate outliers are cases that have unusual patterns of scores. It is much harder to screen for multivariate outliers with the methods mentioned above. The computation of the Mahalanobis distance can be used. The distance of each case from the centroid point is calculated for the mean of all variables. A (very conservative) probability estimate for a case being an outlier $p>0.001$ is used with the Mahalanobis distance method (Tabachnick, 1989).

Homogenous (unimodal) populations are somewhat rare in geochemical data within an urban environment. None have been found in this work. There will most likely be at least two populations present, one being a background population and the other, a population representing a pollution source such as emissions from motor vehicles, a scrap yard, an incinerator or other types of industry such as gas works or newspaper printing works. Plotting the data on a histogram can show which values are anomalous to the dataset. This procedure is effective when the two populations are separate but when they overlap, as commonly occurs in urban environments, difficulties arise in distinguishing between which levels represent a contamination source and which ones indicate threshold values between background (or baseline) and anomalous values (Brooks *et al.*, 1995). One way to view if different populations exist within the dataset is through cumulative probability plots.

If the cumulative frequency is plotted on probability paper, each population is represented by a straight line or curve. The intersection of these lines or curves (as shown in figure 2.3) represents a level that might be taken as an arbitrary indication of the threshold level between background and anomaly.

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that have unusual patterns of scores. It is much harder to screen for multivariate outliers with the methods mentioned above. The computation of Mahalanobis distance is used (Korre, 1997). The distance of each case from the centroid point is calculated for the means of all variables. A (very conservative) probability estimate for a case being an outlier $p<0.001$ is used with the Mahalanobis distance method (Tabachnick, 1989).

Missing values constitute another problem when dealing with geochemical datasets. They occur when the variable has not been measured in a sample, the sample was lost or became contaminated or the variable is below the detection limit of the analyte in a sample. There are a number of approaches to the treatment of missing values. If the proportion of missing values is low, it may be reasonable to replace them with the variable mean; in this case the sample will not affect the overall variability of the dataset. If the missing values all belong to a single variable or sample and exceed 25% of the data it is recommended that the variable or sample be removed (Reimann *et al.*, 2002). All missing values in this dataset result from the concentration falling below the IDL; therefore they are replaced with the values calculated for the ADL.

4.13 Metadata in GIS

Just as measurement uncertainty is an important concept in analytical science, metadata within a GIS database is one of the key components of a geoinformation infrastructure (ESRI, 1997). It describes and documents spatial data as well as assisting users of a GIS system in searching for and archiving data. Metadata describes data using terminology that defines potentially disparate data and facilitates consistent collection, indexing, querying, and publishing. Metadata documents content, quality, source organizations, data format and organization, collection schedule, uses, data currency, spatial references, and distribution mechanisms for the data (ESRI, 1997). It also makes spatial information more useful to all types of users.

ArcCatalog is an application for locating, browsing, and managing spatial data. It automatically associates metadata with all geographic datasets and creates metadata for any dataset supported by ArcInfo as well as any other dataset identified and

catalogued by the user (e.g., text, CAD files, scripts, images). The description of a dataset covers the following topics (ESRI, 1997):

- **Identification** - This is basic information about the dataset title, geographic extent, and rules for using the data.
- **Spatial Data Organization** - How is the spatial information represented in the dataset? Is it raster or vector? Does it have a data direct or indirect spatial reference?
- **Spatial Reference** - A description of the reference frame for and means of encoding coordinates in the dataset. This includes the map projection, coordinate system, and datum--both horizontal and vertical.
- **Data Quality** - Metadata items, such as positional and attribute accuracy, completeness, consistency, and methods used to produce the data, provide criteria for assessing the quality of the dataset.
- **Content** - Information about the objects in the dataset including the names and definitions of features and attributes.
- **Distribution** - The contact information and other items needed for obtaining the dataset.
- **Metadata Reference** - This describes the currency of the metadata and the organization responsible for the metadata.

These items describe a dataset, and they can be used in different ways. A standard provides a common set of metadata elements or variables that document geospatial data and provides definitions and a common terminology. A content standard makes metadata transparent to users. ArcCatalog™ is an integral part of the GIS so when data are updated in the GIS it is automatically updated in the metadata files (ESRI, 1997).

CHAPTER 5

Review of secondary data evaluation techniques

5.1 Spatial and Statistical evaluation techniques

A sound statistical interpretation of data is crucial for any successful geochemical investigation. This is important because the researcher should be in the very least able to decide which statistical procedures should be used. Once the methods of quality control and data screening have been implemented and satisfactory results achieved, the elements with an acceptable bias and precision can then undergo more vigorous statistical techniques to aid in the interpretation of geochemical data within a particular environment.

The choice of statistical tests which one can apply to a dataset should depend firstly on the research question and secondly, on the type of data which one wishes to analyse. The first step in data analyses (as stated in chapter 4) should generally consist of a careful study of the distribution of the measured variables. Exploratory data analyses should be the first step in the analyses of geochemical or environmental data. It provides a number of simple graphical techniques for the study of the data in detail prior to the use of more advanced statistical techniques.

Univariate methods allow the distribution of points along a line to be described and statistical statements to be made about the distribution. For example histograms, box plots and one dimensional scatter diagrams were used to provide an insight into the data structure. Bivariate methods were used to describe and analyse the shape of the scatter for the purpose of investigating the relationship between the data points and/or relationship between two variables. The main techniques for doing this are regression and correlation analysis. In correlation analysis, (used in this work) the extent to which two variables are associated or vary together is assessed. This is done however, without any suggestion that one of the variables is dependent in the other. Descriptive statistics, namely the mean, geometric mean, median, standard deviation, geometric standard

deviation and correlation matrix were also reported. The geometric mean and geometric standard deviation were used to predict the baseline values as described in chapter 6.

Virtually all geochemical and environmental data are inherently multivariate in nature. Many variables may be needed to fully characterise the geological object, or soil concentrations or conditions. Multivariate methods allow the simultaneous analysis of any number of variables. They reduce the dimensionality of the data to imaginable and plottable 2 or 3D data; so that valid diagrams can be drawn to illustrate what a particular method is showing (Swan and Sandilands, 1995). Multivariate statistical methods are widely employed to identify pollution sources and to apportion natural versus anthropogenic contributions (Brooks *et al.*, 1995; Facchinelli *et al.*, 2001; Reimann *et al.*, 2002; Li *et al.*, 2001). A geochemical dataset can be viewed as a data matrix, with the concentration of the elements as columns and the soil samples as rows. Multivariate analysis considers the variability of several random variables simultaneously (Manly, 1994).

5.2 Secondary evaluation techniques - Multivariate statistics

A data matrix is a rectangular array of numbers, organised into columns and rows and operated on as a single unit (Davis, 1973). The principal operations on matrix and subsequent calculations for principal component analysis (PCA) and R-mode factor analysis (FA) are discussed in the following section from Davis (1973), Manly (1994) and Swan and Sandilands (1995).

5.2.1 The data matrix, eigenvalues and eigenvectors

The data, consist of measurements on m variables (elements in geochemical data) made on each of n items (samples) are set out in an n x m matrix. Each row represents one or a series of observations. In geochemical data it is common for there to be more items n (or observations) than variables m (elements being measured), so the column matrix would be $n<m$. The aim of multivariate statistics is basically that of data reduction in which a selection of complex variables can be reduced to a smaller number of important factors to test a theory or explain the processes occurring in the system under investigation.

There are two related models by which to do this: principal component analysis (PCA) and factor analysis (FA). Both methods can be used on either the *correlation matrix* or

the *covariance matrix*. The first step in a PCA and FA is to calculate a matrix of variance and covariance from the original data. The data matrix [X] is multiplied by its transpose $[X]^T$ resulting in a square matrix. This results in a correlation matrix. The variance-covariance matrix is the starting point for PCA and FA.

The scatter in multivariate data will show a trend in a certain direction. This can be visualised by enclosing the data in an ellipse. One axis is placed through the longest part of the ellipse, representing the major axis and a second at right angles through the shortest part of the ellipse, representing the minor axis. This creates a pair of axes at right angles to each other that provide an alternative reference frame for the data scatter, and is referred to as the *principal axes of the ellipse*. An *eigenvalue* is a measure of the total test variance that is accounted for by a particular factor. The orientation of the axes are called *eigenvectors*, both eigenvalues and eigenvectors are calculated by manipulations on the variance-covariance matrix (Manly, 1994; Swan and Sandilands, 1995; Kinnear and Gray, 2001).

5.2.2 Factor analysis (FA)

Factor analysis is a technique used for the interpretation of relationships between the variables in a multivariate collection of data. It allows the data to be expressed in terms of a number of factors which are less than the number of original variables being measured (Brooks *et al.*, 1995). The term *factor* is equivalent to *controlling processes* in geochemistry (Reimann and Filzmoser, 1999).

A FA usually takes place in three stages: (Kinnear and Gray, 2001):

1. A *matrix of correlation coefficients* is generated for all possible pairings of the variables (in other words, the tests)
2. *Factors* are extracted from the correlation matrix. The most common method is called *principal factors*.
3. The factors (axes) are rotated to maximise the relationships between the variables and some of the factors and minimise association with others.

Each factor extracted, successively accounts for a decreasing proportion of the data variance. The analysis can be carried out by examining the relationship between the

samples (*Q mode*) or the variables (*R mode*). With geochemical data sets, were the variables are element concentrations soil or dust samples, the latter can lead to explanations of the data variability in terms of geochemical inter-elemental associations (Brooks *et al.*, 1995).

In factor analysis, there are two main methods for extracting the common factors; principle factor analysis (PFA) and maximum likelihood method (ML). PFA works in principle like a principal component analysis but with a reduced correlation or covariance matrix. Only the common structure of all variables, but not any special behaviour or uniqueness of each single variable is used. ML in contrast, uses a more complicated statistical optimisation procedure to extract the factors (Reimann *et al.*, 2002). In PFA a normal distribution is not essential, but it should be noted that the method is based on the correlation and covariance matrix, and these are strongly affected by non-normally distributed data and the presence of outliers.

The relationships between the variables and the new factors are termed *factor loadings*. The factor loadings are used to find element associations which are used in turn to label the factor. A FA requires the researcher to select the number of factors (p) to be extracted. This assumes however, some prior knowledge of the dataset. Methods for choosing the number of factors (p) to be extracted are outlined below. The first 3 approaches use a precise method for the determination of p, the last requires some visual interpretation (Manly, 1994; Brooks *et al.*, 1995).

1. *Percentage of total variance explained* - Factors that account for a certain percentage of total cumulative variance, this is usually 70-90%.
2. *Kaiser rule* - Factors whose eigenvalues are greater than the mean eigenvalue.
3. *Eigenvalue > 1* - Factors which have an eigenvalue > 1, or factors which have a greater variance than the original standardised variables.
4. *Scree plot* – the eigenvalue number is plotted against the value of the eigenvalue. The first few eigenvalues have high values but consecutive eigenvalues have lower values. The plot shows a curve. The point of interest is where the curve connecting the points begins to flatten out. The number of eigenvalues before this point, are kept. Usually, this point also has an eigenvalue less than 1.

One of the outputs from a factor analysis is a table of communalities. Each variable will have a *communality value*, which is the squared multiple correlation (R^2) between the variable and the factors emerging from the factor analysis. It represents the proportion of variance of the test accounted by the factors. In other words, a high communality value indicates that a large proportion of the variance in that variable is explained by the extracted factors. If the data are suitable for FA, the variables will have a high communality, i.e over 0.6 or 60% of the variability in that variable is contributing to the factors extracted (Kinnear and Gray, 2001).

The next step commonly followed in a factor analysis states rotation of the factors. In rotation, the factor axes are rotated around the fixed origin until the loadings meet certain criteria. Rotating the axes changes the factor loadings emphasising the variables that have a strong correlation to the factor. The most common method is *varimax*. This method maintains independence among the mathematical factors. Geometrically, this means that during rotation, the axes remain *orthogonal* (i.e. they are kept at right angles) Rotation is said to "clean up" the factors for interpretation but does not change the mathematical relationships (Manly, 1994).

The final step is to plot the *factor scores*. Factor scores are the coefficient between the original sample and the new factor. The variables have been reduced to a smaller number of variables. A sample with a high factor score is contributing highly to the variance defined by that factor (Manly, 1994). The factor scores are saved as a new variable in the dataset, and are plotted on a scatter plot. The cases are labelled by sample number so as to allow the identification of groups or clusters within the data.

5.2.3 Principal component analysis (PCA)

Principal component analysis is a form of factor analysis in which the aim is to account for as much variance as possible in the successive components (Brooks *et al.*, 1995). It takes p variables X_1, X_2, ...X_p and find combinations of these to produce indices Z_1, Z_2,...Z_p that are uncorrelated. The lack of correlation means that the indices are measuring different "dimensions" in the data. PCA seeks a linear combination of variables such that the maximum variance is extracted from the variables. It then removes this variance and seeks a second linear combination from the residual correlations which explains the maximum proportion of the remaining variance, and so

on until all variance is accounted for (Manly, 1994). Principal components are the eigenvectors of a variance – covariance matrix. The *variance* (deviation from the mean) is reported along the diagonal or trace of the matrix and the *covariance* (measure of variability between variables) are found in the off diagonal positions of the matrix. A successful PCA explains the majority of the variance in the data by a few (for example between 1 and 6) principal components. However, it must be stated that PCA does not always work in the sense that a large number of original variables are reduced to a small number of transformed variables. If the **original variables** are uncorrelated, then the analysis is invalid. The best results are obtained when the original variables are highly correlated, either positively or negatively.

As with FA, PCA should be carried out in stages. This is necessary to ensure a valid outcome. An important pre-requisite is to log transform the data if it is not normally distributed. The variance-covariance matrix should then be generated. Once this is done, PCA can be used to extract the eigenvalues. The output data are then assessed. The next step would then be to rotate and extract the factors from factor analysis. This then leads to the final stages in the analysis. These include examining the factor loadings, saving the factor scores and plotting the scores so as to characterise the data.

5.3 Limitations and differences between FA and PCA

Geochemical data do not generally display a normal distribution but are strongly skewed. One of the main assumptions of multivariate statistics is that the data possess a multivariate normal distribution.

Outliers reflect locations where anomalous values are occurring either because of underlying geological processes or due to anthropogenic activities which may be important to the investigation. Log transformation of the data may cause the outliers to conform to a normal distribution, thereby fulfilling the requirements of the correlation matrix.

Standardisations of variables is another technique commonly used in datasets that have different units. This is done to avoid measurements taken from a larger scale from having a disproportionate impact. Closed number system or data closure is a property of geochemical datasets (Reimann *et al.*, 2002). Element concentrations are reported as a

portion either in weight percent or mg/kg. There are no data conversion methods that can overcome this problem; researchers are thereby reminded to be aware of these data constraints during interpretation of the work (Reimann *et al.*, 2002).

One of the most important decisions when carrying out multivariate statistics is the choice between FA and PCA. The major difference between these two techniques is that PCA performs a transformation of the data with limited statistical assumptions whereas FA assumes a statistical model with certain pre-requisites, such as that the data displays a multivariate normal distribution (Reimann *et al.*, 2002). PCA accounts for the maximum variance of all variables, while FA is based on the correlation structure of the variables and does not account for maximum variance. The model in FA allows for the common factors to not explain the total variation of the data. This thereby suggests that FA permits the existence of some distinctive factors that have may have a completely different behaviour to the majority of all the other factors. Unusual variables will therefore not enter the common structure. PCA, on the other hand, will always show the total structure, as the variables are forced into the result (Reimann *et al.*, 2002). In other words, PCA analyses variance, whereas FA analyses covariance (communality) (Korre, 1997). FA is therefore better suited to detect common structures in the data. So, in geochemistry, the likelihood of detecting common processes determining element behaviour appear to be better when using FA.

5.4 Geostatistics

Geochemical and environmental data tend to show **spatial dependence**. The environment is the outcome of actions and interactions of different processes and factors (natural and anthropogenic), which operate at different scales, ranging from micrometres to thousands of kilometres. In rural areas the concentration of elements in soil is largely controlled by lithogenic and pedogenic factors, as opposed to urban areas where anthropogenic activities have a greater influence of trace metal input into soils. The anthropogenic release of metals is heterogeneous and spatially discontinuous (Webster and Oliver, 2001). Numerical analysis techniques for environmental data, such as baseline surveys in soils and dusts provide a quantitative description of the data. They provide no insight into the spatial distribution of the data. The spatial distribution is the most important attribute common to all variables measured, so its consideration is essential when analysing any geochemical or environmental data.

Spatial analysis techniques and geostatistics are, in the majority of cases, interlinked. Geostatistics literally means the statistical analysis of natural phenomena. However, in the past few decades, geostatistics as a subject has evolved from this concept, to encompass the attribute of location in space, which all geo datasets possess. The spatial features of a geo-dataset include location of anomalous or extreme values, degree of continuity and overall trend (Webster and Oliver, 2001). These features, or variables (Z) are measured at different locations (S). These features describe phenomena within their geographic distribution, whether it be natural, an ore grade within an ore body, or anthropogenic; the distribution of pollutants around an industrial site (Thornton, 1991). Korre (1997) describes the basis of geostatistics as "*the idea of considering the observed values of a variable at a given set of positions as a realisation of a stochastic process in space*".

The spatial description of a geo dataset is commonly done in stages as outlined below (Shaw, 2000):

1. *Data postings* – the numbers are plotted directly on graphs in which X and Y axes represent spatial coordinates
2. *Symbol maps* - symbols plotted on graphs or maps in which X and Y axes represent spatial coordinates
3. *Contour maps*
4. *Moving window statistics* - to determine whether the mean value and the standard deviation change from location to location
5. *Proportional effects* - scatter plots between moving window means and standard deviations – there should be no relationship (homoscedastic) if the data are normally distributed, but mean and standard deviation will be correlated if the data are log-normally distributed (heteroscedastic – Webster and Oliver, 2001)
6. *Variograms* - these provide a visualisation of the spatial continuity of a variable based on the assumption that two data points which are close to each other are more likely to have similar values than two data points which are further apart. The semi-variogram is a graph of the relationship between the distance between sample points (the lag distance, h, plotted on the x axis) and the semi-variance between those points
7. *Interpolation Techniques*. GIS packages provide the means to visualise spatial data sets by calculating "missing values" between the measured locations

obtained in a spatial sampling survey. The techniques used to achieve this are referred to as interpolation techniques and include trend surface analysis, contour plotting, surface interpolation, Thiessen polygons and kriging.

The spatial variation of elements in soil may be lithogenic or anthropogenic but can be said to be ultimately geographically controlled. Element concentrations are displayed on maps as a means of interpreting the underlying controls influencing geochemical variability. The basic hypothesis behind geostatistical methods is that things that are closer together are more alike than things that are further apart (Johnston *et al.*, 2001). The concentration of elements in soils displays spatial dependency. This therefore means that the variance between locations increases with distance. Once this relationship has been modelled, it is used to predict the concentration of an element in unsampled areas. Variograms and kriging are tools used for this purpose.

5.4.1 Variograms and kriging

When samples such as soils, dusts, flora or water, are collected, each sample has a geographic location which is allocated through a coordinate system. *Autocorrelation* is defined as the spatial correlation between an element's concentration in a soil sample with its concentration in a neighbouring sample. The correlation within a variable is measured by covariance. Because the concentration of an element in soil is believed to be more comparable in samples which are closer together than in samples that are further apart, it is assumed that there is some underlying factor that controls this spatial relationship which can be mapped. Autocorrelation of the variable Z is measured between a pair of points S_1 and S_2. It is assumed that variance of Z is smaller when the distance between the points (S_1-S_2) is smaller and vice versa. This relationship is plotted and modelled by a variogram. Kriging is a statistical method used to interpolate or predict the values of a variable in unmeasured locations. It requires the construction of a semi-variogram before it can be applied (Johnston *et al.*, 2001; Webster and Oliver, 2001).

5.4.1.1 Semivariograms and Variograms

The semivariogram finds the rate of change of a variable along with distance and orientation. If the data are auto correlated then the variability between the sample pairs

increase as distance increases. Figure 5.1 below illustrates the components of a semi-variogram.

The sill is the maximum semi-variance between data points at large separation distances. The range represents the lag or distance between data points at which the sill is reached. The nugget is the minimum semi-variance between the data points observed when samples are taken adjacent to each other. The lag is the horizontal distance between the sample points. The difference between sample pairs increase with distance until there is no spatial relationship between samples and the semivariogram cloud (x on the graph) flattens out. Samples that lie within the range have autocorrelation. Homogeneous data that possess a strong geographic relationship have a large range whereas heterogeneous data with a week spatial control will have a smaller range.

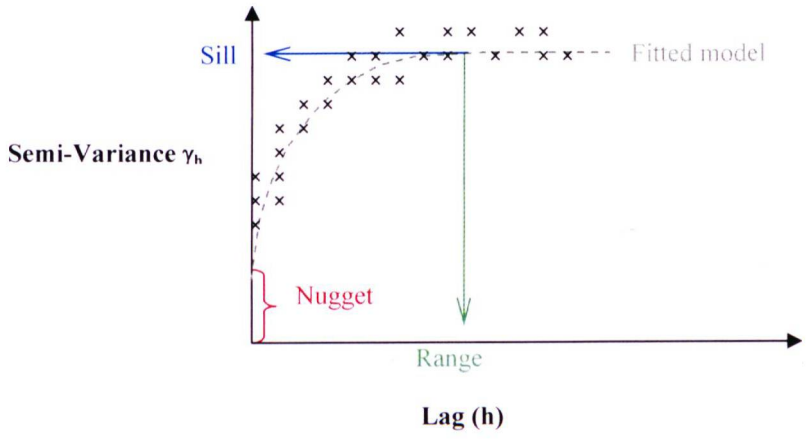


***Figure 5.1* The semi-variogram.**

Source: redrawn from Shaw (2000); Webster and Oliver (2001)

At zero distance the semivariogram (variability of Z) is equal to zero, and the model goes through the origin. This is very often not the case in heterogeneous soil samples. The nugget, as stated above is the variance of Z at zero distance. According to Johnston *et al.* (2001) there are two factors responsible for variation at zero distance; measurement error and micro-scale variation. Measurement error can be estimated by taking duplicate samples obtained from the same location (chapter 4). In order to define characteristic qualities for the semivariogram, a model is fitted through the data (grey dotted line in figure 5.1). This is done by defining a line that provides the best

fit through the points. The researcher needs to find a line such that the weighted squared difference between each point and the line is as small as possible. This is referred to as the weighted least-squares fit. This line is considered a model that quantifies the spatial autocorrelation in your data. There are two main types of variogram models, those that reach a plateau and those which do not. The more common models used include, linear, spherical, exponential and Gaussian.

The variogram shows how the concentration of an element changes with distance between samples. However in most sampling strategies, duplicate samples account for 10% of the data, so in most cases only one measurement has been made at any one point. The mean therefore is unknown. In order to overcome this problem it is assumed that the variable comes from the same population and so the mean is calculated from repeated measurements of the variable Z (Johnston *et al.*, 2001). This assumption is defined as stationarity. It is where the mean value is assumed to be constant between samples and is independent of location. Second order stationarity is the assumption that the covariance is the same between pairs and intrinsic stationarity is the assumption that the variance of the difference is the same between two sample pairs which have the same distance and direction apart. This may not always be a reasonable assumption for regionalised data and trend. Assuming a constant mean has problems particularly in regional dataset (Webster and Oliver, 2001).

5.4.1.2 Kriging

Kriging is a geostatistical method based on the statistical models of autocorrelation (the statistical relationship among the measured points) and variograms. It weights the surrounding measured variables to derive a prediction for an unmeasured location. It uses a *local* weighted averaging procedure, where the data have different weights according to their positions with respect to the unknown point and to each other (Oliver, 1996). The weights are based on the distance between measured points, the prediction location, and the overall spatial arrangement. Ordinary kriging is the most general and widely used method. It assumes the constant mean is unknown. This is a reasonable assumption unless there is scientific reason to reject it.

Universal kriging assumes an overriding trend in the data and it can be modelled by a deterministic function, a polynominal. This polynominal is subtracted from the original

measured points and the autocorrelation is modelled from the random errors. Once the model has been fitted to the random errors, before making a prediction, the polynominal is added back to the predictions, in order to provide more meaningful results. Universal kriging should only be used however, when it is known that there is a trend in the data and a scientific justification can be given to describe it.

Threshold and indicator kriging assign binary values to measured data. The creation of binary data may be through the use of a threshold for continuous data, or it may also be the case that the observed data are 0 or 1.

Simple kriging assumes μ is a known constant; if μ is known then the error, ε, is also known resulting in a better autocorrelation and therefore better predictions. More assumptions are made in this method. The assumption of exactly knowing the mean μ is often unrealistic. However, sometimes it can be plausible to assume a physically-based model gives a known trend.

Probability kriging uses indicator kriging to put data into categories. It does this by using additional data from the measured samples to determine the probability of an unknown value. First the measurements are grouped into binary values and then the proximity to the threshold is analysed.

Finally, cokriging uses information on several variable types. The main variable of interest is $Z1$, and both autocorrelation for $Z1$ and cross-correlations between $Z1$ and all other variable types are used to make better predictions. It is appealing to use information from other variables to help make predictions, but it comes at a price. Cokriging requires much more estimation, which includes estimating the autocorrelation for each variable as well as all cross-correlations. It uses the relationship of a second variable to assist the prediction of a first.

When running kriging models, certain options may be modified which will produce more valid results for the dataset in question. Parameters of the semivariogram and kriging model are changed so as to find the optimum parameters to estimate a particular surface. For example, setting the neighbourhood search area, defines the neighbourhood shape and the constraints of the points within the neighbourhood that will be used in the prediction of an unmeasured location. The neighbourhood search area is recommended

to be small in heterogeneous data to reflect local relationships. Altering the size and number of neighbours can be done in the prediction to optimise the kriging model. Kriging methods generally require a normal distribution. The identification and handling of outliers will thereby influence the creation and interpretation of the surfaces produced. This influence can be large and possibly lead to biased results in the surrounding areas, so it is recommended that their removal or inclusion in such models be related to the purpose and scope of that particular investigation.

Another way of modifying the model to better relate it to a particular dataset is associated to spatial trends. If it is accepted that measurements of the natural phenomena have some geographical trend, then a regional trend can be removed in order to allow the local relationships to be modelled and replaced before the final surface is produced. This can be described as anisotropy. It is the difference in autocorrelation with direction, and it cannot be explained by a regional trend. The method of cross-validation is when the surface is approximated, a point then removed and the surface estimated again without it, (all input parameters are kept constant). A plot of measured values versus predicted values is displayed. This is done because kriging methods are known to underestimate samples with a high value and overestimate low values, thereby affecting the decision making process. Since the data contain errors, the interpolation of points for a particular urban area can lead to mistakes in policy regulations if and when the points are close to a threshold value. For example, if a residential or commercial location has two adjacent values that are separated by a short distance, with Pb values of 450 mg/kg and 480 mg/kg (DEFRA/EA guideline value 450 mg/kg) it would be difficult to conclude that either location is safe or unsafe according to the guideline values. Furthermore the influence of surrounding values may result in a surface which is classified as safe. Factor analysis is used for the analysis of the Gibraltar data.

5.5 Geographic Information Technologies (GIT)

Geographic information technologies are tools used for collecting and processing geographical information. There are three main types of GIT, namely *global positioning systems* (GPS), *remote sensing* and *geographic information systems* (GIS). In this project, two of these technologies have been used, GPS and GIS.

A GPS consists of a system of earth-orbiting satellites transmitting precisely timed signals. These signals are received by a special electronic device (commonly known as a hand held GPS), which provides direct measurements of positions on the Earth's surface. The location is expressed in latitude/longitude or other standard system (e.g. Easting and Northing) (Grossinho, 2001).

A GIS consists of hardware and software, with procedures of automated data, designed to support the capture, management, manipulation, analysis, as well as the modelling and display of spatially referenced data for solving complex planning, management and research problems. Analysis using GIS is important because it integrates spatial as well as other types of information, provides a consistent analysis framework for geographically referenced data, provides new and insightful ways of manipulating and displaying data as well as allowing the viewing and analyses of data based on geographical proximity and relationships.

The GIS project in this work has been developed as a decision support system. This support system will convey environmental information to assist various Government departments in Gibraltar.

5.5.1 Steps in a GIS project

GIS allow strategic planning, development control and pre-application assessment (Grossinho, 2001). The GIS project will assist in the modelling of urban regeneration based on the "suitable-for-use" approach adopted by various EU governments. The GIS project will offer various options to assist government departments in the integration of EU directives with the Gibraltar regulatory system. ESRI ArcGIS software has been used in this project (ESRI, 2002).

One of the most important aspects of a GIS is the quality of the primary data. Spatial features are captured from a number of different sources. Figure 5.2 illustrates the different data automation techniques. Data can be imported into a GIS in a tabular form, as ASCII text files, or in the form of images from aerial photographs, satellite images (raster data) and CAD drawings (other vector data). Features can be digitally drawn directly into a GIS by a method of digitisation (paper maps or onscreen digitising). The features are stored as different layers, which then can be linked together.

One of the primary objectives in any GIS database is to analyse the spatial relationships and distribution of the data collected. It is therefore essential that the different features within the database are compatible in scale and detail. Similarly, time is another key factor to bear in mind. Urban development is an ongoing process which leads to rapidly changes landscapes.

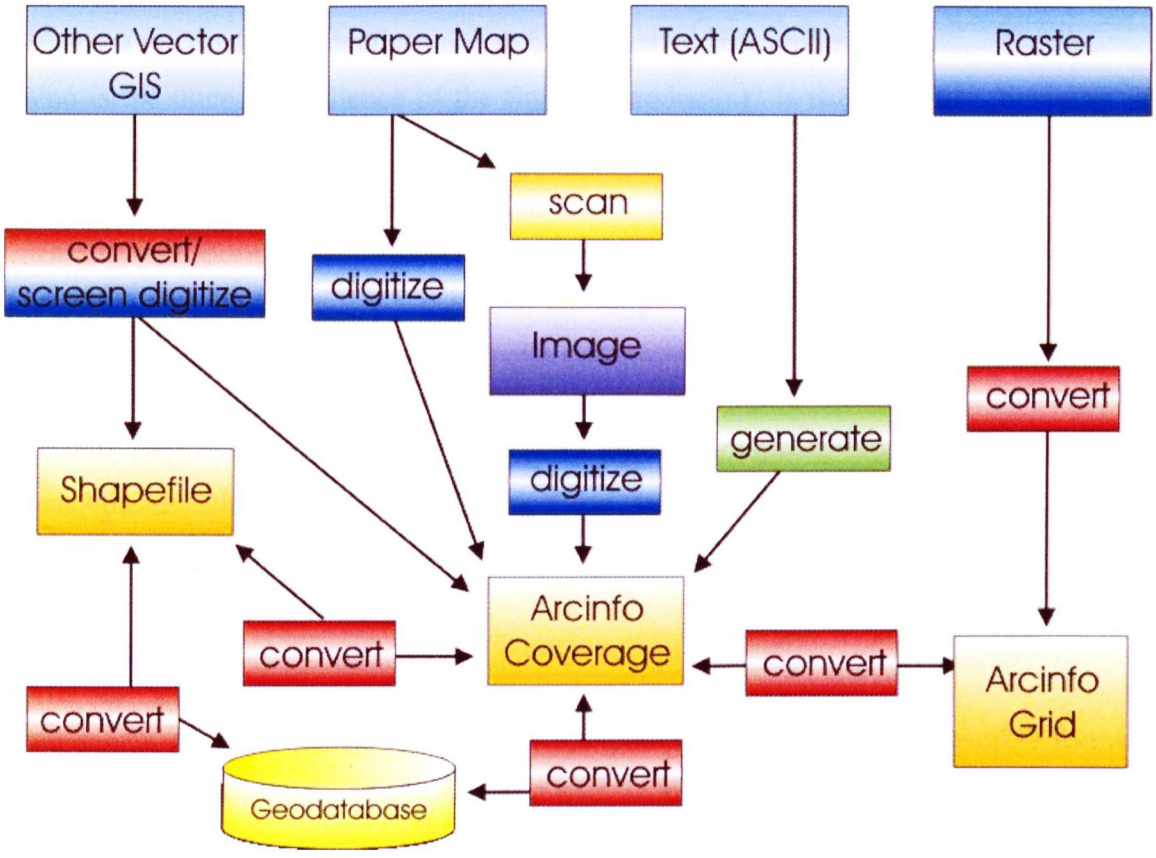


Figure 5.2 Data automation methods in a GIS.

Source: modified from ESRI (1990)

The date of the primary data source is important particularly in relation to geographical features as such projects can use a series of geological, geographical and land use data (both past and present) to evaluate any spatial relationships.

One of the key tools of a GIS is data handling capabilities (figure 5.3). Once the features have been captured into a GIS they can be analysed and modified to suit the requirements of the project. A GIS allows a great degree of flexibility to the categorisation and display of data.

5.5.2 Defining a GIS project

The first step in the development of a GIS project involves determining the project objectives, by posing a series of questions (Grossinho, 2001):

•What is the problem? How can it be solved? What is the role of GIS?
•What are the needs of the user or client?
•What are the final products that need to be created: charts, reports, maps?
•Who is the intended audience of the finished product(s)? Is it technicians, planners, or the general public?
•What data are necessary? Will the data be used for other purposes?

The answers to these questions establish the scope of the project. Figure 5.3 illustrates the steps to be followed in the creation of a GIS project.

The next step is to design the database. No digitised maps of Gibraltar were available when this investigation began; therefore these were produced in order to allow spatial distributions of elements to be assessed.

5.5.3 Digitising

Over recent decades, geographic data in computer automated GIS compatible formats have now become widely available. The data acquired usually require some degree of processing, simplification, or additions to meet the needs of the project. For example, error can be inherited from the original data and subsequent data processing may therefore be necessary. Error may often be overlooked in a GIS project so a method of quality control should be applied to the database. This is done by cataloguing the origin and quality of the original dataset and the procedures applied to them in the form of metadata files (section 4.13). The data input involve the digital encoding of both geographic and attribute data. For attribute data, this is done in the form of spreadsheets and database management systems. For geographic data, this is done through coordinate entry, scanning and digitizing (Grossinho, 2001).

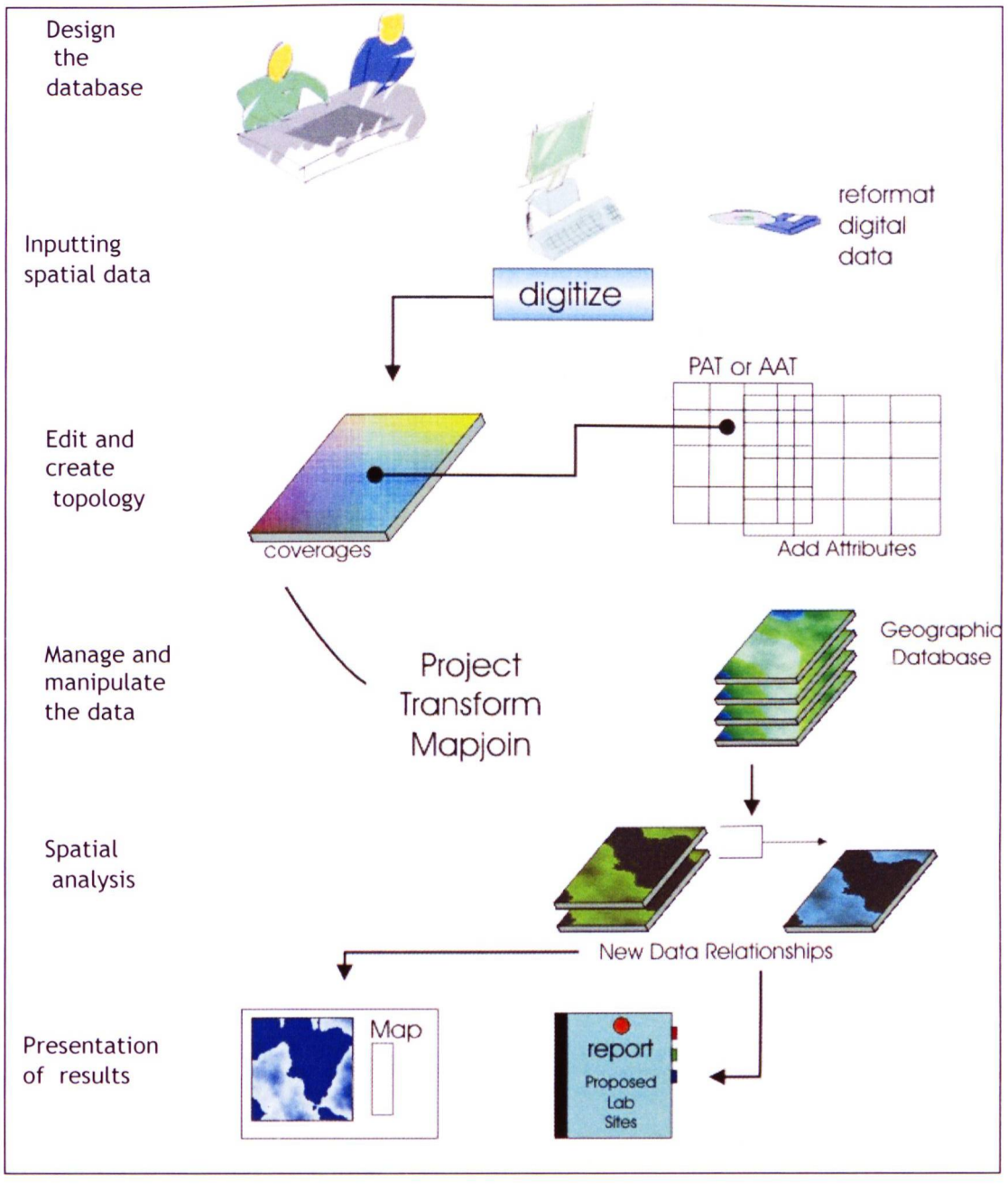


***Figure 5.3* A GIS project. Building the database.**
Source: modified from ESRI (1990)

Digitising is the process of capturing spatial data manually (digitising can be done manually using a digitising tablet or via onscreen through a scanned map); it consists of tracing a paper map and generating a computer file that can then be operated with a software package. Several different (paper) maps of Gibraltar were obtained from the Department of Trade and Industry (DTI), Gibraltar and have been digitised using a Calcomp Drawing Board III digitising tablet and the GIS program ArcGIS; Arc Info 8. The tablet and software were studied beforehand in order to ensure the digitising was carried out and done correctly. An "A0" sized map was fixed onto the tablet. All

features on a paper map can be stored digitally as either points, lines or polygons, (definitions are given below) once they have been formatted in an *x y* coordinate system. Once the data are captured, it exists in a digital format, which can then be reformatted and used by many applications. A series of control points (tics) were selected with the digitizing puck and a tic coverage was created. Tic coverage consists of a series of easily identifiable reference points identified by known coordinates on a map and is used to orient the coverage (using a minimum of 4 Tics increases accuracy) (figure 5.4). The points chosen corresponded to the corners of the map, but can be any areas with the map, such as a road intersection or a lighthouse or mountain peak. The corners of the map were geo-referenced using a master tic file, which was based on the real world co-ordinates (UTM grid) given on the paper map. The tic file also contains data like the number of rows and columns on the scanned map, which allows the projection of the data on screen. The various layers of information, or different maps which were used, were each digitised as a separate coverage, in other words as a separate layer, which can then be over-layed or superimposed onto any other layer (figure 5.5).

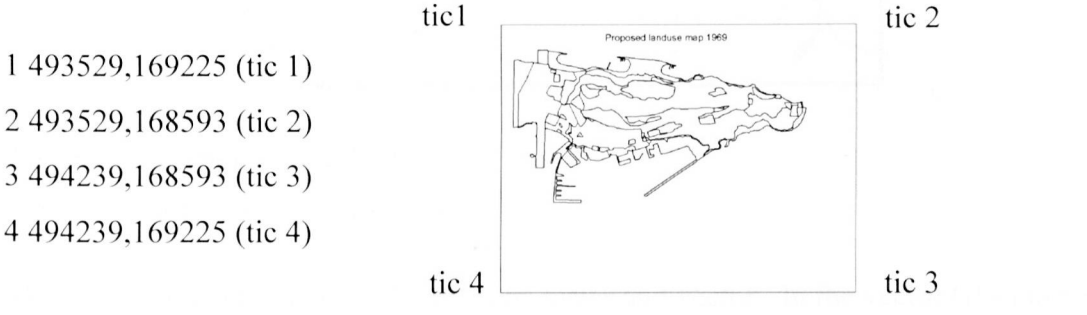


Figure 5.4 Control points on a map

The original data file with the grid co-ordinates (master tic file) were used for each coverage that was created from a given map to ensure greater accuracy when overlaying data. For example, the coastline, road network, buildings and contours were all taken from a single map. The geology was digitised from a separate map which would have its own master tic file. Similarly, land use was digitised from another map which again would have its own master tic file. All the paper maps used for the digitising process had the same scale. The reason why a master tic file was created each time a new map was fixed onto the tablet is because the physical location of the map on the tablet would change. The actual digitising process was done in a series of stages. The features to be digitised were "traced" with a digitising puck. Figure 5.5 is a schematic illustration of a

digitising tablet and puck. The digitising tablet has a series of grid wires on the inside (figure 5.6, bottom half). These grid wires create a magnetic field which is detected by the puck. *x y* coordinates are fed directly into GIS in the form of digitizing units. This allows for a high level of precision in coordinate recording. These units are then converted into **real world coordinates** through the tic file.

The more information which is digitised onto the project, the more this will allow for a further vigorous investigation into the spatial distributions of element concentrations across Gibraltar.

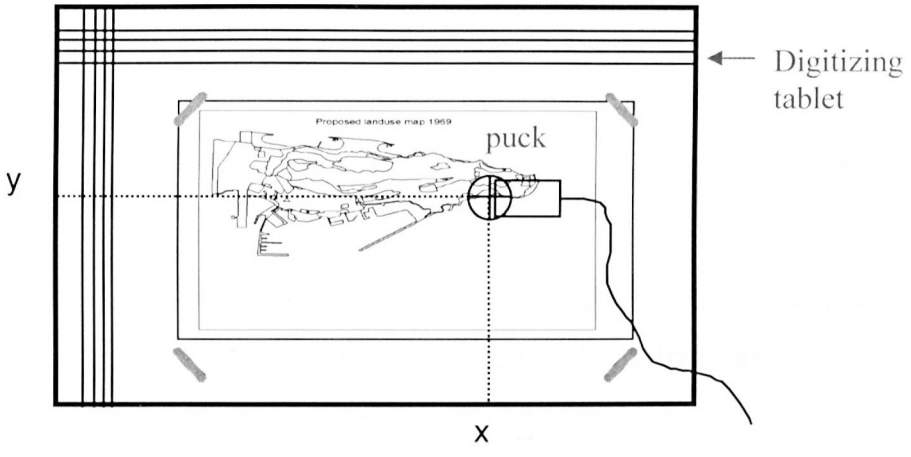


***Figure 5.5* A Digitising tablet.**

Source: modified from Grossinho (2001)

There are two main types of GIS models; raster and vector. In the vector GIS model, real world objects are represented as points, lines and areas. Points identify locations, lines connect points and areas (polygons) consist of connected line segments (figure 5.6). The information which is acquired from the tablet is the converted into point, line or polygon coverages.

Errors can occur during the digitising processes. These can be in the form of undershoots, overshoots or spurious polygons. Any digitized map requires considerable post-processing. This includes checking for missing features, connecting lines, removing overlaps in lines or polygons and verifying the precision of the tic files (Grossinho, 2001). The latter is extremely important as it will ensure an exact overlay of the different data layers.

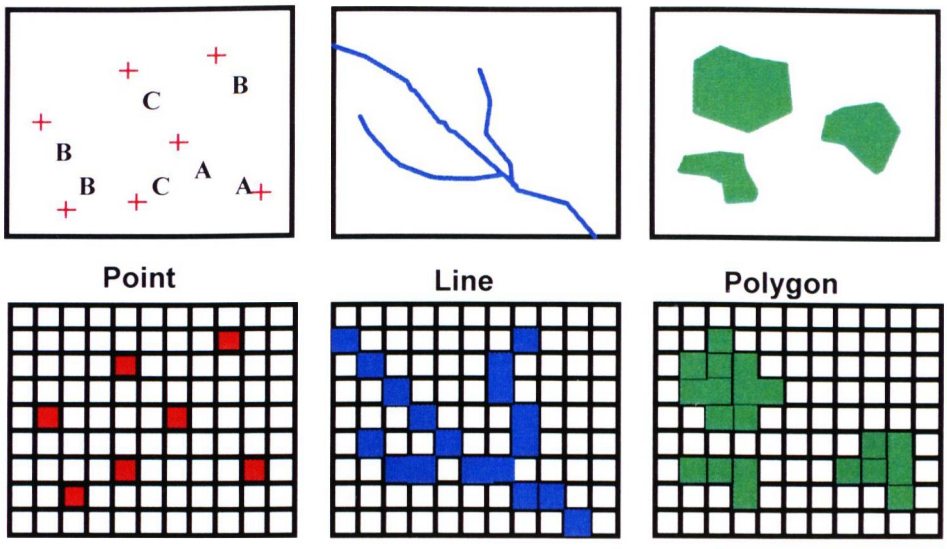


***Figure 5.6* Points, lines and polygons.**

Source: Grossinho (2001)

5.5.4 Data layers

A GIS database will consist of a series of layers (coverages) that can be overlaid to provide information concerning spatial patterns. Figure 5.7 illustrates an example of the different types of layers that might be found within a GIS database.

The purpose of this project is to conduct a baseline geochemical survey of Gibraltar. This then means that the geochemical data are a key aspect of the GIS analysis. The GIS project is used to display geographical and geochemical data, analyse trends in the geochemical data and interpolate surfaces. Geochemical data for soils and dusts, the results of the multivariate statistics and the partitioning of trace metals in sequential extractions can be displayed as layers in the GIS along with other geographic information, including road networks, green areas, buildings, industrial locations etc. Geological, pedogenic and anthropogenic features are the underlying controls on geochemical variability in urban soil and dusts. This thereby dictates the extra data layers which are necessary to make a full geochemical interpretation using GIS as a tool. For example, geological layers represent the parent material and the land use layer indicates anthropogenic activity (Grossinho, 2001). Historic and contemporary land use is used to interpret the extent and impact of anthropogenic activity.

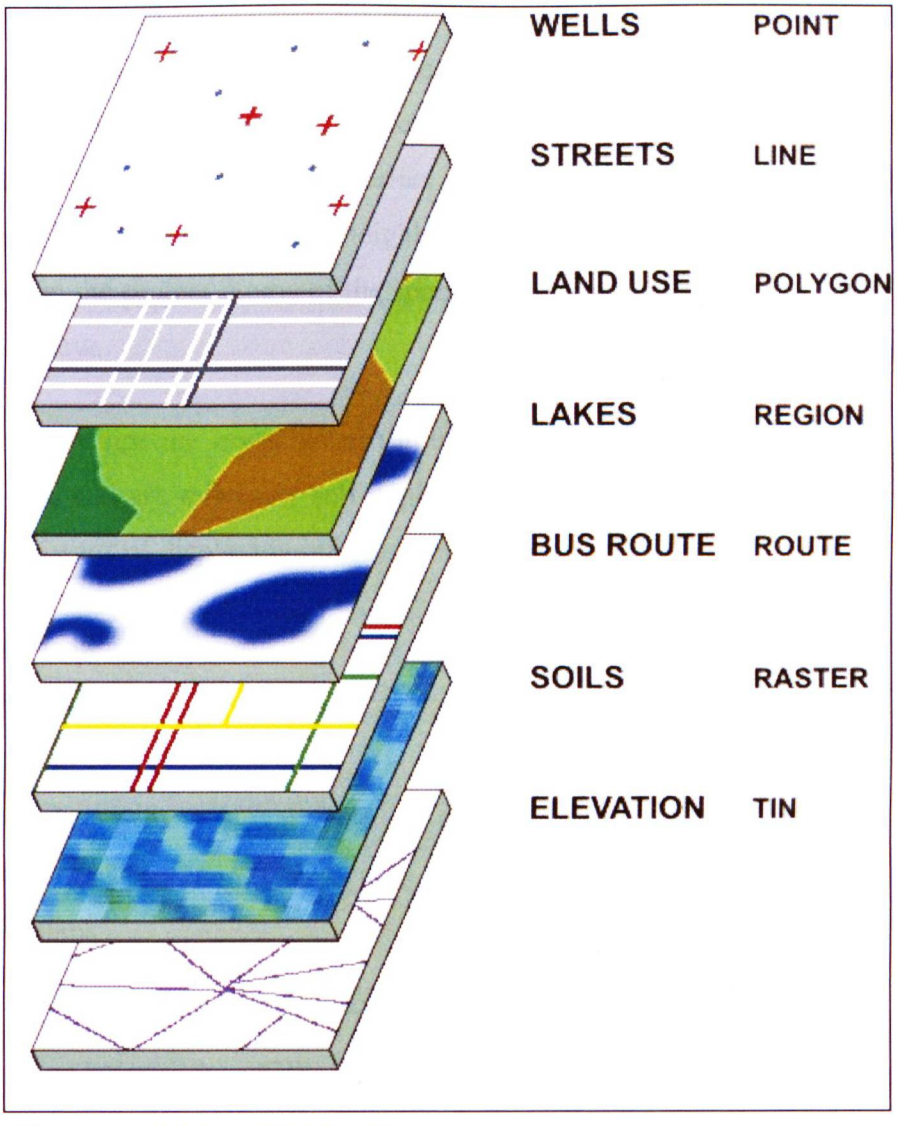


***Figure 5.7* Layers within a GIS database.**

Source: modified from ESRI (1990)

The next step in the creation of a GIS project involves the analyses of the data. Data analysis on a GIS project will include at least one of three GIS functions (Grossinho, 2001):

- Geometric modelling – calculating distances, generating buffers, calculating areas
- Coincidence modelling – overlaying datasets looking for spatial coincidence (necessitates vertical integration) – cartographic modelling
- Adjacency modelling – allocating, path finding, redistricting – derivation of new datasets and layers as answers to questions

This project uses GIS tools for trend analysis and surface interpolation. Trend analysis allows spatial data to be analysed for regional trends; geostatistical techniques mode the autocorrelation and estimate element concentrations over the surface of a region (section 5.5.2 above). Further analysis involves the showing of the geographic distribution of features and the development of queries (spatial, locational, aspatial or attributional) (Grossinho, 2001). Additionally, neighbourhood analysis and overlay analysis can be carried out on the project. Some of the spatial evaluation techniques used in this work are described below.

Spatial relationships are investigated through queries. The following terms are used in GIS analysis, and are relatively self-explanatory. They provide a good indication as to the different ways of displaying information within a GIS:

- Adjacent to
- Connected to
- Near to
- Intersects with
- Within
- Overlaps

When creating queries in a GIS, the different features are selected by their attributes, through geographic relationships, or both. Buffers (demarcated areas or rings extending out from a central point showing distances from that point) are created to assess the impact to something within a given catchment area. For example, the decrease in Pb concentrations with distance from a road can be evaluated if a buffer area is selected from the road and point-in-polygon operations identify Pb concentrations within industrial land use areas. Similarly, polygon overlay allows the researcher to combine ecological surveys within nature parks. Geocoding/address matching allows the researcher to identify areas within a map with greater accuracy.

Modelling allows the researcher to identify or predict a process that has created or will create a certain spatial pattern. Diffusion modelling relates to the spread of a contaminant source within soils for example. Interaction modelling can be related to the migration of elements within different environmental media or locations within a city. Finally "What-if scenarios" allow questions to be asked before a decision is made. Such a

question might be - "If the incinerator is built in this location, what areas will become susceptible to contamination?"

Polygon overlay allows subsets to be created within a dataset. For example, a layer of for example incinerator locations can be superimposed onto another layer showing the location of samples with Pb concentrations above 500 mg/kg. When these locations coincidence a subset can be created. Once the analysis is complete, and the researcher is content with the information which has been produced, the research is documented in the form of presentation quality maps, charts and statistical summary tables, which can be incorporated into a report.

5.6 Chapter conclusions

From a methodological perspective, each of the techniques discussed in this chapter can be used as effective tools for the interpretation of data, as long as the limitations to each method are noted and carefully considered. For example a normal distribution is required before multivariate analysis and methods of kriging can take place. Therefore data transformation and the management of missing values are essential prior to any analysis. However, when any tool or method is used in isolation, the results obtained may not truly reflect all the different aspects which influence and function within a particular environment. Multivariate statistics, when combined with GIS, provide a very powerful instrument for the identification of factors controlling the variability of geochemical data and interpreting the results. Confirming and refining hypotheses related to geochemical interpretations from statistical outputs is best achieved when several methods are used to compliment each other.

CHAPTER 6

Analytical results and discussion

6.1 Introduction

The first step in data analyses should generally consist of a careful study of the distribution of the measured variables as it provides a number of simple graphical techniques for the study of the data in detail, prior to the use of more advanced statistical techniques.

Table 6.1 Media sampled and analysed from Gibraltar in this research project

Site description	Number of samples
Rocks	9
Soils	187
Beach sands	12
Raised beaches	4
Wind blown sands (WBS)	17
Cave sediments	3
Samples high in fly ash and shot blasting sand	13
Red sands	10
House dusts	80
Street dusts	83

Table 6.1 shows the numbers and types of samples that have been collected and analysed in this study. The "total" elemental concentrations of 26 Elements (Li, Na, K, Be, Mg, Ca, Sr, Ba, Al, La, Ti, V, Cr, Mn, Mo, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb, P, S, As) were determined by ashing in a nitric/perchloric acid mixture followed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analysis. A chemical sequential extraction technique was used to assess partitioning of elements within the soil phase, thereby giving an indication into any potential bioavailability. This was also applied to dust samples (see section 4.4.1). Although it is understood that the phases applicable to soils and sediments are unlikely to be found as such in dust samples, a series of

sequential extractions can give valuable information concerning the extractability and thus mobility of metals in the dusts. This chapter will discuss some preliminary results on the samples collected and their distribution across Gibraltar.

6.2 Soils

A total of 246 samples (excluding duplicates) were taken throughout Gibraltar (figure 4.1). The soils were taken from MOD and civilian areas, and included local natural soils and garden soils which are commonly imported from Spain. The accuracy of the analytical methods was assessed by comparing the accepted values for the reference materials with the values obtained for those materials from the analytical run. Figures D1 and D2 in appendix D show the percentage recovery for the HRM and NIST SRM reference materials for the nitric/perchloric acid digestion and sequential extraction process. Most elements have an overall recovery rate of between 80-120%. The recovery was generally higher for the HRM reference materials than for the NIST SRM reference materials. Also elements whose concentrations were close to the analytical detection limit of the instrumentation, such as Cd had lower recovery rates.

In each analytical batch, 10% of the samples were analysed in duplicate and were randomly included in the batch. Each duplicate was independently taken through the analytical procedure (see section 4.8.4). The precision was calculated by comparing the mean value and the absolute difference for each pair of duplicate results using a control chart (Thompson and Howarth, 1976).

All element concentrations are presented in mg/kg. Both the arithmetic (AM) and geometric means (GM) were used to assess the central tendency and variation of the data. The AM and arithmetic standard deviations (SD) are best used as estimates of geochemical abundance of an element (Chen *et al.*, 1999), they are good estimators of location and spread for data which follow a normal distribution. The standard deviation (SD) is a measure of data scatter about the mean, the larger the value the greater the scatter. When dealing with a skewed distribution, (as geochemical data often display) the median, GM and geometric standard deviation (GSD) are better maximum likelihood estimators of the central tendency of the elemental data (Chen *et al.*, 1999). The median value also shows the central tendency and dispersion of the data. Measures of central tendency indicate the location of the distribution. When data conform to a normal

distribution the mean and median values will be the same or approximately the same. As stated in chapter 5 (section 5.3), geochemical data do not conform to a normal distribution. The reason for the positive skew in environmental and geochemical datasets is often that the samples represent more than one population or process. In such cases, the median (or middle value) is a much better indicator of the spread of the data. The geometric mean is very commonly used as an alternative. When the data are positively skewed as most geochemical datasets are, the median value < arithmetic mean. Skewness and kurtosis are statistics that describe the shape and symmetry of the distribution. They indicate how much a distribution varies from a normal distribution. A high kurtosis value for example indicates that the distribution is peaked. Percentiles are values of a quantitative variable that divide the data into groups so that a certain percentage is above and another percentage is below that value. Quartiles (the 25th, 50th, and 75th percentiles) divide the observations into four groups of equal size. The 95th percentile is also given which illustrates the value below which 95% of the observations fall.

In order to ease the statistical analysis of the data, soil, beach sand, raised beach, wind blown sand, cave sediment, red sand and samples high in fly ash and shot blasting sand are all referred to as soil samples unless stated otherwise. The extreme outlying values have been removed from the dataset for statistical analysis so as to minimise the likelihood of erroneous of biased results when assessing the spread of the data. This explains why n = 238 in table 6.2 and in the GIS maps in section 7.3. Molybdenum has not been included in the statistical analysis due to unacceptable levels of precision. Results for Ag, Cd and to a lesser extent La, Co, Cr and Mn (in soils, rocks, house and street dusts) need to be interpreted with caution due to high numbers of samples falling below or close to detection limit (appendix C contains the IDL for the SEQ analysis) and leading to an unacceptable precision. The IDL for Cd is set at 0.2 mg/kg, however, any data below 2 mg/kg warrants caution in the analysis (section 4.10). The Cd soil data has a 75th percentile value of 2 mg/kg, which illustrates the need for caution when reviewing the data.

The descriptive statistics (table 6.2) show that most elements have a large range of concentrations. The median value is smaller than the arithmetic mean for all elements indicating a skewed distribution. The anthropogenic elements such as Pb have a maximum value of 8507 mg/kg but the median value is 131 mg/kg and a GM value of 86

mg/kg. Similarly Cd has a maximum value of 17 mg/kg but a median value of 1 mg/kg. The elements Mg, Ca, Al and Fe have a very large standard deviation which suggests that the measurements are scattered widely about the arithmetic mean. Most elements have a positive skew and show a non-normal distribution. This illustrates the presence of outlying values in the dataset. This can be seen from the histograms in figures D5 and D6 in appendix D. All the elements show a strong positive skew (skewed to the right). The soil data for all elements show that there are at least two populations present. The main population contains most of the data range, and the subsequent population(s) referring to specific sites where some form of activity (anthropogenic or natural) has occurred or is occurring. These subsequent populations represent (extreme) outlying values which when plotted on a frequency distribution produce a highly skewed graph as seen in Appendix D, figures D5 and D6. The problem lies in that these values affect the distribution of the data, and the histograms then fail to show the distribution of the main population. For this reason, the histograms in this chapter show the distribution of the main population of the dataset ($n \leq 238$), and the histograms of the complete dataset ($n=246$) are found in appendix D. The histograms in this chapter have had the main outlying values removed until the samples remaining belong to the main population. This then means that the total number of samples displayed in each histogram will vary according to the element in question.

The major elements Na, Ca, Ba, Al, La, Ti and Mn display a lower kurtosis value to the other elements in the dataset illustrating a frequency distribution curve with a more flattened peak (figure 6.2 and 6.3). Kurtosis is the extent to which observations cluster around a central point. A normal distribution has a kurtosis value of 0. A positive kurtosis indicates that the observations cluster more and have longer tails than those, which exhibit a normal distribution. The kurtosis values are generally quite high, with Be, Sr, V, Ni, Ag and S displaying values above 100, showing the distribution to have a very strong peak as can be seen from the corresponding histograms for these elements (figure D5 and D6 in appendix D and figures 6.2 and 6.3). All the elements in the dataset have a skewness value greater than 1. In general a skewness value greater than 1 indicates a distribution that differs significantly from a normal, symmetric distribution. A positive skewness value (a value greater than 0) indicates a positively skewed distribution. The range of values of skewness are from 0.31 for Ti to 15 for Be. As with the values for kurtosis, Be, Sr, V Ag, Cd and Pb display the highest numbers.

***Table 6.2 Descriptive statistics for soils (0-15 cms) from Gibraltar* (n=238) (results in mg/kg)**

	AM	Median	SD	GM	Skewness	Kurtosis	Min	Max	25th percentile	50th percentile	75th percentile	95th percentile
Li	20	14	20	13	4	25	<0.04	192	8	14	24	49
Na	461	353	412	348	3	9	4.04	2608	244	353	481	1330
K	5488	4360	4709	3909	3	10	<1	32000	2592	4360	7170	13800
Be	109	0.72	1674	0.67	15	239	<0.02	25878	0.44	1	1	2
Mg	9937	7360	11439	6760	5	36	2.4	114000	3920	7360	11800	24700
Ca	51098	44403	44521	29930	2	5	<0.2	299408	17000	44403	74300	125000
Sr	86	74	127	63	13	183	<0.01	1914	43	74	102	173
Ba	182	145	160	122	2	8	<0.02	1070	82	145	237	503
Al	22669	18418	17777	16188	2	11	2	131000	11300	18418	29400	50300
La	14	14	8	11	1	6	<0.1	56	9	14	19	26
Ti	487	465	221	409	0.31	0.12	<0.04	1220	342	465	639	864
V	62	36	188	34	10	109	<0.1	2212	23	36	61	109
Cr	125	113	114	87	7	77	<0.2	1446	65	113	164	259
Mn	335	317	186	274	1	2	<0.1	1160	219	317	409	668
Fe	25593	17100	50933	15321	7	48	10	435000	10600	17100	25400	48300
Co	10	7	27	6	9	88	<0.1	284	4	7	10	16
Ni	46	39	49	37	9	104	<0.2	648	31	39	49	81
Cu	288	38	1548	30	7	45	<0.02	12500	13	38	65	411
Ag	0.58	0.30	3	0.23	14	215	<0.01	40	0.08	0.30	1	1
Zn	502	168	1471	153	7	49	<0.42	12700	63	168	375	1500
Cd	1	1	2	0.2	5	30	<0.01	17	0.30	1	2	6
Pb	368	131	866	86	7	56	<0.6	8507	20	131	359	1680
P	1220	926	1683	678	7	74	<0.4	20500	302	926	1580	3300
S	930	657	1693	463	9	104	<0.2	22000	238	657	1140	2290
As	16	9	31	9	8	83	<0.2	351	5	9	18	49

(Please note Cd and Ag data to assessed with caution due to number of samples below IDL and proximity of most sample concentrations to IDL. Cadmium concentrations below 2 mg/kg to be assessed with caution)

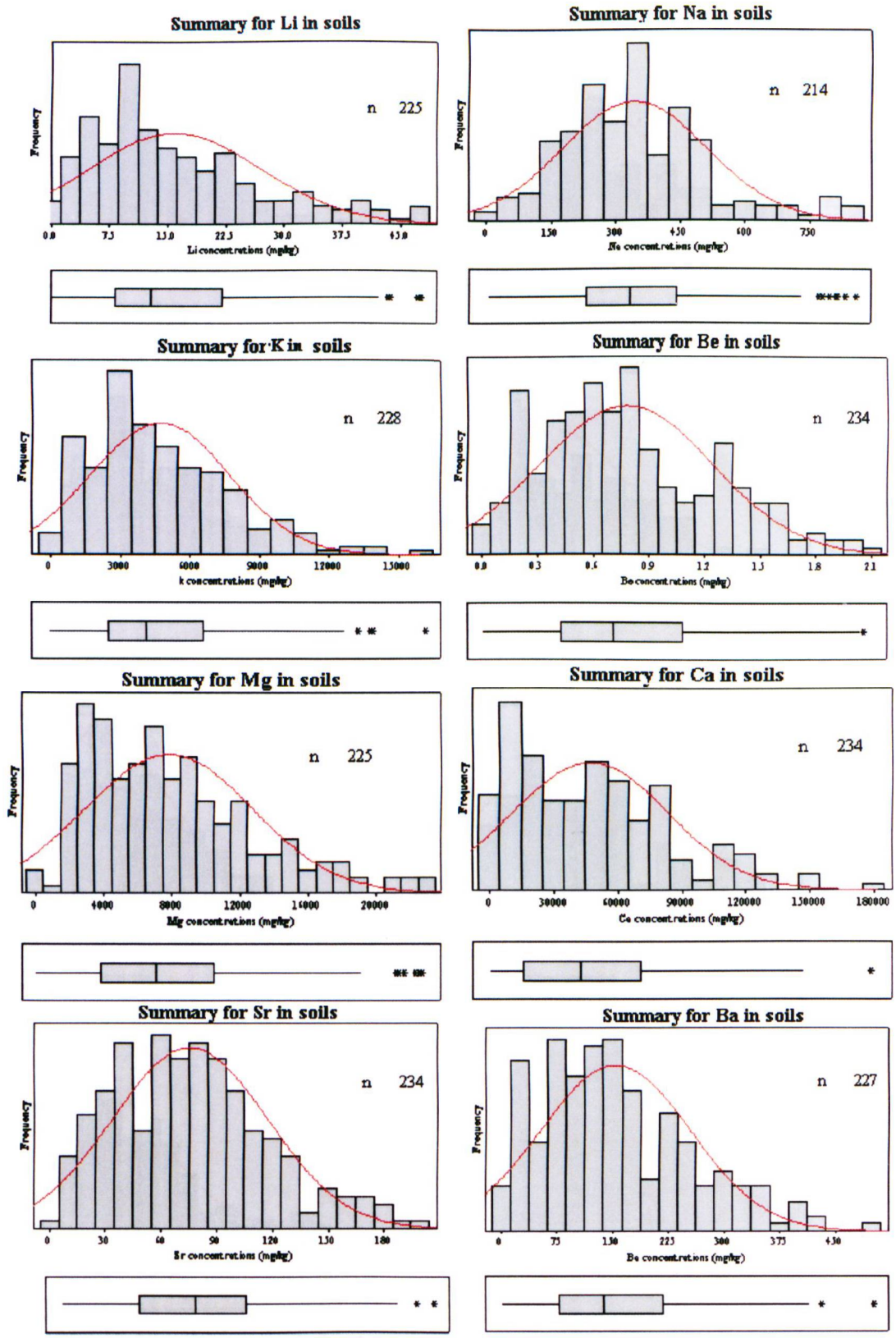


Figure 6.1 Graphical summary for Li, Na, K, Be, Mg, Ca, Sr and Ba in soils from Gibraltar.

(Histograms presented in this chapter show the main population of the data, extreme outlying values have been removed to allow an accurate assessment of the distribution of the majority of the samples in the dataset. The value of *n* in each histogram varies according to the number of outlying values that were removed).

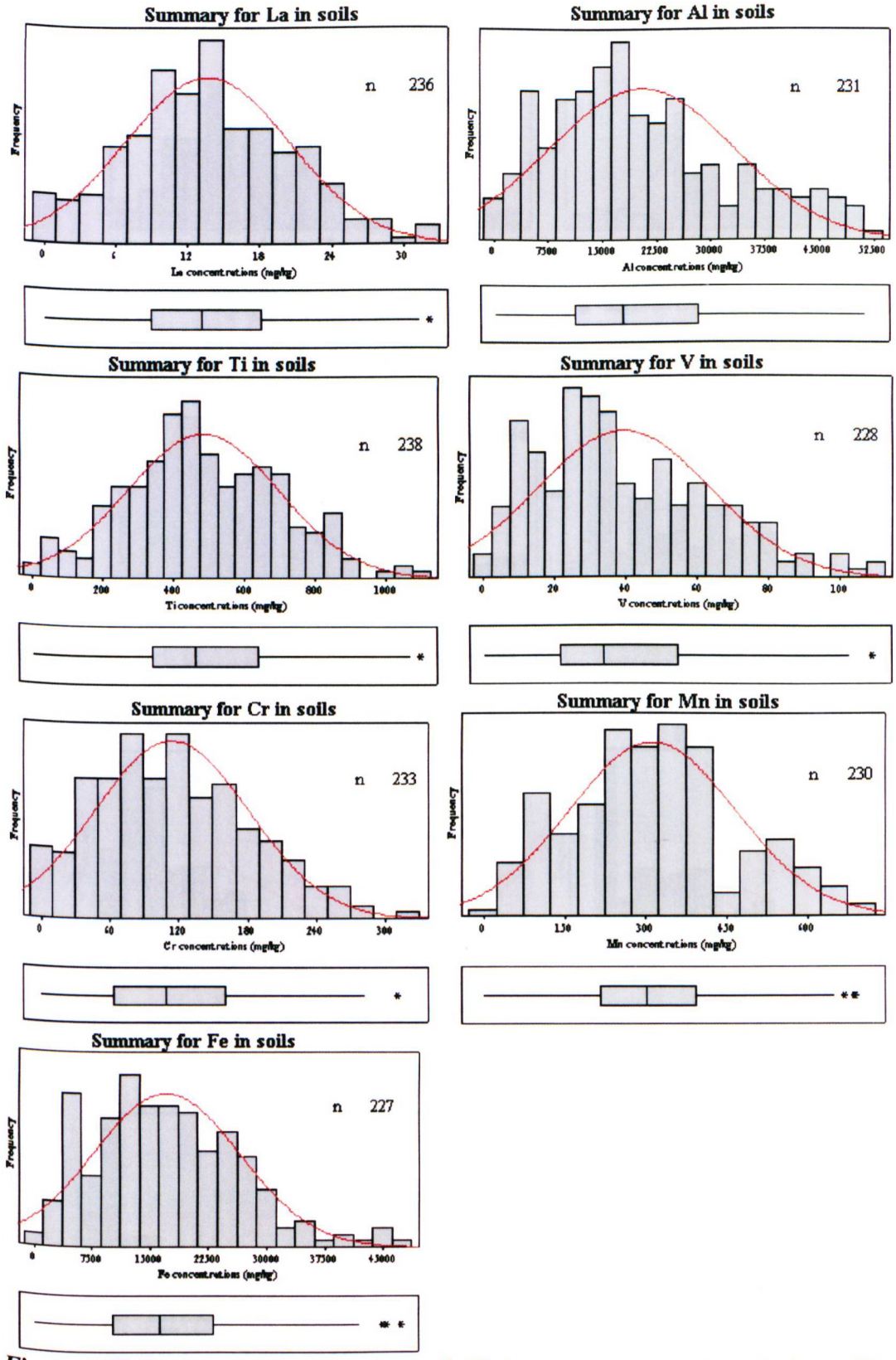


Figure 6.2 Graphical summary for La, Al, Ti, V, Cr, Mn and Fe in soils from Gibraltar.

Box plots have been used in combination with histograms to illustrate outlying and very high values for each element. The diagrams were calculated using Minitab v14. Using box plots together with histograms allows the identification of the location of outlying and extreme values in relation to the

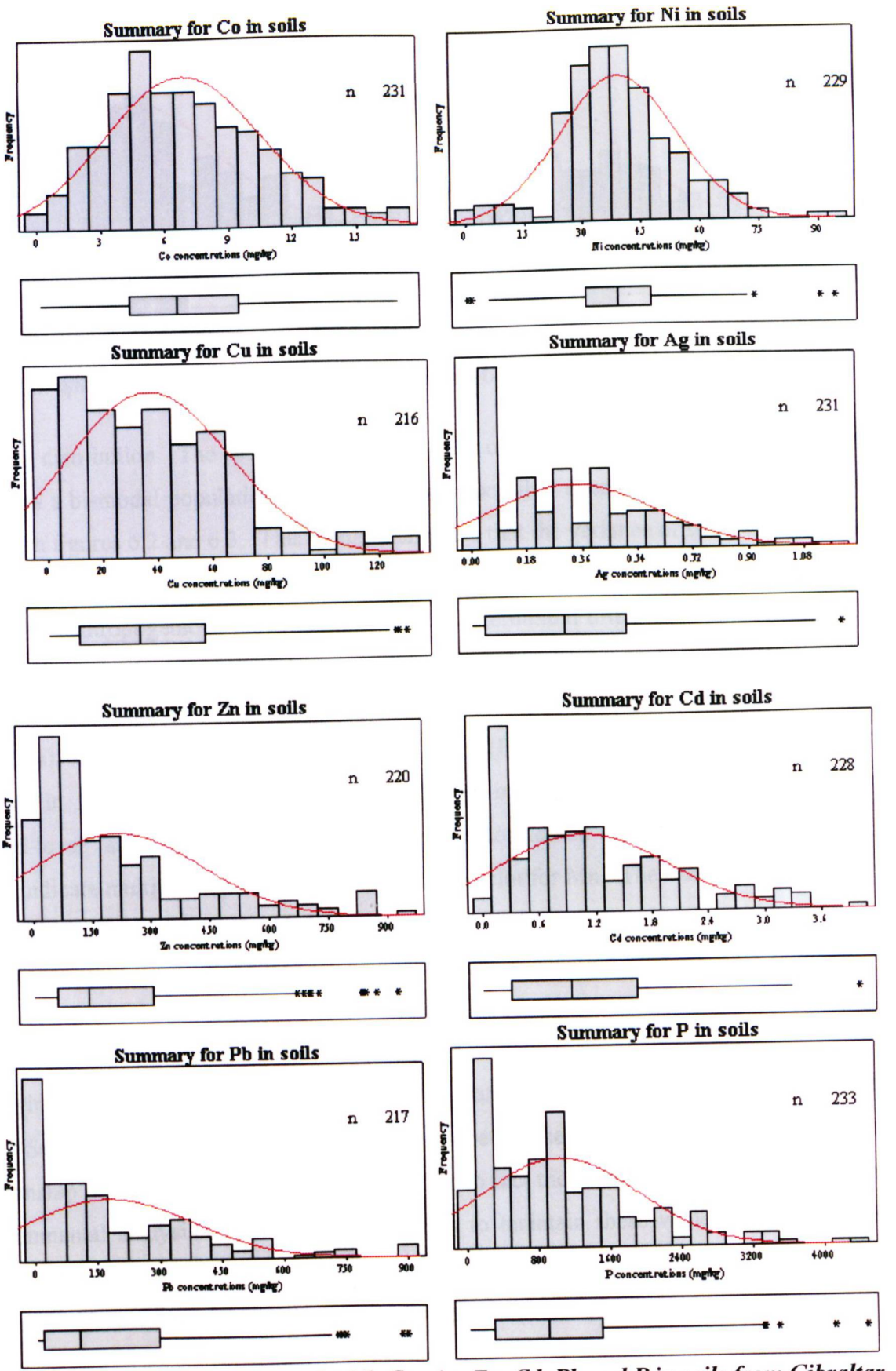


Figure 6.3 Graphical summary for Co, Ni, Cu, Ag, Zn, Cd, Pb and P in soils from Gibraltar.

(Please note Cd data to be assessed with caution due to number of samples below IDL and proximity of most sample concentrations to IDL. Concentrations below 2 mg/kg to be assessed with caution)

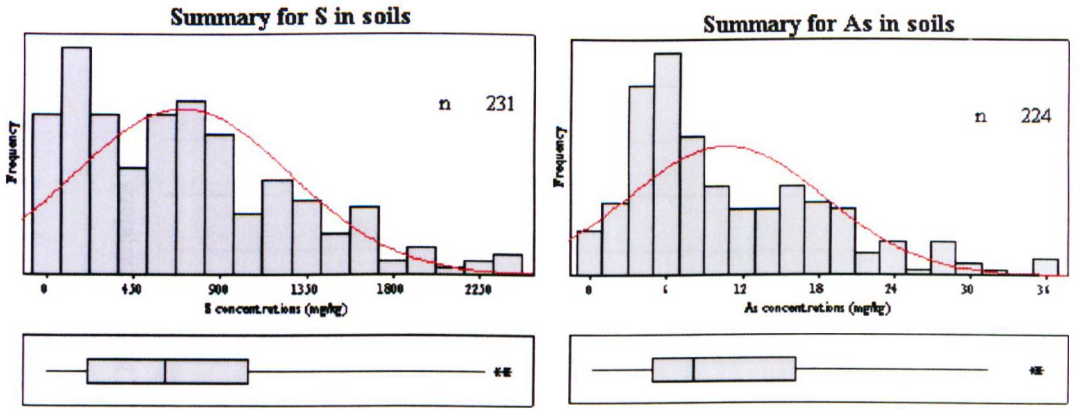
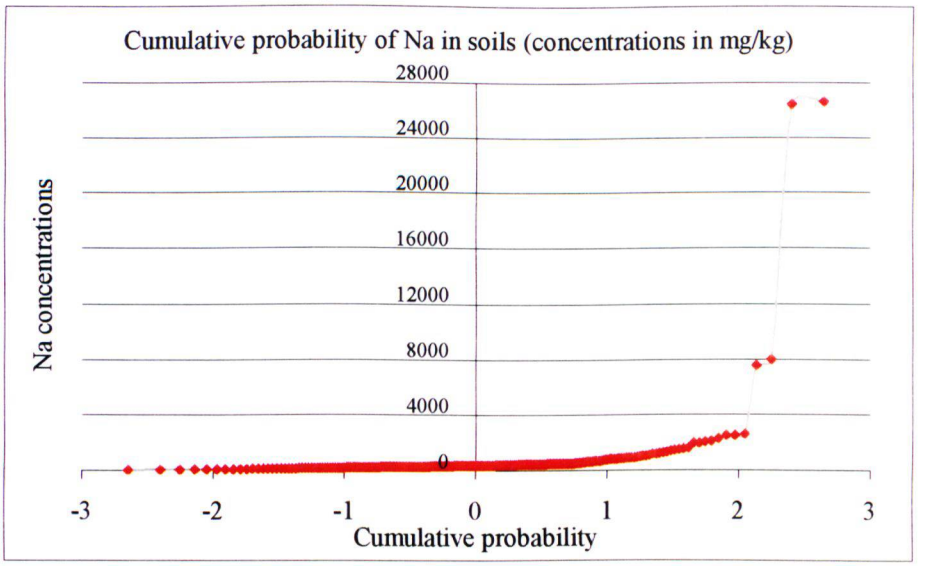


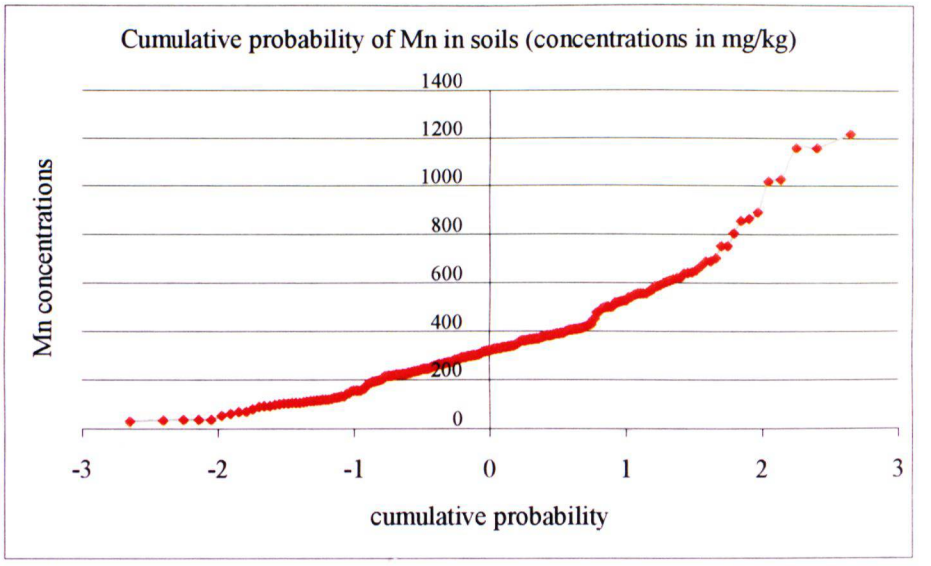
Figure 6.4 Graphical summary for S and As in soils in Gibraltar.

overall data distribution. The spread of the distribution of elements such as K, Ca, Ba, La, Al and Mn suggests a bi-modal population and in some cases possibly even a tri-modal population as can be seen from figures 6.2 and 6.3. This would then mean that the variance of some of these elements come from two or more populations which would indicate two or more distinct sources, either geological or anthropogenic or both. Another way to determine if different populations exist within the dataset, is by calculating cumulative probability plots. These plots were calculated for all elements in soils, house dusts and street dusts. Figure 6.5 illustrates the plots calculated for a major element (Na), a trace element (Mn) and a heavy metal (Pb). Further cumulative probability plots are shown in figure D7 in appendix D. A change in gradient indicates samples within the "threshold-level" above which remaining samples are considered anomalous. Several changes in the trend indicate multiple-populations as shown by the plot for Mn. The histograms for Na, and Pb in appendix D showing the spread of the entire dataset, show the same pattern to the cumulative plots below in that most of the dataset belongs to one population, and extreme outlying values belong to another.

The outlying values in the box plots can be identified and the corresponding samples ascertained as outliers. Samples which are designated as outliers, whether they are range outliers[1], spatial outliers[2] or relationship outliers[3] (Lalor and Zhang, 2001) are in fact the samples that spark the most interest in environmental analysis. It is thereby important to maintain these values in further statistical analysis. However because these values result in a non-normal distribution, the data are log transformed before further statistical analysis takes place.

[1] range outliers are those which are considered to be either too high or too low when compared with the population of the majority of samples
[2] spatial outliers are usually defined as observations that are extreme with respect to their neighbouring values
[3] relationship outliers are observations that fall outside of the values expected from correlations within the dataset





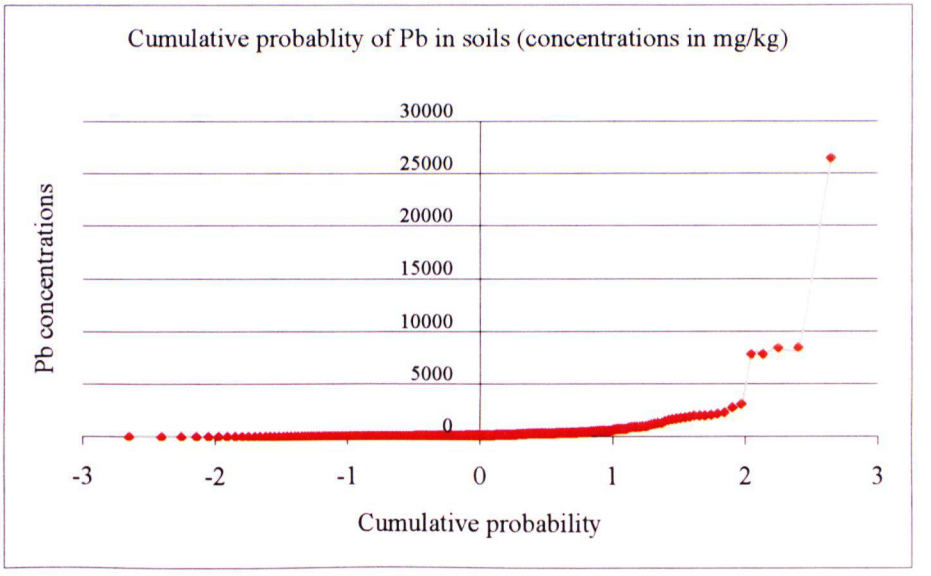


Figure 6.5 Cumulative probability for Na, Mn and Pb in soils from Gibraltar.

The reason for this is that (as stated in section 4.10) multivariate statistics and indeed most classical statistical tests are based on the assumption of a normal distribution. Other (non-parametric)

statistical methods are available which are suited for data with skewed distributions. The reason for not using such tests is that firstly, once the data were log transformed it conformed to a normal distribution and secondly, the power of these tests (non-parametric) is not as significant, and so parametric statistics on log normally distributed data are believed to provide more powerful statistical tools. When the data are log transformed, the effects of the outlying values are minimised and the spread of the data approach a more accepted normal distribution.

6.2.1 Kolmogorov-Smirnov (KS) test

There are several methods that can be used when testing for a normal distribution. The easiest method is to plot a histogram and check for the typical bell shaped curve. Another method is by using probability plots (P-P). The cumulative proportions of a variable are plotted against those of any number of test distributions. If the observed data cluster around the line, then a normal distribution is observed. Figure 6.6 shows an example of some P-P plots for Li, Mg and Pb.

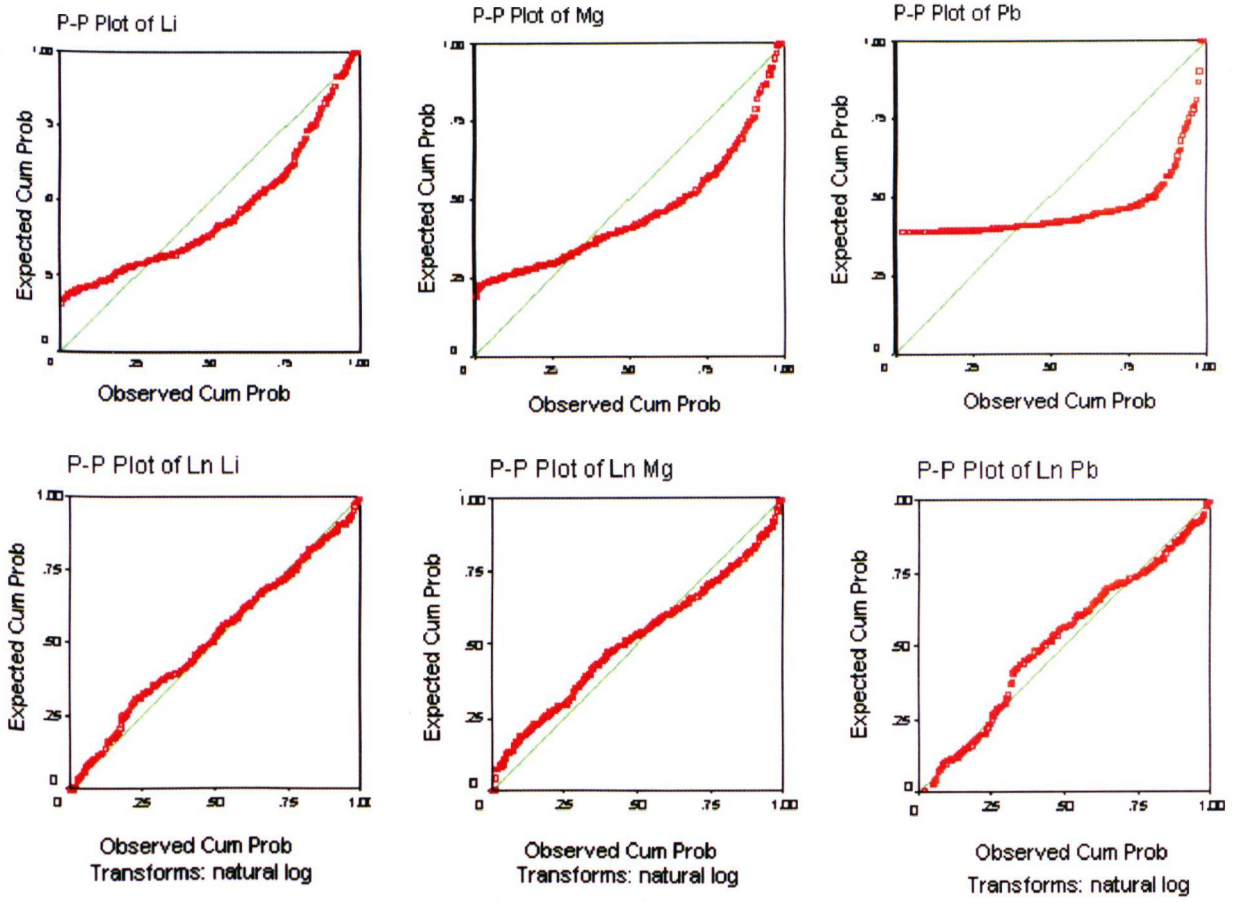


Figure 6.6 P-P plots for Li, Mg and Pb in soils from Gibraltar.

As stated in section 4.11, these plots provide a good first impression of the data distribution. However in order to demonstrate that the data deviate significantly from a normal distribution, a more formal statistical test needs to be applied.

The KS test compares the observed cumulative distribution function for a variable with a specified theoretical distribution, in this case a normal distribution. It is based on the maximum absolute difference between the observed cumulative distribution functions for both sets of samples. It compares an observed cumulative distribution function to a theoretical cumulative distribution. If the observed frequency distribution exceeds the theoretical distribution then the data are assumed to deviate from the normal model. Large significance values (>.05) indicate that the observed distribution corresponds to the theoretical normal distribution. Table 6.3 shows the results of the KS test on both untransformed and log transformed (Ln) data. The results show that once the data underwent logarithmic transformation, most elements conformed to a normal distribution. Silver and Cd do not display a normal distribution even after logarithmic transformation. Different logarithmic transformations were attempted on the data and the results were always the same. The reason for this is attributed to the fact that for these two elements, more than 25% of the data fell below the IDL. As stated in section 4.10, if more than 25% of the values fall below detection, then there is no chance that these data will approach a normal or lognormal distribution.

Table 6.3 Kolmogorov-Smirnov (KS) test applied to element concentrations in soils.

	Untransformed data	Ln data		Untransformed data	Ln data
Li	×	✓	Mn	×	✓
Na	×	✓	Fe	×	✓
K	×	✓	V	×	✓
Be	×	✓	Co	×	✓
Mg	×	✓	Ni	×	✓
Ca	×	✓	Cu	×	✓
Sr	×	✓	Ag	×	×
Ba	×	✓	Zn	×	✓
Al	×	✓	Cd	×	×
La	✓	✓	Pb	×	✓
Ti	×	✓	P	×	✓
V	×	✓	S	×	✓
Cr	×	✓	As	×	✓

× data do not correspond to a normal distribution., ✓ data correspond to a normal distribution.
Ln = natural log

6.2.2 Chemical partitioning of elements in soils

Studies dealing with total metal concentrations are valid when dealing with mass balance studies.

***Table 6.4 Descriptive statistics of Li, K, Be, Ca, Sr, Ba, Al, La, Ti, V and Cr in soils from Gibraltar.* (n=32) (results in mg/kg)[4]**

	Li	K	Be	Ca	Sr	Ba
Step 1						
GM	0.05	124	0.2	2253	5.7	5
SD	18	3317	0.01	3093	6.4	15
Range	0.04-2.14	7.5-27500	0.01-0.03	57-21000	0.8-33	0.5-90
Step 2						
GM	68	77	0.04	14421	16	13
SD	1	177	0.01	18606	22	15
Range	0.04-4.08	1-1460	0.01-0.136	120-64800	0.5-95	1.3-84
Step 3						
GM	55	97	0.2	5737	7.3	15
SD	2	269	0.01	19450	15	43
Range	0.1-16	19-1900	0.02-0.6	93-136000	0.3-82	0.8-255
Step 4						
GM	7	25	0.1	349	1	4
SD	0.3	54	0.04	1132	2.8	25
Range	1.8-26	4.3-252	0.01-0.2	3.2-6490	0-21	0.1-207
Step 5						
GM	0.05	3789	0.5	1360	21	106
SD	18	5226	0.4	2763	21	339
Range	2.1-85	90-26700	0.01-2.4	242-13300	2.2-122	2.3-1900

	Al	La	Ti	V	Cr
Step 1					
GM	23	0.1	0.3	0.1	0.2
SD	109	0.1	1.9	1.5	0.3
Range	2-818	0.1-.75	0.14-14	0.1-12	0.2-2.5
Step 2					
GM	15	0.3	0.1	0.1	0.4
SD	141	0.4	0.7	2.7	1.3
Range	2-872	0.1-1.4	0-3.2	0-22	0.2-8
Step 3					
GM					
SD	590	1	0.7	3.5	1.4
Range	2018	1	7.9	11	8.9
	160-16400	0-4.2	0-53	0.6-892	0.1-54
Step 4					
GM	415	0.4	5.6	2.2	3.4
SD	531	1	7.2	11	3.3
Range	13-2650	0-6.4	0.2-37	1.5-619	0.1-19
Step 5					
GM	14063	5	984	984	89
SD	8620	2	1139	1139	62
Range	920-48800	1-13	2.5-6320	2.5-6320	3-275

GM = Geometric Mean. SD = Standard Deviation

However, when an investigation relates to the fate and effect of metals, the total metal concentration is of limited importance in calculating the extent of plant uptake as well as the consequent phytotoxicity and entry of metals into the food chain (Li, 1993). The form of a trace metal in soil

[4] Step 1 = Soluble and Exchangeable phase, Step 2 = Carbonate phase, Step 3 = Bound to Fe-Mn oxide fraction, Step 4 = Bounds to organic/sulphide fraction, Step 5 = Residual fraction. (for further details refer to section 4.4.1).

has been identified as one of the most important properties in determining the solubility, mobility and availability of metals to humans and the wider environment (Tessier *et al.*, 1979). One aim of the chemical extraction technique is to quantify the fraction of soil contamination available for root uptake (Kennedy *et al.*, 1997). Metals in the soil solution are an intermediate source between plant roots, and it is assumed that there is a dynamic equilibrium between the species in the soil solution and the solid phase (Davis, 1994). The concentration and speciation of metals in the soluble phase and the controls effecting the concentration and speciation are important when assessing the availability and exposure to receptors in the environment. The availability of metals to biological organisms and the wider environment are largely dependent on the solubility and of a metal and the dissolution of the solid phase.

The accuracy and precision of the analytical methods is discussed in section 4.4.2. Most elements have an overall recovery rate of between 80-120% (figures D2, appendix D). The precision was generally not satisfactory as the majority of elements in most steps had a precision exceeding 10%. Reasons for this include low concentration values in the samples in the different steps, the heterogeneous nature of the sample as well as the few duplicate pairs used in the analysis. Therefore assessing which extraction steps have (statistically significant) higher concentrations of each of the elements is problematic and rather difficult. This then means that without such certainty, only general trends are discussed. Tables 6.4 and 6.5 report the GM, SD and range for all elements in steps 1 to 5 of the sequential extraction procedure.

Element partitioning in sequential extraction sequence is reported in mg/kg. The concentration in each step is a proportion of the original gram of sample. Loss of material during the chemical procedure has been mentioned as one of the main causes of error in this method. Error from re-precipitation and incomplete dissolution of material are other important causes of error during data interpretation (section 4.4.3).

***Table 6.5 Descriptive statistics of Mn, Fe, Co, Ni, Cu, Zn, Pb, P, S and As in soils from Gibraltar.* (n=32) (results in mg/kg)**

	Mn	Fe	Co	Ni	Cu
Step 1					
GM	4.4	18	0.1	0.2	0.3
SD	12	133	0	0.5	4.4
Range	0.3-85.2	1-949	0.1-0.3	0.2-3.3	0.08-32
Step 2					
GM	54	21	0.2	0.4	0.4
SD	38	348	2.5	2.9	212
Range	8-185	1-2180	0.1-2.6	0.2-216	0.35-1710
Step 3					
GM	89	1258	1.6	4.9	1.2
SD	120	16527	11	14	287
Range	3.3-717	288-100000	0.1-64	0.3-113	0.16-2280
Step 4					
GM	4.2	103	0.4	2.8	6.1
SD	5	398	2	3.1	4.2
Range	0.1-22	1-1980	0-12	0.2-17	0.38-2180
Step 5					
GM	93	11376	3.7	29	15
SD	80	68313	39	51	1212
Range	9.5-548	60-36800	0.1-216	0.2-433	0.35-6900

	Zn	Pb	P	S	As
Step 1					
GM	0.5	1	5.9	32	0.2
SD	4.5	5.2	14	1561	0
Range	0-26	0.6-31	0.4-65	3.7-12800	0.2-0.20
Step 2					
GM	19	20	23	39	0.2
SD	655	729	130	902	0.6
Range	0-4470	0.6-4980	0.4-692	2.4-7470	0.2-4.8
Step 3					
GM	60	25	80	34	0.5
SD	1111	483	278	3984	7.8
Range	0.9-4880	0.6-2950	5.3-1980	0.2-929	0.1-48
Step 4					
GM	4.6	6.4	44	168	0.3
SD	114	197	145	222	0.4
Range	0-835	0.3-1610	0.2-747	6-1050	0.1-2.2
Step 5					
GM	43	23	418	89	14
SD	2016	363	639	601	39
Range	2.9-11000	0.6-1600	40-3260	9.5-3070	0.2-226

GM = Geometric Mean. SD = Standard Deviation (Please note Cd and Co samples displayed concentrations below IDL in all five steps)

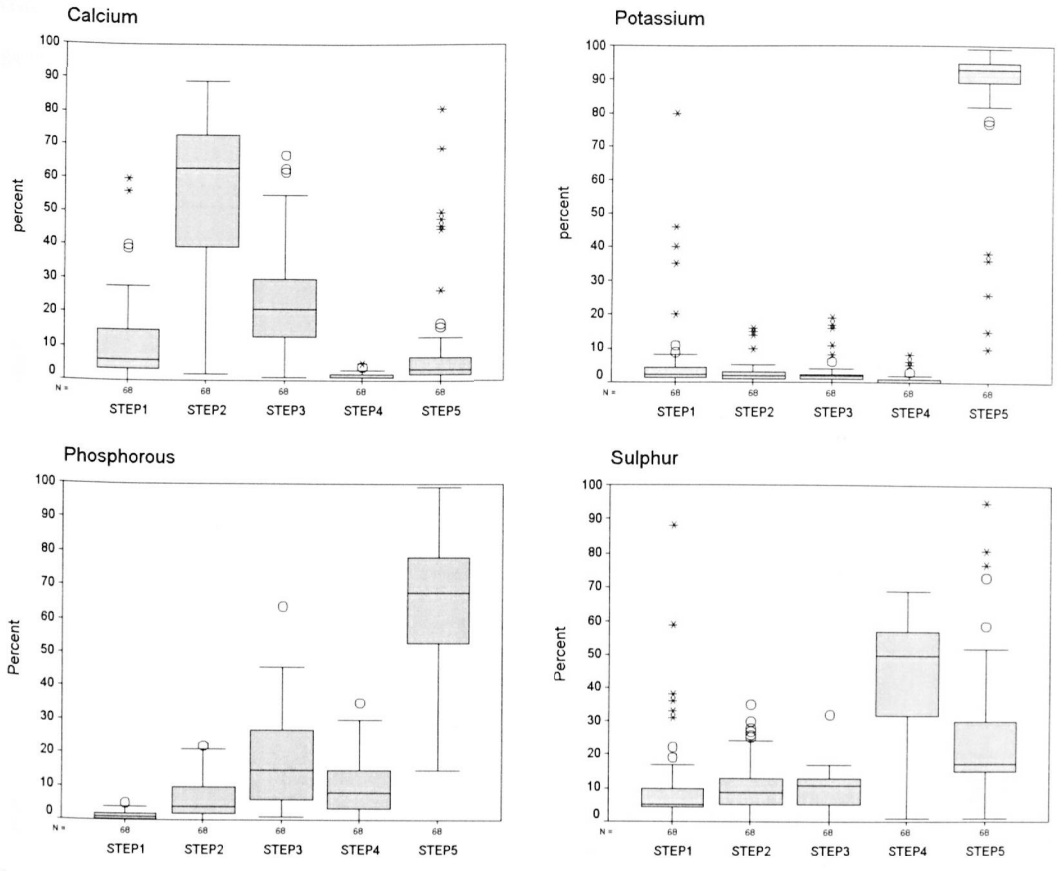


Figure 6.7 Box plot diagrams illustrating the partitioning of the major elements Ca, K, P and S in soils across a five step sequential extraction procedure. Results in percentage of total value.

The partitioning of elements in sequential extraction is also reported as a percentage of the total value from the bulk analysis. Each batch contained 36 samples, which included the duplicates and reference materials. The mean of the duplicate results has been included in this chapter but the reference materials have not, thereby explaining why n=32. Results are displayed in mg/kg and are absolute concentrations of each of the elements in each step. Figures 6.7 – 6.10 display box plots showing the partitioning of elements in each step as a percentage of the total value.

The partitioning of calcium, potassium, phosphorous and sulphur

The partitioning of the major elements Ca, K, P and S is shown in figure 6.7. The majority of the calcium was extracted in steps 1-3 with the percentage in steps 4 and 5 being very low. The variability of Ca in step 2 was high and negatively skewed. This is represented by the large depth of the box with the median value closer to the top end of the box. Calcium is partitioned in the following step order 2>3>1>5>4. Calcium is also a major constituent in carbonate rocks. In soils it is very strongly associated with the carbonate phase (step 2) and this indicates the strong influence of the carbonate phase on heavy metal chemical forms in soils as calcite ($CaCO_3$), (Li *et al.*, 2001)

which is a primary mineral in the geology and soils in Gibraltar. During alteration, Ca becomes associated with clay minerals.

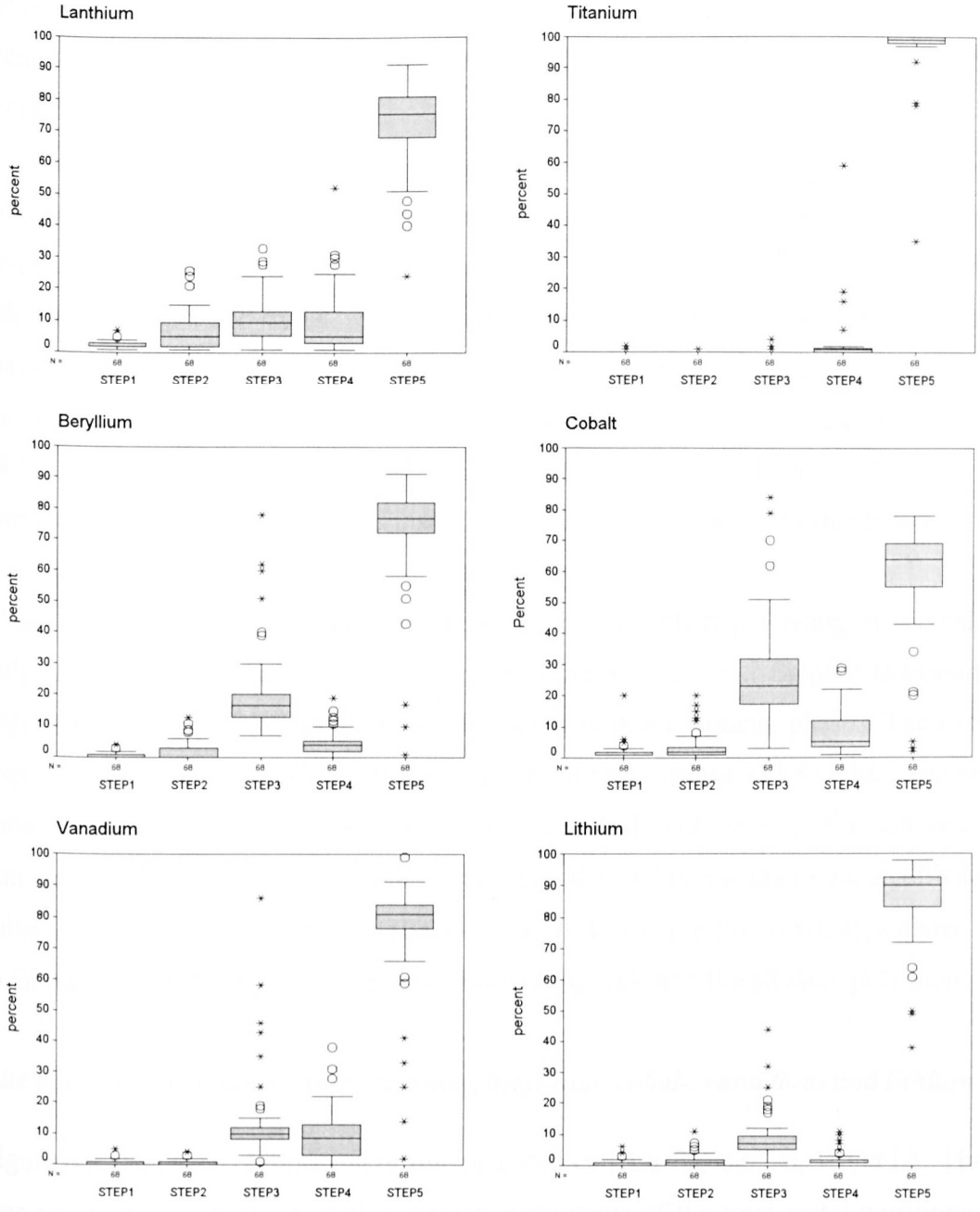


Figure 6.8 Box plot diagrams illustrating the partitioning of the trace elements La, Ti, Be, Co, V and Li in soils across a five step sequential extraction procedure. Results in percentage of total value.

Secondary precipitation of $CaCO_3$ in soils incorporates trace metals such as Be and Sr into the structure, and provides a pH buffering capacity to the soil. Calcareous (carbonate rich) soils (such as those found in Gibraltar) (see section 6.2.4) have a pH range between 7.3 and 8.5 (Lindsay, 1979). The concentration of Ca in soils in Gibraltar can be attributed primarily to the underlying

geology, but also to the anthropogenic input from the weathering of cement and the break down of construction material. The partitioning of Ca in all extraction steps reflects the mobility of Ca in natural systems and the possible redistribution and re-precipitation of Ca during the experimental procedure. Li (1993) reports the partitioning of Ca into step 3 in soils from the Pb mining region in Derbyshire, UK. This was attributed as the incomplete dissociation of the carbonate phase in soils formed over limestone.

Potassium occurs in primary minerals such as alkali feldspars, which alters to clay minerals. It is partitioned in the following order 5>1>2=3>4. The majority of P was partitioned into step 5 followed by step 3 and step 4. Steps 1 and 2 are of minor importance in the partitioning of P. The majority of P was partitioned into step 5 followed by step 3. Phosphorous forms stable Al, Fe and Ca phosphates in soil, the most common form in soils is the orthophosphate species (Lindsay, 1979). Phosphate has been applied to soils as an *in-situ* remediation technique, with the aim to immobilise Pb by the formation of insoluble Pb-phosphate species (Cotter-Howells, 1996a).

Almost half of the total S was partitioned into step 4 with step 5 being of secondary importance. Sulphur was partitioned in the following step order 4>5>2=3>1. Sulphur is essential to biological organisms and therefore had a strong association with the organic phase. The occurrence of S in step 5 may represent sulphide minerals pyrite (FeS_2), galena (PbS), chalcopyrite ($CuFeS_2$) and sphalerite (ZnS) which are dissolved by concentrated acids in step 5 (Deer *et al.*, 1992). The atmospheric deposition of SO_2 from the burning of fossil fuel leads to the acidification of soils and subsequent mobilisation of metals (Raiswell *et al.*, 1980), but this is not anticipated to be a problem in Gibraltar soils due to the calcareous nature of the soils and the alkaline pH range.

The partitioning of lanthanum, titanium, beryllium, cobalt, vanadium and lithium

Figure 6.8 shows the partitioning of the trace elements La, Ti, Be, Co, V and Li. The majority of La was partitioned into step 5, with a smaller percentage of the total metal partitioned into the other four steps. It was partitioned in the following order 5>3>4>2>1.

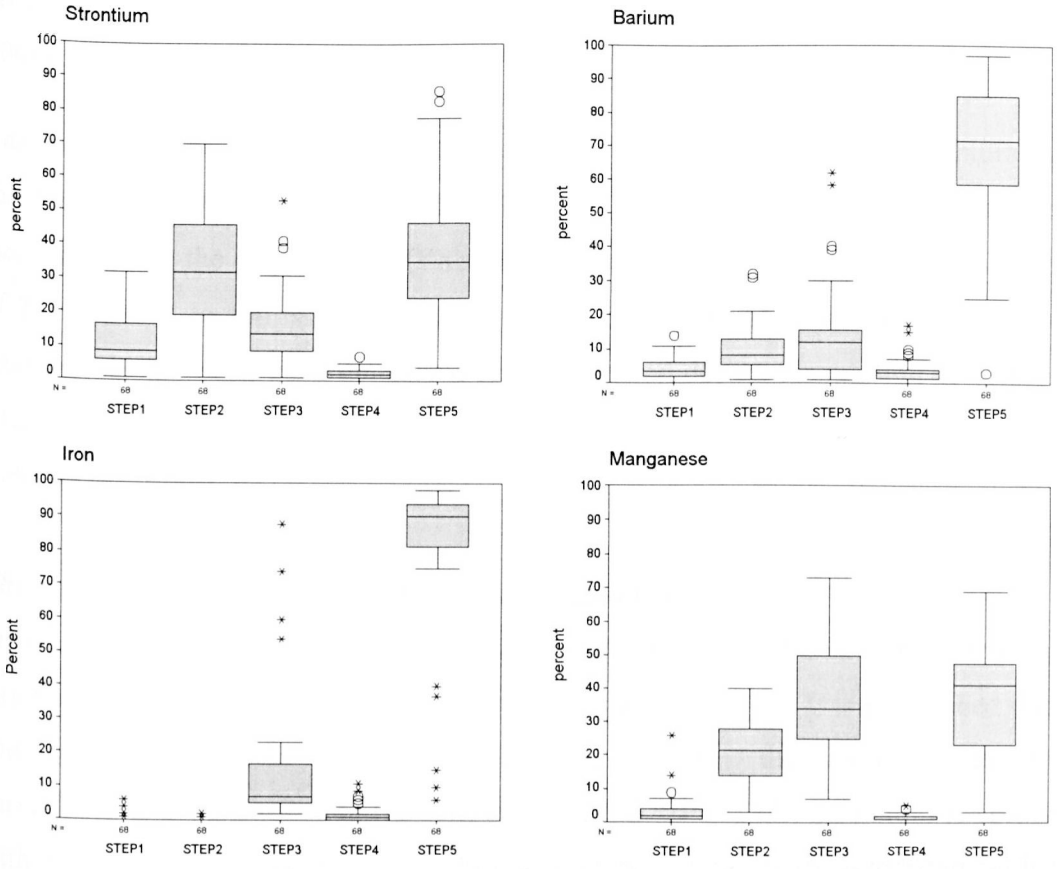


Figure 6.9 Box plot diagrams illustrating the partitioning of the trace elements Sr, Ba, Fe and Mn in soils across a five step sequential extraction procedure. Results in percentage of total value.

Lanthanum is a member of the rare earth elements and its concentration in soil mirrors that of the geological parent material. Most of the Ti was partitioned into steps 5 with a very small percentage into step 4 and nothing in steps 1 to 3. The majority of Ti, Li and V were partitioned into the fifth step. Titanium and V occur in soils as primary minerals which are resistant to weathering. The concentration of Ti and V in soil mirrors that of the parent material. This is further shown by the results of the factor analysis (section 6.6.4.1) were these elements were strongly associated with the lithogenic factor. Titanium is commonly found as an oxide, TiO_2, is found in sedimentary rocks and small amounts of Ti can be associated with clay minerals (Deer *et al.*, 1992). A large portion of Be was partitioned into step 5, followed by step 3. It was partitioned in the following step order 5>3>4>2>1. Cobalt is largely partitioned into step 5 followed by step 3, with very small amounts in step 4, 2 and 1. Cobalt is associated with Fe and Mn in rock forming minerals (Kabata-Pendias and Pendias, 2001). This relationship has been observed in the partitioning of Co in step 3. The majority of V (76%) was partitioned into step 5 followed by step 3 and 4. It was partitioned in the following order 5>3>4>2=1. Vanadium replaces Fe and Mn ions in ferromagnesian minerals rich in shales and soils developed over a shale-rich parent material, as is found in some areas of

Gibraltar. It accumulates in clay minerals and organic material (Kabata-Pendias and Pendias, 2001).

The majority of Li was partitioned into step 5 (85%) followed by step 3. Lithium was partitioned in the following step order 5>3>4=2>1. Lithium is highly mobile in soil and becomes strongly associated with the clay fraction (Kabata-Pendias and Pendias, 2001). The anthropogenic addition of Ti, Li and V to soil is minor. Titanium is a component of alloys and paint and Li of electronic components and batteries. Vanadium can be released during the burning of fossil fuels, and small amounts are used in components of catalysts as well as in the electronics and dyeing industries (Leep *et al.*, 1995).

The partitioning of strontium, barium, iron and manganese

Figure 6.9 shows the partitioning of the trace elements Sr, Ba, Fe and Mn. Strontium is partitioned more evenly across the five steps as opposed to other elements. It is partitioned mainly into steps 5 and 2. The box widths are large in both cases indicating the majority of the data have a large variability. It is partitioned in the following order 5>2>3>1>4. Strontium is commonly associated with Ca in rock forming minerals; during alteration it becomes associated with oxides, organic matter and clay minerals (Kabata-Pendias and Pendias, 2001). Barium is partitioned largely into step 5 followed by steps 3 and 2. Barium is an alkaline earth element, which has a geochemical association with K^+. The underlying parent rock controls the concentration of Ba in soil (Kabata-Pendias and Pendias, 2001). Anthropogenic inputs of Ba to soils include oil and fuel additives to diesel and unleaded petrol. The concentration of Ba in vehicle emissions is reported to be high and has been proposed to be a valuable tracer of traffic pollution (Monaci and Bargagli, 1997). During alteration, Ba forms secondary carbonates, sulphides and associations with clay minerals. It is not mobile in soil (Kabata-Pendias and Pendias, 2001) and this is illustrated by the fact that in the Gibraltar soils it was highly partition into step 5, the residual phase.

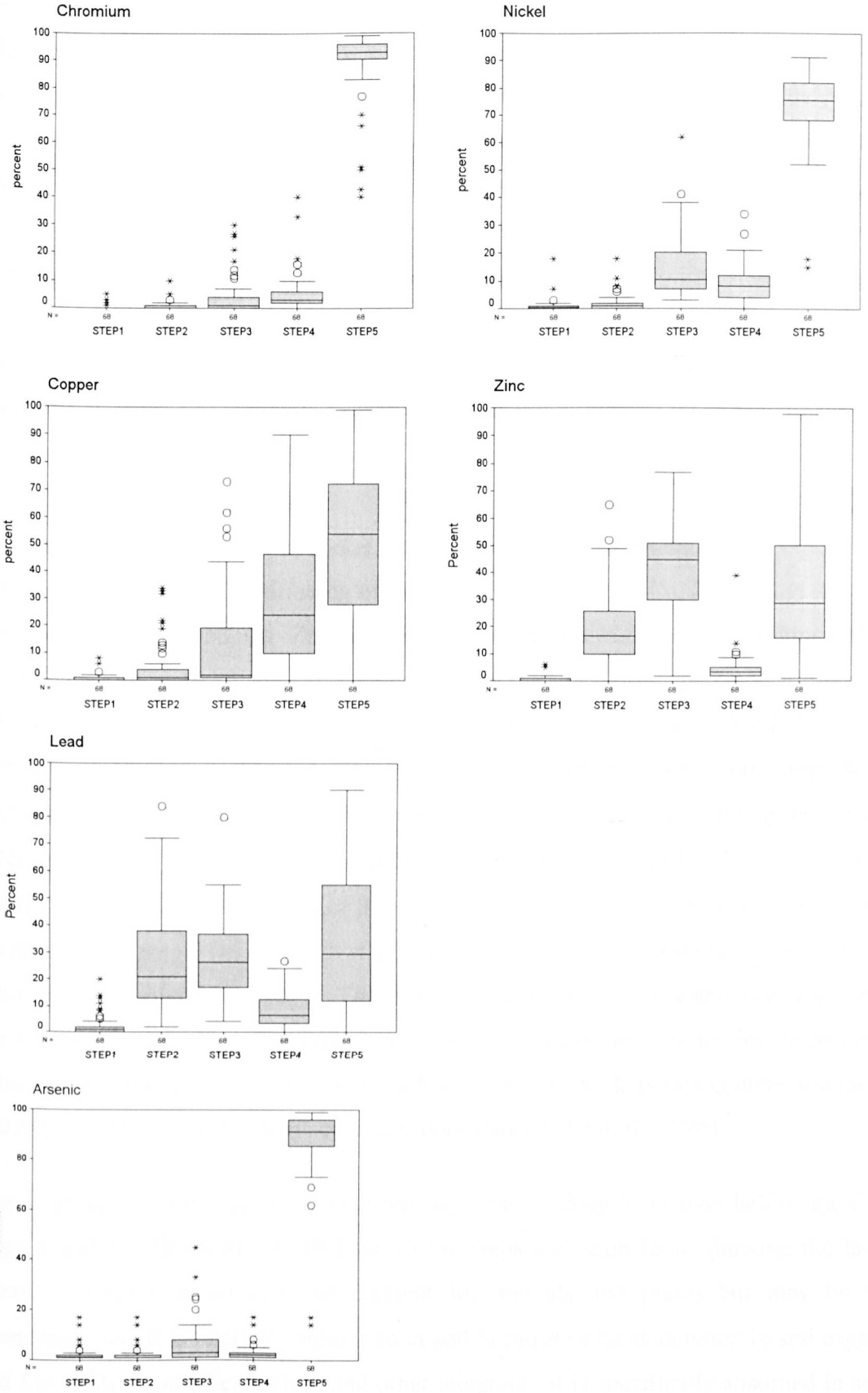


Figure 6.10 Box plot diagrams illustrating the partitioning of the heavy metals Cr, Ni, Cu, Zn, Pb and As in soils across a five step sequential extraction procedure. Results in percentage of total value.

Iron was mainly partitioned into step 5 (84%) followed by steps 3 and 4. It partitioned in the following order 5>3>4>1=2. Iron is a major constituent of rock forming minerals. As with Sr the box for step 5 is large, showing the variability in the data. Iron and Mn are widely distributed in the soil profile, they occur in primary minerals, clay, are associated with organic matter and form amorphous oxides and hydroxides. The latter is an important phase in the scavenging and fixing of metals and other cations in soil (Hawkes and Webb, 1962). Manganese, as was the case with Sr is partitioned more evenly across the 5 steps. It is partitioned mainly into steps 5 (38%), 3 (36%) and 2 (22%). The box depths are large in the three cases indicating the large variability in the data. The appearance of Mn in step 2 however, may be attributed to the partial dissolution of Mn oxides, which are more readily reducible than Fe oxides in soil or the release of specifically adsorbed Mn^{2+} ions (Gibson and Farmer, 1986).

The partitioning of chromium, nickel, copper, zinc, lead and arsenic

Figure 6.10 displays the partitioning of the heavy metals Cr, Ni, Cu, Zn, Pb and As. The content of the heavy metals Cr, Ni, Cu, Zn, Pb and As in soil is the result of the combined effects from the underling parent material, the redistribution within the soil profile and associations made within the soil phase, as well as inputs from anthropogenic sources (see section 2.4.2.1, 2.5.1 and 2.5.2). The majority of Cr was partitioned into step 5 (88%) with the other four steps being of minor importance. Chromium is a major constituent of alloy steel, containing between 10-26% Cr (McGrath, 1996). Chromium in roadside dust and soil can result from elevated concentrations in coal fly ash and from corroded break linings in vehicles (West *et al.*, 1999). Nickel was also largely partitioned into step 5 (>70%) with step 3 being of secondary importance. Nickel partitioned in the following step order 5>3>4>2>1. The content of nickel in soil depends very much on the nature of the parent material. The most important factor determining the distribution of Ni between the soil solid and solutions phases appears to be pH, while factors such as clay content and the amount of Fe and Mn oxides in the soil are of secondary importance (McGrath, 1996).

The majority of Cu is partitioned between steps 3 to 5. Step 5 has over half of the Cu followed by steps 4 and 3. The boxes in all three of the steps are again large showing the large variability present. Copper is an essential element for animals and plants but may be toxic in high concentrations. It is relatively immobile in soil because of its association to soil organic matter, Fe and Mn oxides, soil silicate clays and other minerals. It is specifically absorbed in soils, making it one of the trace metals which moves the least (Alloway, 1995). Zinc and Pb also display a large variability in the distributions. The variability of Zn was found to be quite high over steps 5, 3 and 2. In oxidising acid conditions Zn is mobile and associated with oxides and hydroxides in acid soil

and organic matter in alkaline soil (Kiekens, 1995). Lead was partitioned into the following step order 5>2>3>4>1. The percentage of exchangeable (step 1) Pb is very low. These results are in broad agreement with other studies in urban areas (Harrison *et al.*, 1981, Li *et al.*, 2001). Lead has a strong tendency to be adsorbed on to particles of clay or organic matter, and in this form is largely immobile and biologically inert (Thornton, 2001). The main compartments for Pb in soil are the soil solution, the adsorption sites of the clay-humus exchange complex, precipitated forms, secondary Fe and Mn oxides and alkaline earth carbonates, the soil humus and silicate lattices. The majority of As, was partitioned into step 5 with the step 3 being of minor importance. In oxidising environments, the mobility of As is controlled by the coprecipitation with Fe oxides. Arsenic is associatiated with Fe in steps 5 and 3 (Hawkes and Webb, 1962).

Tessier *et al.* (1979) suggested that the mobility and bioavailability of metals decrease in order of the extraction sequence, from readily available to unavailable. The exchangeable fraction (step 1) may show the form in which metals are most available for plant uptake. Step 2 showing the metals that become more available under lower soil pH. Metals in step 3 are more tightly bound to the soil constituents and less easily passed onto the soil solution. Metals in step 5 are considered to be bound to the lattice of minerals and so unavailable to plants and animals. Steps 5 and 3 are the dominant phases for most elements. Sulphur, Sr, Ca and Li are the exceptions.

6.2.3 Geochemical baselines

Baseline concentrations are a better measure of the variation in trace element concentrations than observed ranges of background concentrations, as the distorting effects of a few values can be minimised by log-transformation of the data (Dudka *et al.*, 1995). The use of baseline concentrations as alternative criteria for assessing possible trace element contamination in soils (Chen *et al.*, 1999), or the use of the upper baseline limit to assess the background concentration with an acceptable degree of confidence (Dudka *et al.*, 1995; Chen *et al.*, 1999) is increasingly being suggested (see section 2.6.2). Baseline values are shown below in table 6.6. They were calculated for element concentrations in Gibraltar using the method described by Dudka *et al.* (1995) and Chen *et al.* (1999) of the GM/GSD^2 (lower baseline) and $GM*GSD^2$ (upper baseline). These baseline values are for Gibraltar at this point in time, for the years 2001-2003.

Two sets of baseline ranges have been calculated during this study, one in 2001 after a year of investigation and another set in 2003. This was done because of a change in land use at one of the sites sampled which had affected the concentrations for six separate samples taken at that site. A site believed to be possibly contaminated known as the East Side reclamation was sampled during

the initial reconnaissance survey in June 2000 and re-sampled at the beginning of the baseline survey between April and June 2001. This was the only site which had undergone a change in land use, and so was the only site to be re-investigated.

Table 6.6 Baseline values for soils in Gibraltar (mg/kg) for 2 years

(Values in bold show upper baseline ranges which have changed between 2001 and 2003).

	2001		2003	
Elements	Lower baseline	Upper baseline	Lower baseline	Upper baseline
Li	2	92	2	92
Na	60	**2366**	74	**1648**
K	528	**30380**	525	**29084**
Be	<0.02	5	<0.02	5
Mg	*867*	**53570**	851	**53665**
Ca	1662	**552500**	1643	**545250**
Sr	10	433	10	404
Ba	13	**1240**	13	**1175**
Al	1972	**137700**	1912	**137060**
La	1	68	2	70
Ti	72	**2530**	72	**2322**
V	5	244	5	240
Cr	10	**802**	9	**838**
Mn	54	**1460**	53	**1410**
Fe	1767	**146501**	1836	**127829**
Co	1	**45**	1	**35**
Ni	9	**165**	9	**159**
Cu	0.8	**1517**	1	**977**
Ag	<0.01	3.6	<0.01	3
Zn	7	**4600**	8	**2954**
Cd	<0.01	**13**	<0.01	**9**
Pb	1	**6550**	1	**5026**
P	57	**8500**	56	**8230**
S	27	**9300**	29	**7318**
As	1	**97**	1	77

The reclamation site on the East Side was being used as a landfill for the bottom (inert) ash of the incineration process. Asbestos and other waste products such as building rubble and wood debris were also dumped onto this site. The landfill dimensions were height c.7m above sea level, length c.600m and width c.90m. As this was not a proper landfill site there were no liners at the site and whatever was placed there can potentially leach directly into the sea. The results from the soils samples taken at that site showed elevated concentrations for a range of elements, with these concentrations greatly exceeding guidelines values (Mesilio, 2000). The reclamation is now complete and the area has been paved over. There is a road on the site, vegetation is growing on new soil and there are plans to create a Marina. The soils and flora at the site were re-sampled during August 2003 as part of an ecological MSc project at Imperial College (Conti, 2003). The

new soil and there are plans to create a Marina. The soils and flora at the site were re-sampled during August 2003 as part of an ecological MSc project at Imperial College (Conti, 2003). The results from the new soils on the site showed normal concentrations for both media. Soil concentrations at that site fell markedly and were now comparable to the rest of the dataset for Gibraltar. The recent change in land use in the east side of Gibraltar, and its subsequent effects on element concentrations in soils provides a good example of one of the arguments made in this work in respect to the validity of baseline maps due to the temporal variability of metal inputs to soils. This change in land use has resulted in different values for the baselines calculated and the resultant geochemical maps differ as well. This is an important factor which should be considered when baseline ranges and geochemical maps are used for policy implementation and for the management of contaminated land. It is interesting to note how the upper baseline limit for the heavy metals: Cr, Ni, Cu, Zn, Cd, Pb and As, have changed as a result of the management of this site.

A t-test was carried out to verify whether there was a statistically significant difference between the baseline values calculated for 2001 and 2003. The results were that *there is no significant difference* for the changes in baseline values for any of the elements analysed between those years. The fact that the alteration in upper baseline values is not statistically significant does not necessarily mean that this alteration (brought about as a result of land use changes) is not an important factor in itself. For example, an owner of a piece of land who is investigating if Pb concentrations within his property fall within the baseline values for Gibraltar, could face savings in terms of possible remediation costs. This would be due to the decrease in the upper Pb baseline value (6550 – 5226 mg/kg) between the years 2001 and 2003 resulting from a change in land use at the East Side reclamation site. An additional point to take note of however is that the change (decrease) in concentrations found for some of the elements in table 6.6 between the years 2001 and 2003 could be due to sampling error. This factor has not been concretely established and so should be considered when interpreting such results.

Table 6.7 compares the calculated baseline values for the year 2003 with the min and max values obtained for the soil dataset. Calcium, Ba, Al, La, Ti and Mn are the only elements with maximum concentrations below the upper baseline value. The maximum concentrations for the remaining elements exceed this calculated value. Interestingly, the 95th percentile concentration for all twenty-six elements is lower than the upper baseline value. This suggests that a few isolated, possibly contaminated samples (or sites) are responsible for the overall exceedences of the upper baseline value in Gibraltar. GIS mapping can now be used as a secondary step in the identification of these samples/sites (refer to section 7.3).

The calculated baseline ranges for some elements can be quite large. Since baseline is defined as 95% of the expected background range then the following explanation is provided. The small size of Gibraltar means that no soils will have been un-affected by anthropogenic activity of some sort and therefore no soils which could be classed as true "background" exist. The long history of incineration in Gibraltar and general industrial activities around the Bay of Gibraltar (sections 3.6 and 3.7) further supports the latter statement. Therefore in most cases the baseline ranges for major and trace elements encompass most of the elemental data. This is not always the case however with the heavy metals as the input of these metals into soils in the urban environment is increased and governed by anthropogenic activity.

Table 6.7 Comparison of calculated baseline values with concentrations obtained for Gibraltar surface (0-15cms) soils. (mg/kg)

Elements	Lower baseline	Upper baseline	Min	Max	95th percentile	Max value within upper baseline range	95th percentile value within upper baseline range
Li	2	92	<0.04	192	49	*x*	✓
Na	74	1648	4.04	2608	1330	*x*	✓
K	525	29084	<1	32000	13800	*x*	✓
Be	<0.02	5	<0.02	25878	2	*x*	✓
Mg	851	53665	2.4	114000	24700	*x*	✓
Ca	1643	545250	<0.2	299408	125000	✓	✓
Sr	10	404	<0.01	1914	173	*x*	✓
Ba	13	1175	<0.02	1070	503	✓	✓
Al	1912	137060	2	131000	50300	✓	✓
La	2	70	<0.1	56	26	✓	✓
Ti	72	2322	<0.04	1220	864	✓	✓
V	5	240	<0.1	2212	109	*x*	✓
Cr	9	838	<0.2	1446	259	*x*	✓
Mn	53	1410	<0.1	1160	668	✓	✓
Fe	1836	127829	1	435000	48300	*x*	✓
Co	1	35	<0.1	284	16	*x*	✓
Ni	9	159	<0.2	648	81	*x*	✓
Cu	1	977	<0.02	12500	411	*x*	✓
Ag	<0.01	3	<0.01	40	1	*x*	✓
Zn	8	2954	<0.42	12700	1500	*x*	✓
Cd	<0.01	9	<0.01	17	4	*x*	✓
Pb	1	5026	<0.6	8507	1680	*x*	✓
P	56	8230	<0.4	20500	3300	*x*	✓
S	29	7318	<0.2	22000	2290	*x*	✓
As	1	77	<0.2	351	49	*x*	✓

x = no ✓ = yes

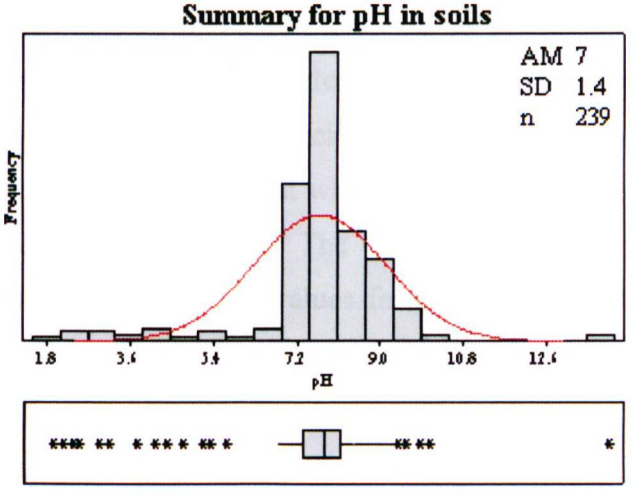
The influence of outlying values on the baseline range was investigated. This was done using robust statistics. In this case, the outlying values were removed and descriptive statistics recalculated each time until the newly calculated GM value was as close as possible to the original median value from the entire dataset. This was done for all elements and the upper limit did not changed significantly, most of the distribution still fell within the baseline range for most elements.

6.2.4 Soil properties

Descriptive statistics for the soil properties pH and loss on ignition are given in Table 6.8. These parameters are important variables when modelling the behaviour of trace metal solubility and potential bioavailability in soils. Soil pH ranges from 4.8 to 10.1 with a median value of 7.6. Loss on ignition is an approximation of the percentage of organic carbon in soil. The organic content of soils has been measured between 2 - 93% with a median of 9.7%.

Table 6.8 Descriptive statistics for the soil properties pH and loss on ignition **(n=246)**

	Soil pH	LOI
Median	7.6	9.7%
Range	4.8-10.12	2%-93%
SD	1.2	12



6.3 Rocks

Nine rock samples were taken to identify what the element concentrations were in regards to the underlying geology. As with the soil samples, they were digested in a nitric/perchloric acid digestion and subsequently analysed using ICP-AES. The samples consisted of limestone,

dolomite, shales and scree breccias. Table 6.9 shows the descriptive statistics for the elemental data in rocks. Elements like Mg, Ca, Al, Fe, and S have a large standard deviation, which suggests that the measurements are scattered widely about the arithmetic mean. The median value is smaller than the arithmetic mean for all elements, except La, indicating a skewed distribution. Calcium, Sr, La, Cu, Cd and P have a negative kurtosis indicating a frequency distribution curve with a flattened peak. All the elements in the dataset except Ca, La, Cu and Cd show a skewness value greater than 1. A negative skewness value indicates a negatively skewed distribution. Most elements have a positive skew and show a non-normal distribution.

Table 6.10 compares average abundance of some minor and trace elements in rocks and soils. It compares data for Gibraltar with data reported by Alloway (1995). Values for element concentrations in rocks are generally lower in Gibraltar than those reported by Alloway (1995). Cadmium concentrations in Gibraltar shales (as compared to reported shale values) are the exception. Reasons for this are not known, however, the smaller population, that is to say number of rock samples collected in Gibraltar, or the facies of the rock samples collected, that is to say the different types of beds within the bedrock could suggest possible explanations. It can also mean that element concentrations in rocks in Gibraltar are actually lower than reported world means, although further samples would need to be collected before this could be conclusively proven. The latter suggestion is re-enforced by the fact that the Ag data displayed high % bias values and poor precision in the quality control analysis. The samples collected by Alloway (1995) may have been taken from rocks on different land uses and soil textures, factors that also need to be considered when comparing concentrations. The rock samples taken in this study from Gibraltar were from exposed rock outcrops, mainly in the Upper Rock and southern areas of Gibraltar. The values obtained do appear to be however, in agreement with the fact that sedimentary rocks are supposed to yield low concentrations of heavy metals. The Gibraltar soil data when compared with the Alloway data for agricultural soils, the high values for Be, Ag, As, Cd, Cu, and Zn reflect the inclusion of some contaminated samples.

***Table 6.9 Descriptive statistics for the rock samples* (n=9) (results in mg/kg)**

	AM	Median	SD	GM	Skewness	Kurtosis	Min	Max	25th percentile	50th percentile	75th percentile	95th percentile
Li	2.6	0.4	4.5	0.8	1.6	0.8	0.3	11	0.3	0.4	5.4	11
Na	165	85	192	109	2.0	3.5	42	608	63	85	227	608
K	491	52	858	122	1.7	1.0	27	2170	45	52	973	2170
Be	0.2	0.1	0.2	0.2	1.6	0.7	0.1	0.5	0.1	0.1	0.3	0.5
Mg	7712	4290	7801	5304	2.1	5.1	1070	26700	3175	4290	10075	26700
Ca	382100	382000	39203	380239	-0.7	-0.7	316000	422000	349000	382000	417500	422000
Sr	68	48	33	61	0.5	-1.8	36	120	40	49	96	120
Ba	12	3.4	16	6.7	1.6	0.6	2.6	41	3.2	3.4	24	41
Al	2700	172	4993	429	1.6	0.8	86	12000	123	172	5720	12000
La	7.4	7.5	4.6	5	-0.1	-0.2	0.6	14	4.0	7.5	10	14
Ti	42	4.4	75	9	1.6	0.9	2.2	185	2.9	4.4	85	185
V	5.1	1.2	8	2	1.6	0.8	0.6	20	0.9	1.2	10	20
Cr	10	1.0	19	1.5	1.9	2.7	0.2	55	0.2	1	18	55
Mn	20	4.6	29	8	1.6	0.9	2.5	77	3	4.6	41	77
Fe	1470	94	2711	236	1.6	0.8	40	6520	82	94	3105	6520
Co	2.4	1.2	3	1	1.5	0.7	0.1	8	0.5	1.2	4.4	8.1
Ni	7.7	2.2	12	2.3	1.6	0.8	0.2	30	1.2	2.2	15	30
Cu	2.0	2.4	1.3	0.8	-0.5	-1.0	0.2	4	0.6	2.4	2.9	3.8
Ag	<0.001	<0.001	0.004	0.001	3	9	0.1	0.1	0	0	0	0.1
Zn	6	4.3	4.1	5	1.3	0.3	1.8	14	3.5	4.3	9.3	14
Cd	1.3	1.6	0.7	0.9	-1.1	-0.2	0.1	2.1	0.6	1.6	1.8	2.1
Pb	1.7	0.6	2.1	1	1.6	0.7	0.6	5.4	0.6	0.6	3	5.4
P	290	187	173	248	0.7	-1.3	112	575	157	187	477	575
S	258	116	420	11	1.7	1.8	0.2	1150	0.2	116	472	1150
As	1.1	0.2	1.7	0.4	1.7	1.3	0.2	4.6	0.2	0.2	1.9	4.6

(Please note Cd and Ag data to assessed with caution due to number of samples below IDL and proximity of most sample concentrations to IDL. Cadmium concentrations below 2 mg/kg to be assessed with caution)

Table 6.10 Average abundance for minor and major elements (mg/kg).

Element	Sandstone	Shale	Limestone	Soil	Gib Shales	Gib Limestone	Gib Breccias	Gib Dolomite	Gib Soil
Ag	0.25	0.07	0.12	0.1	0.06	0.04	0.04	0.04	0.58
As	1	13	1	1.5	4.1	0.2	0.2	0.2	16
Ba	-	700	100	100-300	41	3.2	6	5	182
Be	-	3	1	6	0.5	0.1	0.1	0.1	109
Cd	0.05	0.2	0.1	1	2	1.6	1.7	0.6	1
Co	0.3	20	4	1-40	7.7	1.3	0.9	0.4	10
Cr	35	100	10	5-1000	44	1.4	0.2	0.5	125
Cu	30	50	15	2-100	2.7	3.3	0.02	1.5	288
Li	15	60	20	5-200	11	0.32	0.6	0.4	20
Mn	460	850	620	850	70	3.9	18	4	335
Ni	9	68	7	5-500	29	2.3	2.4	0.8	46
Pb	7	20	8	2-200	5.4	0.6	0.6	0.6	368
Sr	20	300	500	50-1000	94	45	120	58	86
Ti	1500	4600	400	5000	174	3.4	6.1	3.1	487
V	20	130	15	20-500	19	1.2	1.9	0.77	62
Zn	30	120	20	20	13	5	3.5	3.2	502

Source: mean values taken from Alloway, 1995; Krauskopf, 1995. (Gib = Gibraltar).

6.4 House dusts

Eighty house dusts samples were taken from households throughout Gibraltar (figure 4.4). As with the soils samples 10% of the samples were analysed in duplicate and were randomly included in the batch. Each duplicate was taken through the analytical procedure independently. The percentage recovery from the reference materials was between 80-120% and the control charts followed the precision model of 10%. Table 6.11 shows the descriptive statistics for the house dust data. The distribution of the data are non-normal as can be seen from figure 6.11-6.14. House dust data, as was the case with the soil and rock data, has a large standard deviation. There again seems to be some outlying values, as can be seen from the box plots below. These outlying values originate from the same few households as will be discussed later in chapter 7, section 7.4. The problem again lies in that these values affect the distribution of the data, and the histograms then fail to show the distribution of the main population. As was done with the soil data, the histograms in this section have had the main outlying values removed until the samples remaining belong to the main population. This then means that the total number of samples displayed in each histogram will vary according to the element in question. The descriptive statistics show that as with the soil data, most elements have a

large range of concentrations. The median value is smaller than the arithmetic mean for all elements except for Be, indicating a skewed distribution. For example Pb has a maximum value of 5000 mg/kg, an AM value of 525 mg/kg but a median value of 246 mg/kg.

The analyses of the elements Na,K, Mg, Ca, AL, Fe, Cu, Zn, Pb, P and S show very large standard deviations suggesting a large scatter about the arithmetic mean. Most elements have a positive skew and show a non-normal distribution.

***Table 6.11 Descriptive statistics for the house dust samples* (n=80) (results in mg/kg)**

	AM	Median	SD	GM	Skewness	Kurtosis	Minimum	Maximum	25th percentile	50th percentile	75th percentile	95th percentile
Li	9.2	7.7	9.1	7.5	5.0	28	1.1	66	5.6	7.7	10	16
Na	7801	7200	5763	6381	3.9	24	990	46600	5080	7200	8875	18420
K	3363	3230	1191	3138	0.4	-0.2	560	6570	2365	3230	4140	5545
Be	0.3	0.3	0.2	0.3	2.6	11	0.002	1.3	0.2	0.3	0.4	0.6
Mg	7382	6730	4659	6509	3.8	21	1390	37100	5290	6730	8040	13470
Ca	64198	48800	52589	50213	2.7	11	8330	350000	30300	48800	83400	172800
Sr	119	98	99	99	5.0	34	17	847	77	98	134	265
Ba	65	57	34	57	1.2	1.3	17	180	39	57	80	139
Al	10504	8510	11033	8332	5.5	36	1120	90700	6105	8510	11300	19620
La	15	9.5	18	11	3.5	13	1.6	109	7.1	9.5	16	58
Ti	544	523	230	495	1.2	2.9	45	1420	396	523	626	1107
V	60	32	221	29	9.0	83	1.9	2060	20	32	46	99
Cr	126	70	182	81	5.2	34	8	1450	51	70	138	421
Mn	168	153	101	142	1.7	3.7	24	550	108	153	199	365
Fe	12948	9050	15168	9545	5.5	40	1570	128000	6375	9050	14400	29080
Co	9	5.9	9.5	6.6	3.1	11	1	60	4	5.9	10	31
Ni	129	76	273	79	6.5	46	7.2	2230	55	76	110	312
Cu	416	214	722	232	4.3	20	14	4410	141	214	335	1395
Ag	5.1	2.9	6.9	2.8	2.8	7.3	0.1	34	1.5	2.9	5.4	27
Zn	1610	957	2532	1025	5.4	35	99	20100	692	957	1635	6134
Cd	3.7	2.8	3.2	3.1	9.0	82	0.3	364	2.0	2.8	4	14
Pb	525	246	740	300	3.6	17	29	5000	145	246	636	2323
P	1431	1190	914	1224	2.2	6	286	5080	845	1190	1690	3667
S	13537	11000	10074	10469	2.1	6.1	810	57400	7745	11000	17000	32840
As	8.3	5.6	8.5	6	4.4	28	0.2	68	4.1	5.6	9	22

(Please note Cd and Ag data to assessed with caution due to number of samples below IDL and proximity of most sample concentrations to IDL. Cadmium concentrations below 2 mg/kg to be assessed with caution)

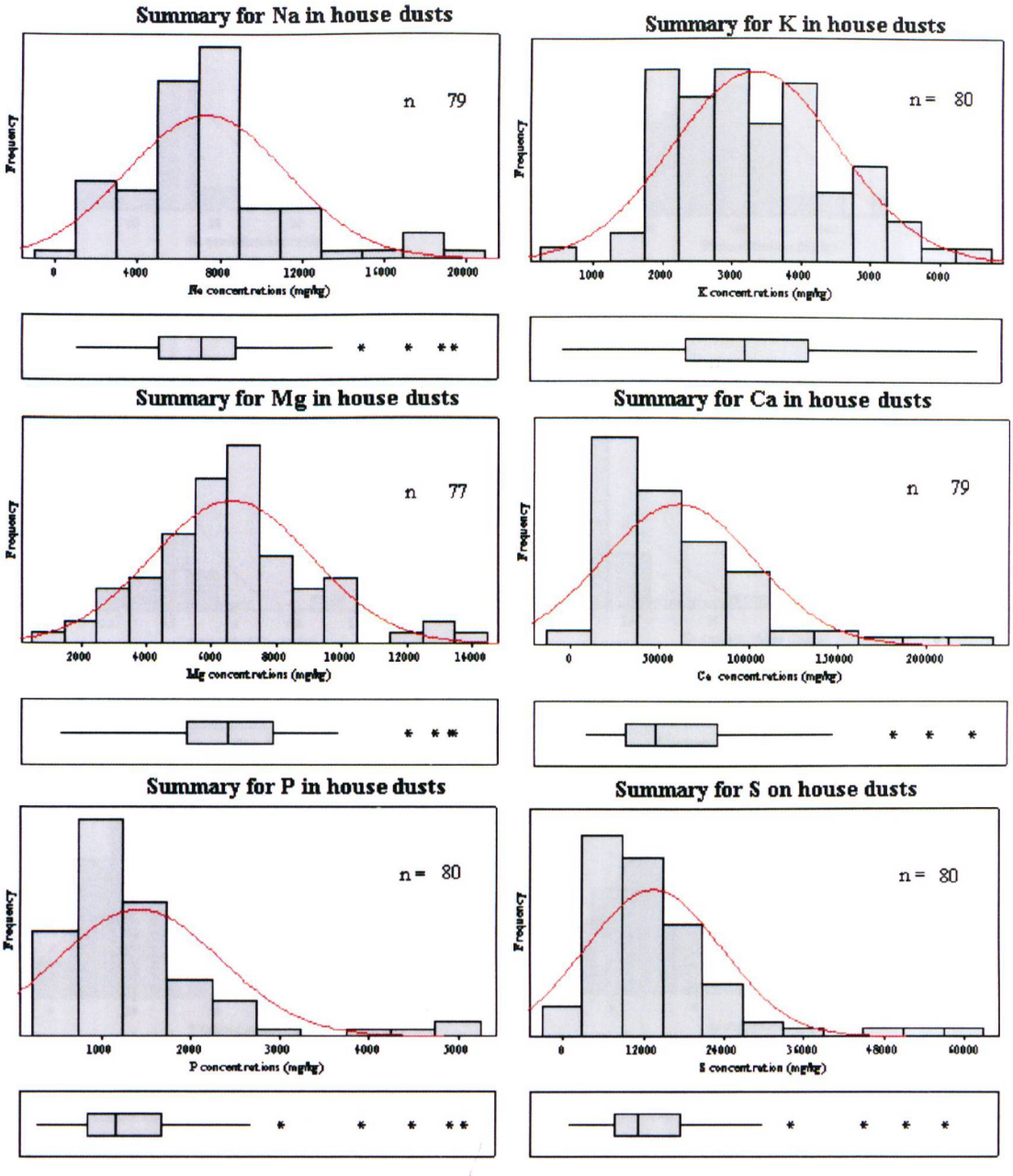


Figure 6.11 Graphical summary for the major elements Na, K, Mg, Ca, P and S in house dusts from Gibraltar.

All elements have a skewness value greater than 1 and only k displays a negative kurtosis value of -0.2. The skewness values range from 0 to 9 and the kurtosis values are high, Ti and Cd showing values above 80. The spread of the distribution of most elements shows a positively skewed distribution with the presence of outlying values.

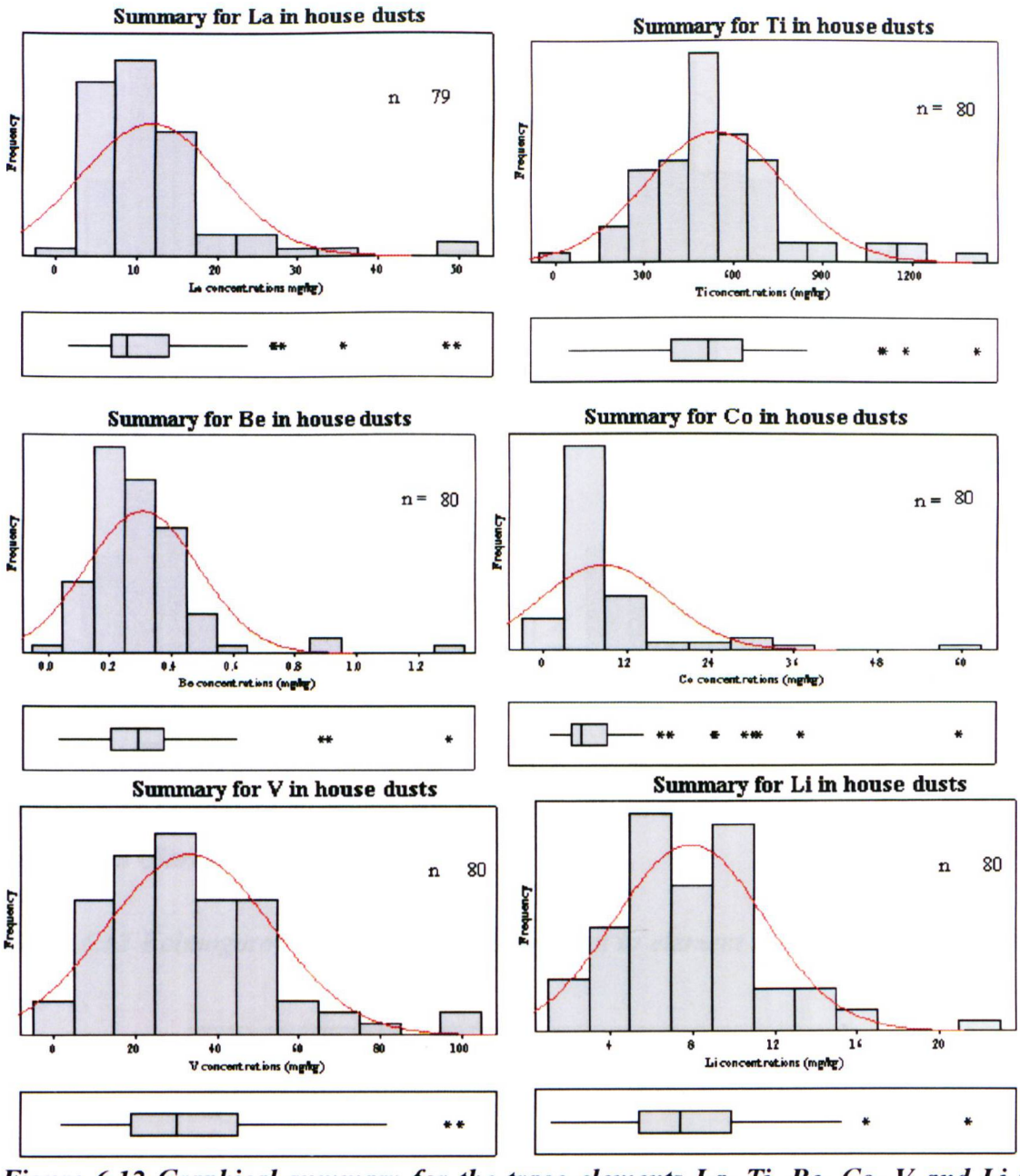


Figure 6.12 Graphical summary for the trace elements La, Ti, Be, Co, V and Li in house dusts from Gibraltar.

The spread of elements such as S, Pb, Mn, and Co, Ti and K, together with the location of the outlying values suggests a possible bi-modal population indicating alternative sources within the household or possible sources from outside the home for these elements. Table 6.12 shows a KS test applied to the house dust data. According to the initial test performed on the data, none of the elements conformed to a normal distribution. Once the data underwent logarithmic transformation, all elements conformed to a normal distribution.

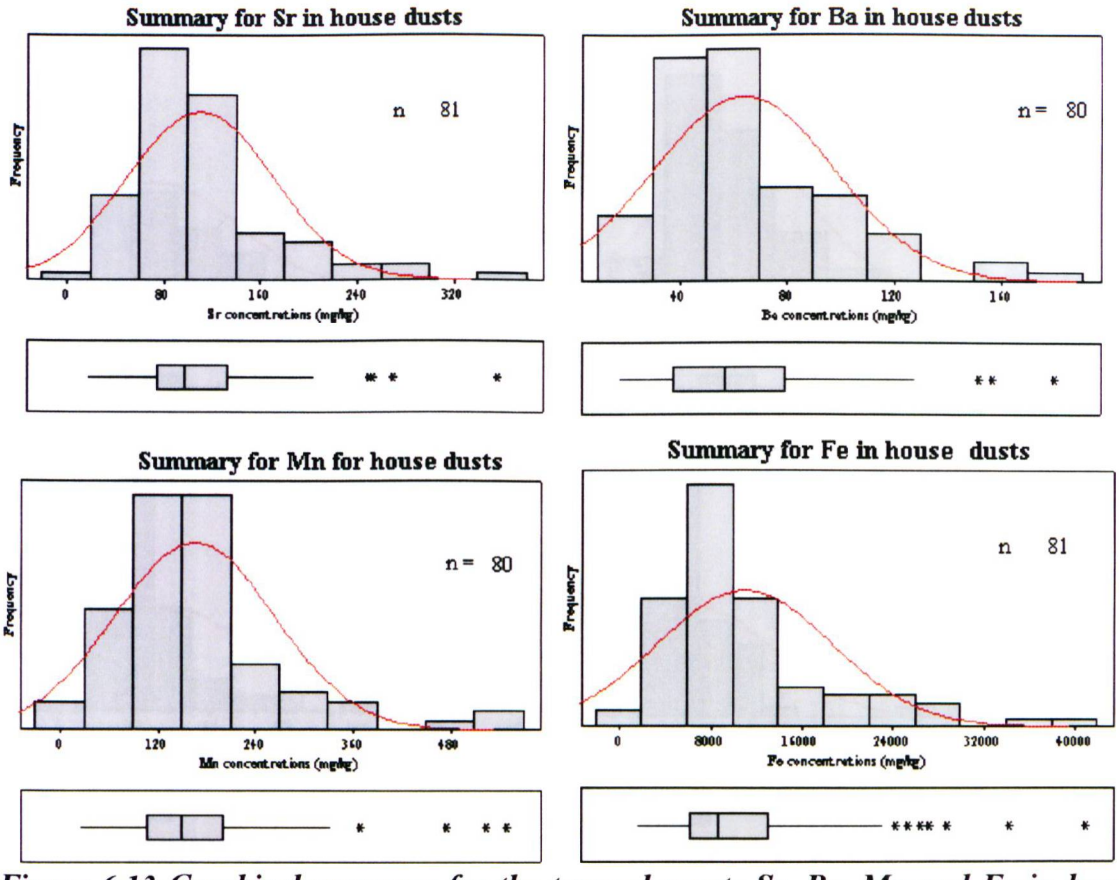


Figure 6.13 Graphical summary for the trace elements Sr, Ba, Mn and Fe in house dusts from Gibraltar.

Table 6.12 Kolmogorov-Smirnov (KS) test applied to element concentrations in house dusts.

	Untransformed data	Ln data		Untransformed data	Ln data
Li	×	✓	Mn	×	✓
Na	×	✓	Fe	×	✓
K	×	✓	V	×	✓
Be	×	✓	Co	×	✓
Mg	×	✓	Ni	×	✓
Ca	×	✓	Cu	×	✓
Sr	×	✓	Ag	×	×
Ba	×	✓	Zn	×	✓
Al	×	✓	Cd	×	✓
La	×	✓	Pb	×	✓
Ti	×	✓	P	×	✓
V	×	✓	S	×	✓
Cr	×	✓	As	×	✓

× data do not correspond to a normal distribution., ✓ data correspond to a normal distribution.

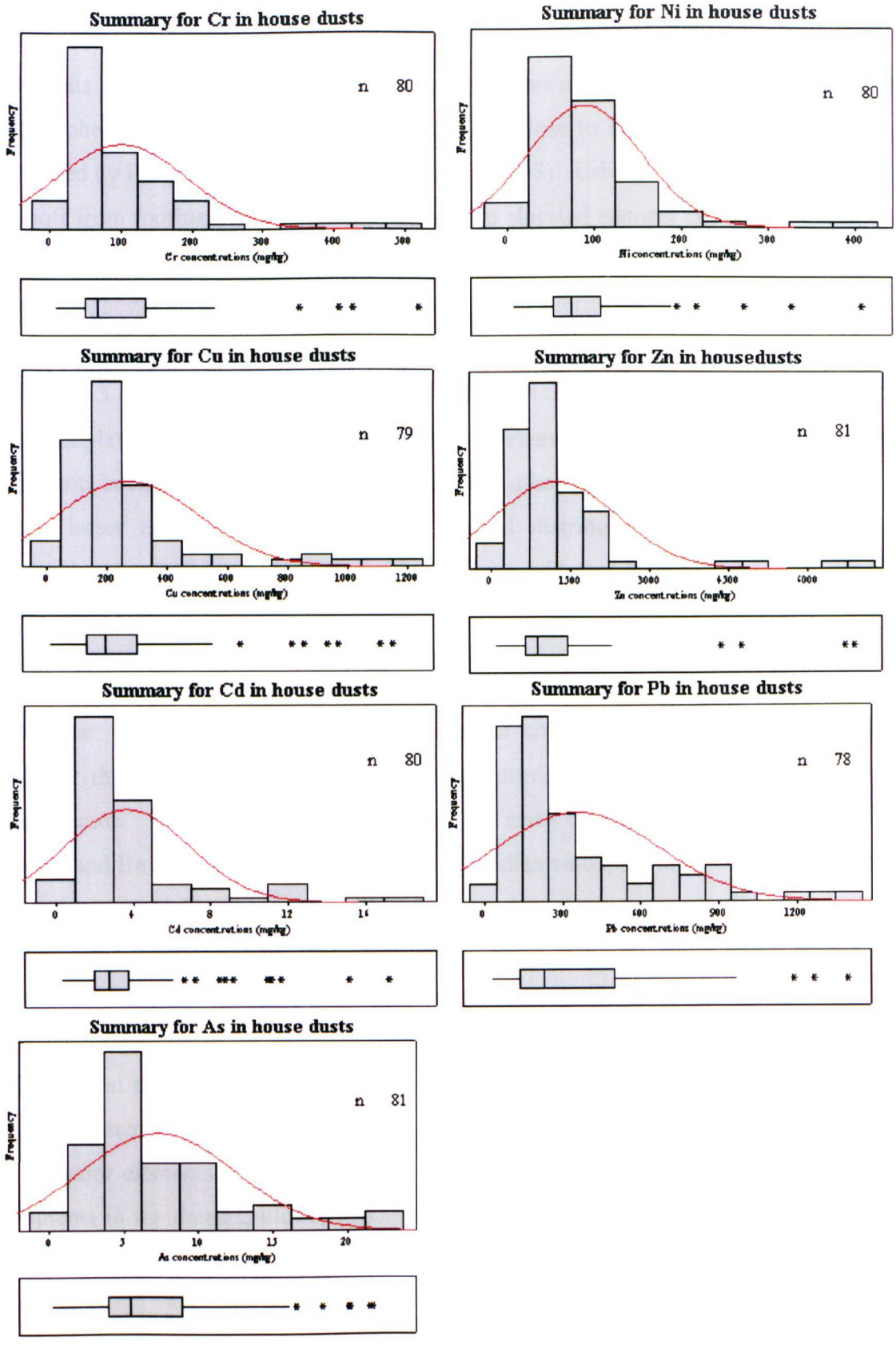


Figure 6.14 Graphical summary for the heavy metals Cr, Ni, Cu, Zn, Cd, Pb and As in house dusts from Gibraltar. (Please note Cd data to assessed with caution due to number of samples below IDL and proximity of most sample concentrations to IDL. Concentrations below 2 mg/kg to be assessed with caution)

6.5 Street dusts

Topsoils and street dusts in urban areas are indicators of heavy metal contamination from atmospheric deposition. Roadside soils that are close to heavy traffic are known to be polluted by Pb and other metals (Culbard *et al.*, 1988). Urban soils and dusts also contain runoff from roofing materials which can lead to elevated element concentrations in these two media. Cadmium, Cu, Pb and Zn are good indicators of pollution in dusts and soils because they appear in petrol, car components, oil lubricants, industrial and incinerator emissions (Alloway, 1995). A total of 83 street dust samples were taken across Gibraltar. Figure 4.3 shows the spatial distribution of samples taken. The data shown in table 6.13 also display large standard deviations for most elements (Co and Cd excluded). Some elements such as As have a normal distribution, other elements like Cu, Zn and Cd (and to a lesser extent Pb) only display a normal distribution when the data undergo logarithmic transformation. Parametric statistics will therefore be used to analyse this dataset.

The descriptive statistics below show that with the soil, rock and house dust datasets in Gibraltar, most elements have a large range of concentrations. The median value is smaller than the arithmetic mean for a large portion of the data indicating a skewed distribution. Elements such as Li, Mg, Al, Fe and Co have a higher median than AM value, and Be and As have an equal AM and median value, the latter suggesting a normal distribution. Table 6.14 does show that As displayed a normal distribution before logarithmic transformation. Elements like K, Mg, Ca, Al, Ti, Fe, P and S have a large standard deviation indicating that the measurements are scattered widely about the AM. As mentioned above, in general terms, a skewness value greater than one indicates a distribution that differs significantly from a normal, symmetric distribution. Elements with a skewness value greater than 1 include Li, Be, Ba, Al, Ti, Cr, Fe, Cu, Ag and Zn. The major elements Ca, Ba, AL, La and Mn display a lower kurtosis value to the other elements in the dataset, illustrating a frequency distribution curve with a more flattened peak. Elements with a negative kurtosis include Na, K, Ca, Sr, La, V, Ni, Ag, Pb, P, S and As.

***Table 6.13 Descriptive statistics for the street dust samples* (n=83) (results in mg/kg)**

	AM	Median	SD	GM	Kurtosis	Skewness	Min	Max	25th percentile	50th percentile	75th percentile	95th percentile
Li	12	13	5.8	10	7.1	1.7	2.5	41	6.80	13	14	20
Na	1043	482	896	680	-1.1	0.7	58	2650	324	482	1790	2610
K	3344	2731	1863	2777	-1.5	0.2	492	7610	1560	2731	5310	5707
Be	0.4	0.4	0.2	0.4	7.7	2.1	0.2	1.5	0.3	0.4	0.5	0.8
Mg	14476	15400	5682	12847	2.8	0.5	460	35900	12250	15400	16500	25710
Ca	86696	79700	37260	76845	-0.3	0.1	9620	203000	55000	79700	121000	131800
Sr	115	90	63	98	-1.4	0.4	21	248	64	90	189	205
Ba	118	110	62	107	15	3.3	25	460	87	110	131	196
Al	12634	14500	6218	11266	4.8	1.5	3170	40100	7320	14500	15500	21480
La	9.4	9.1	4.7	8.1	-0.1	0.6	0.8	24	5.40	9.1	13	18
Ti	521	496	263	473	5.3	2.1	126	1550	348	496	564	1296
V	53	45	38	41	-0.5	0.8	7	138	21	45	69	128
Cr	159	153	98	132	7.7	2.1	14	641	92	153	196	350
Mn	374	327	164	338	1.5	0.8	84	1030	253	327	492	608
Fe	25540	28200	11630	22954	5.6	1.6	3230	74800	17700	28200	30100	44306
Co	7.6	7.8	3.2	6.8	-0.1	0.1	1	17	5.2	7.8	9.9	13
Ni	68	52	36	57	-1.1	0.4	3.4	135	40	52	103	130
Cu	275	211	308	168	20	3.7	5.2	2250	82	211	430	781
Ag	1.0	0.3	1.1	0.4	-0.6	1.0	<0.01	3.6	0.2	0.3	2.08	3.1
Zn	781	484	655	528	2.4	1.3	26	3190	246	484	1300	1608
Cd	1.0	0.7	0.84	0.48	0.0	0.8	<0.01	3.50	0.4	0.7	1.8	2.5
Pb	898	392	874	433	-1.6	0.5	17	2626	147	392	1950	2190
P	963	680	685	715	-0.3	0.6	80	3280	372	680	1650	1850
S	2993	1380	2721	1830	-1.5	0.6	129	7960	769	1380	5970	7254
As	8.4	8.4	4	7.4	-0.8	0.3	1.4	17	4.8	8.4	11	16

(Please note Cd and Ag data to assessed with caution due to number of samples below IDL and proximity of most sample concentrations to IDL Cadmium concentrations below 2 mg/kg to be assessed with caution)

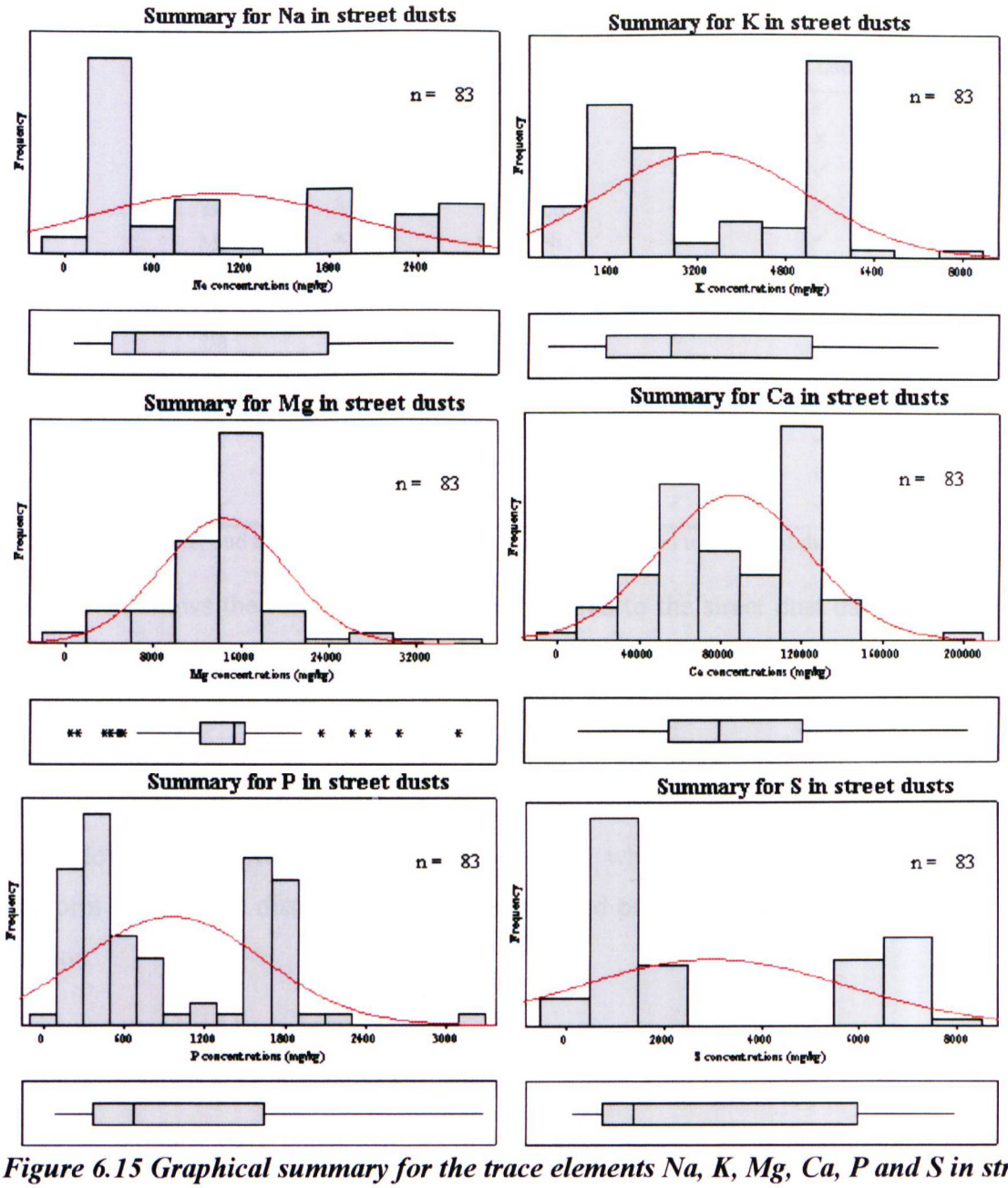


Figure 6.15 Graphical summary for the trace elements Na, K, Mg, Ca, P and S in street dusts from Gibraltar.

The spread of the distribution of the elements Na, K, P, S, V, Sr, V, Sr, Ni, Zn and Pb clearly indicates a bimodal distribution, meaning that the variance of some of these elements come from two or more populations which would indicate two or more distinct sources, again either geological, anthropogenic or both. Outlying values are present in the distribution of La, Ba, Mn, Fe, Cr, Cu and Zn. The large variability in the street dusts dataset is illustrated by the multiple populations present as seen from the cumulative probability plots in appendix D as well as the large widths of the box plots (figures 6.15-6.18) for most of the elements including Na, S, K, Sr, Ni, Pb and Cd.

Table 6.14 Kolmogorov-Smirnov (KS) test applied to element concentrations in street dusts.

	Untransformed data	Ln data		Untransformed data	Ln data
Li	×	✓	Mn	✓	✓
Na	×	✓	Fe	×	×
K	×	✓	V	✓	✓
Be	×	✓	Co	×	✓
Mg	×	✓	Ni	×	✓
Ca	×	✓	Cu	×	✓
Sr	×	✓	Ag	×	×
Ba	×	✓	Zn	×	✓
Al	✓	✓	Cd	×	×
La	✓	✓	Pb	×	✓
Ti	×	✓	P	×	✓
V	×	✓	S	✓	✓
Cr	×	✓	As	✓	✓

× data do not correspond to a normal distribution., ✓ data correspond to a normal distribution.

Table 6.14 shows the results of the KS test applied to the street dust data. Aluminium, La, Mn, V, S and As conform to a normal distribution before the data underwent logarithmic transformation. Iron, Ag and Cd did not conform to a normal distribution even after logarithmic transformation. This may be due to the large number of sources of these elements in the urban environment. In the case of Cd, more than 25% of the sample fell below the analytical detection limit (ADL) which means that the data will not conform to a normal distribution and as mentioned previously, need to be assessed with caution.

6.5.1 Chemical partitioning of elements in street dusts

Selected samples were chosen from the street dust data for sequential extractions using the methodology developed by Tessier and modified by Li (1993), section 4.4.1 and appendix C. The recovery was within the acceptable range of 80-120% (figure D3 in appendix D). Although it is understood that the phases applicable to soils and sediments are unlikely to be found as such in dust samples, a series of sequential extractions can give valuable information concerning the extractability and thus mobility of metals in the dusts. Table 6.15 and 6.16 show the descriptive statistics for street dusts subjected to sequential extraction procedure.

Results are displayed in mg/kg and are absolute concentrations of each of the elements in each step. Figures 6.15 – 6.18 display box plots showing the partitioning of elements in

each step as a percentage of the total value. The recovery of some elements can be less than 100%. As mentioned previously, this is due to the incomplete dissolution of some primary silica phases.

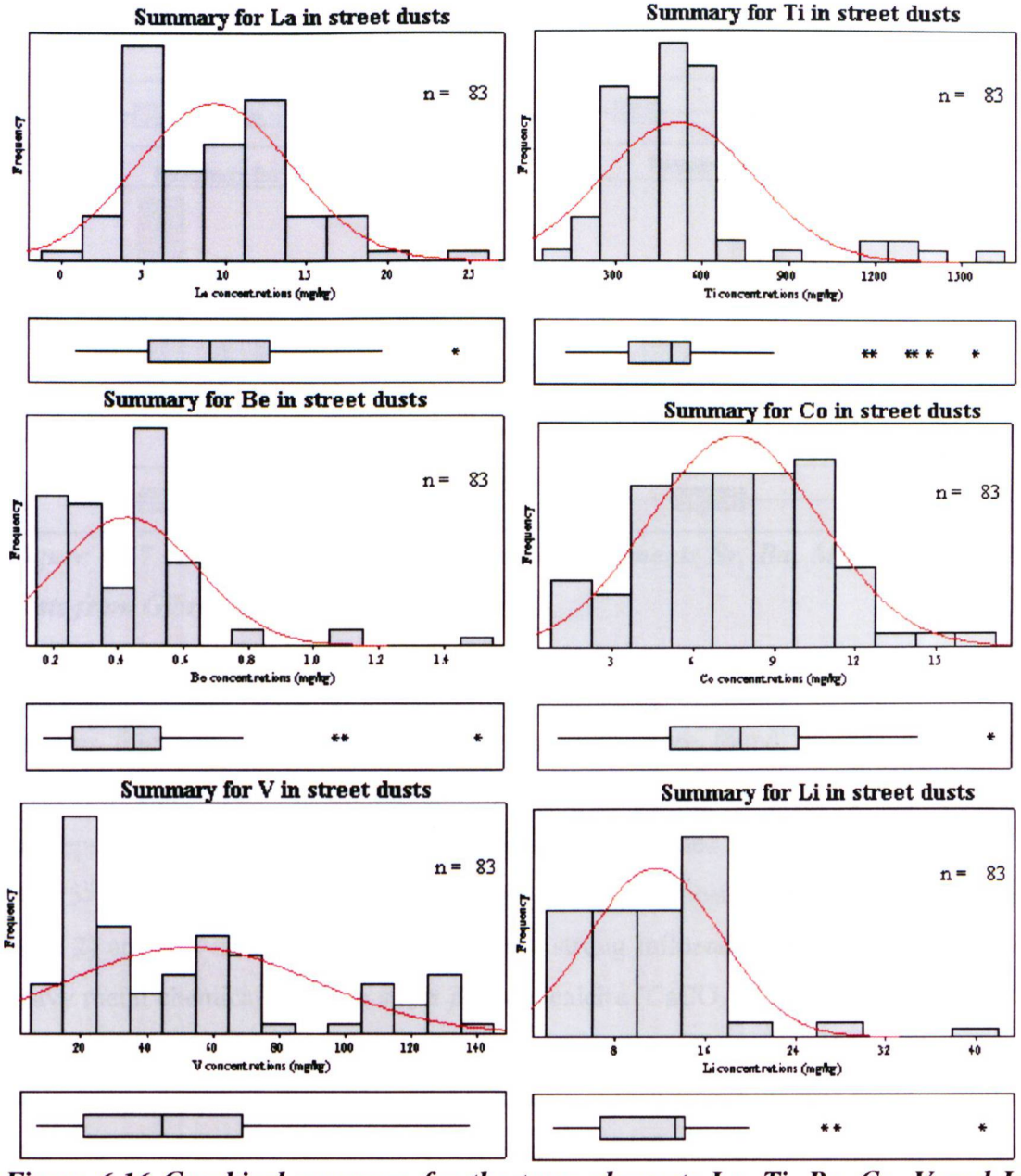


Figure 6.16 Graphical summary for the trace elements La, Ti, Be, Co, V and Li in street dusts from Gibraltar.

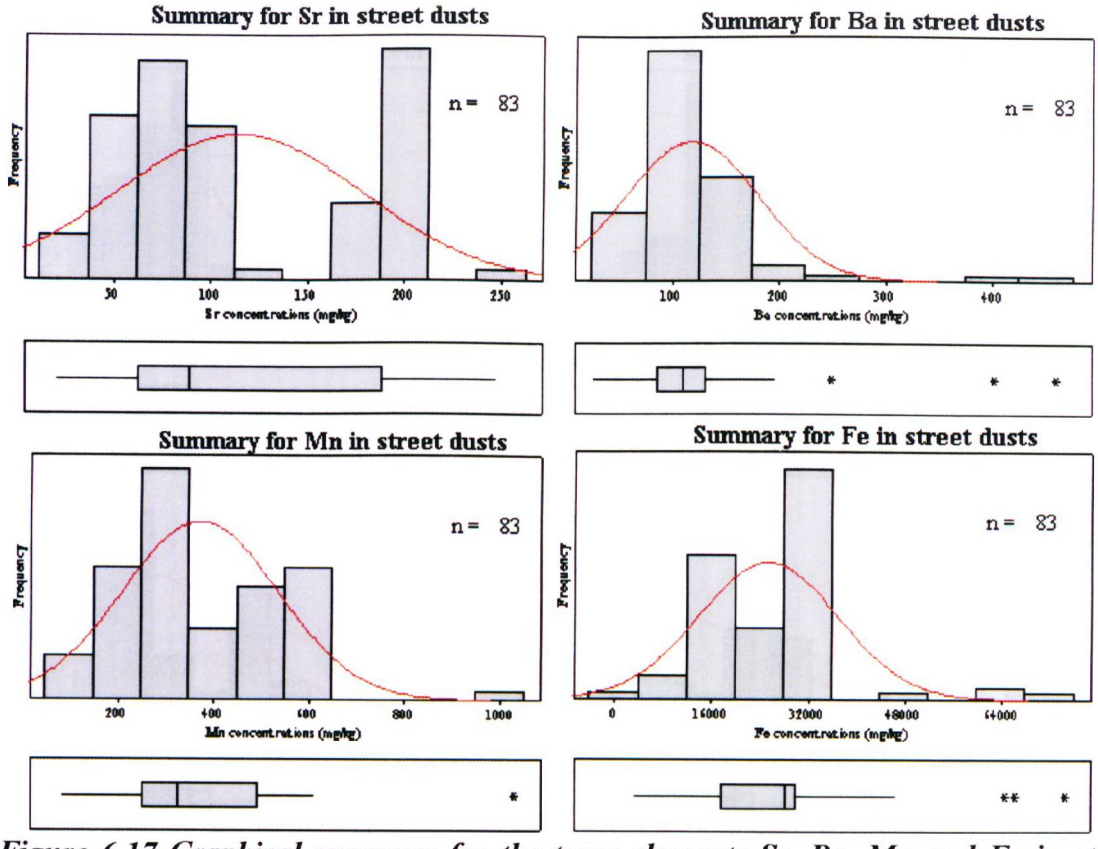


Figure 6.17 Graphical summary for the trace elements Sr, Ba, Mn and Fe in street dusts from Gibraltar.

The partitioning of the major elements Ca, K, P and S is shown in figure 6.19. The patterns found in street dusts are very similar to those found in soils for the major elements. The majority of the calcium was extracted in steps 2 and 3 with the percentage in steps 1 and 5 being very low. Calcium is partitioned in the following step order 2>3>5>1>4. Calcium in street dusts is very strongly associated with the carbonate phase (step 2) and this indicates (as with soils) the strong influence of the carbonate phase on heavy metal chemical forms in street dusts as calcite ($CaCO_3$), (Li *et al.*, 2001) which is a primary mineral in the geology and soils in Gibraltar. It can also be attributed to the weathering of cement. Potassium in street dusts as well as in soils was mainly partitioned into step 5 with the other steps being of minor importance. It is partitioned in the following order 5>1>2>3>4. The majority of P was partitioned into step 5 followed by step 3 and step 4. Steps 1 and 2 are of minor importance in the partitioning of P. It was partitioned in the following order 5>3>4>2>1. Almost half of the total S was partitioned into steps 1 and 3. Sulphur was partitioned in the following step order 1=3>5>2>4. The partitioning of this element was much more evenly distributed throughout the 5 steps than the other major elements.

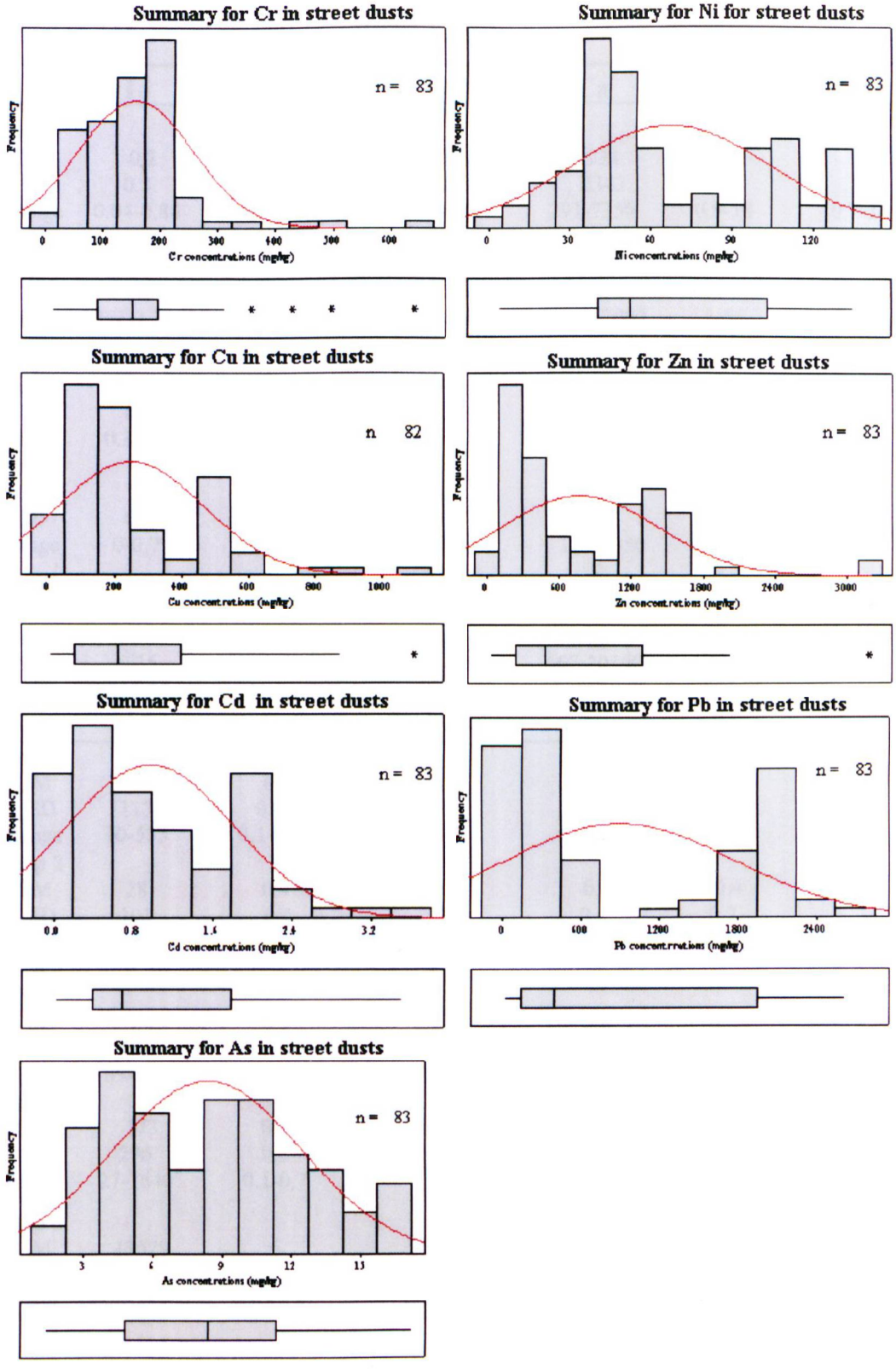


Figure 6.18 Graphical summary for the heavy metals Cr, Ni, Cu, Zn, Cd, Pb and As in street dusts from Gibraltar. (Please note Cd data to assessed with caution due to number of samples below IDL and proximity of most sample concentrations to IDL. Concentrations below 2 mg/kg to be assessed with caution)

Table 6.15 Descriptive statistics of Li, K, Be, Ca, Sr, Ba, Al, La, Ti, V and Cr in street dusts in Gibraltar. **(n=32) (results in mg/kg)**[5]

	Li	K	Be	Ca	Sr	Ba
Step 1						
GM	0.2	291	0.006	1924	5.1	4
SD	0.3	967	0.003	2343	6.1	3
Range	0.04-0.88	37-2610	0.002-0.009	291-7350	0.9-18	0.7-14
Step 2						
GM	0.2	88	0.004	26702	31	11
SD	0.5	233	0.006	12424	16	9
Range	0.1-1.44	1-630	0.002-0.068	2050-47000	2-58	1-33
Step 3						
GM	0.9	89	0.7	20962	19	19
SD	0.5	94	0.5	16816	26	16
Range	0.3-1.9	17-298	0.02-02	3080-35700	2-74	2-64
Step 4						
GM	0.1	9	0	1194	1.7	6
SD	0.2	14	0	1040	2.8	7
Range	0-0.7	2-77	0-0.08	113-3350	0.2-8.4	0.8-20
Step 5						
GM	11	3717	0.3	5071	30	210
SD	5	906	0.1	5466	18	320
Range	6-35	1500-5860	0.2-0.8	667-20500	9-70	48-937

	Al	La	Ti	V	Cr
Step 1					
GM	35	0.1	1.7	1.2	0.2
SD	113	0.03	0.9	0.5	0
Range	10-533	0.1-0.25	0.4-11	0.7-2.5	0.2-0.2
Step 2					
GM	28	0.4	0.1	0.2	0.4
SD	101	0.4	2	0.6	0.7
Range	2-596	0.1-1.6	0.04-12	0.1-2.6	0.2-2.8
Step 3					
GM					
SD	646	0.9	1.7	5.8	0.2
Range	485	0.9	0.9	7.1	12
	189-1500	0.2-2.8	0.5-5.6	0.9-23	0.2-32
Step 4					
GM	173	0.3	9.3	3.1	3.5
SD	296	0.2	10	5.9	3.2
Range	27-1640	0.1-0.7	0.9-35	0.3-19	1-11
Step 5					
GM	13529	6	1177	27	121
SD	5860	2.9	891	22	43
Range	6050-28000	3.3-13	400-3070	8.5-80	45-261

[5] Step 1 = Soluble and Exchangeable phase, Step 2 = Carbonate phase, Step 3 = Bound to Fe-Mn oxide fraction, Step 4 = Bounds to organic/sulphide fraction, Step 5 = Residual fraction. (for further details refer to page 98).

Table 6.16 Descriptive statistics of Mn, Fe, Co, Ni, Cu, Zn, Pb, P, S and As in street dusts in Gibraltar. **(n=32) (results in mg/kg)**

	Mn	Fe	Co	Ni	Cu	Zn
Step 1						
GM	6.7	24	0.1	0.4	1.3	0.2
SD	8.2	110	0	0.5	3.4	27
Range	1.8-42	3.5-503	0.1-0.3	0.2-1.9	0-8.9	0-153
Step 2						
GM	53	50	0.2	0.5	6.4	152
SD	36	251	0.4	1.6	43	321
Range	1.6-127	8-1490	0.1-1.4	0.2-4	0-253	12-1640
Step 3						
GM	73	2289	1.2	6.9	11	183
SD	73	2122	0.7	6.4	56	191
Range	14-257	702-6400	0.1-2.8	1.8-21	0.4-308	45-619
Step 4						
GM	2.5	114	0.2	1.6	43	9.6
SD	2	166	0.2	1.4	63	9.9
Range	0.6-6.4	20-845	0.1-0.7	0.3-4.9	5.2-221	2.3-34
Step 5						
GM	142	15500	4	42	41	63
SD	94	10138	2.5	20	121	53
Range	52-415	4450-52600	1.3-11	18-91	4.7-732	17-293

	Pb	P	S	As
Step 1				
GM	0.7	4.8	243	0.2
SD	1.5	13	1497	0
Range	0.6-9	0.4-40	7.8-5180	0.2-0.3
Step 2				
GM	97	33	123	0.2
SD	291	25	229	0
Range	2.4-707	7.2-119	11-640	0.2-0.2
Step 3				
GM	125	90	103	0.5
SD	370	67	93	0.3
Range	5-894	29-321	37-281	0.2-1.3
Step 4				
GM	20	75	298	0.3
SD	57	127	274	0.2
Range	0.4-261	4.6-328	31-865	0.2-08
Step 5				
GM	69	319	309	11
SD	152	383	419	8.9
Range	3-411	86-1430	42-1190	3.5-35

(Please note Co samples displayed concentrations below IDL in all five steps)

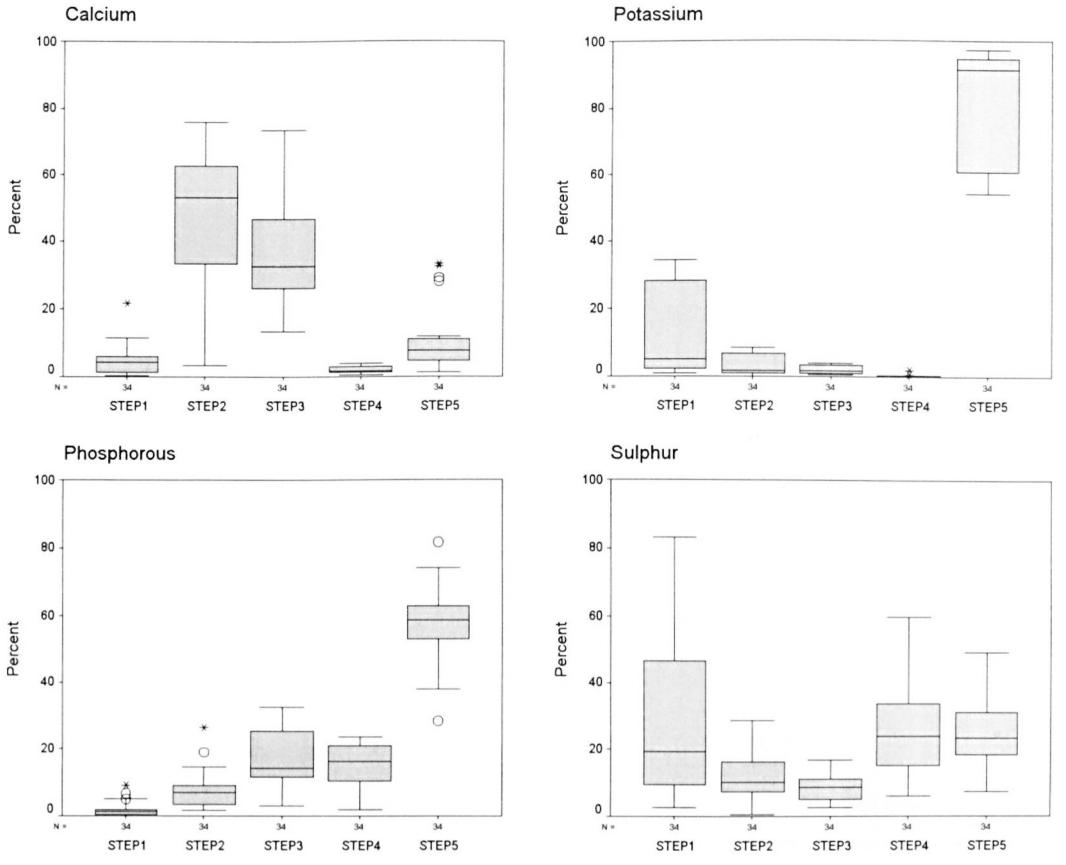


Figure 6.19 Box plot diagrams illustrating the partitioning of the major elements Ca, K, P and S in street dusts across a five step sequential extraction procedure. Results in percentage of total value.

Figure 6.20 shows the partitioning of the trace elements La, Ti, Be, Co, V and Li. As with the major elements similarities can be found between the partitioning of trace elements in soils and street dusts. The majority of La was partitioned into step 5, with a small percentage of the total metal partitioned into the other four steps. It was partitioned in the following order 5>3>2>4>1. Most of the Ti (98%) was partitioned into step 5 with a very small percentage in the other four steps. As with Be in soils, a large portion of Be in street dusts (79%) was partitioned into step 5, followed by step 3. It was partitioned in the following step order 5>3>4>2>1. Cobalt is largely partitioned into step 5 followed by step 3, with very small amounts in step 2, 4 and 1. The majority of V was partitioned into step 5 followed by step 3 and 4. It was partitioned in the following order 5>3>4>1>2. Again as in soils the majority of Li was partitioned into step 5 followed by step 3. Lithium was partitioned in the following step order 5>3>2>1>4.

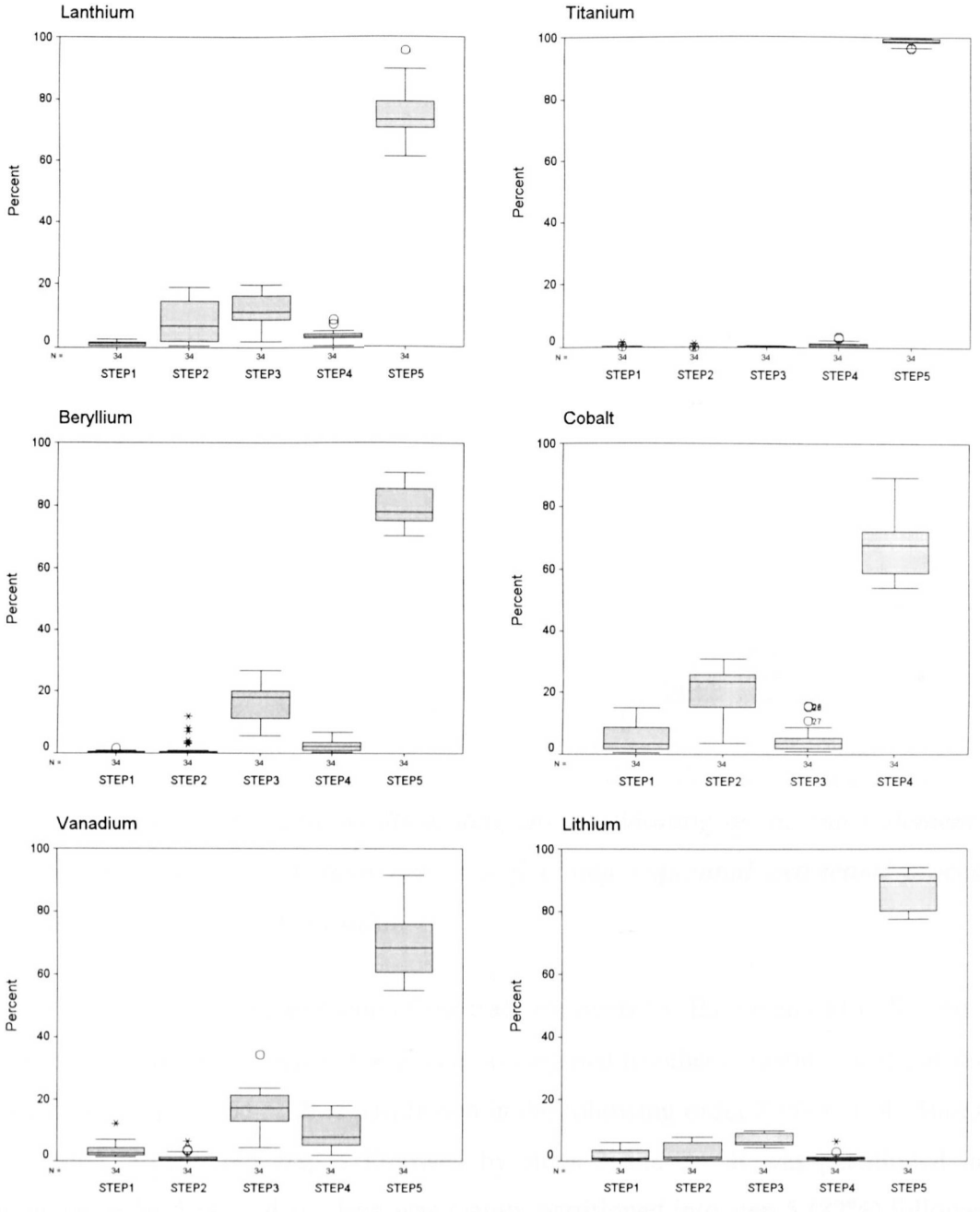


Figure 6.20 Box plot diagrams illustrating the partitioning of the trace elements La, Ti, Be, Co, V and Li in street dusts across a five step sequential extraction procedure. Results in percentage of total value.

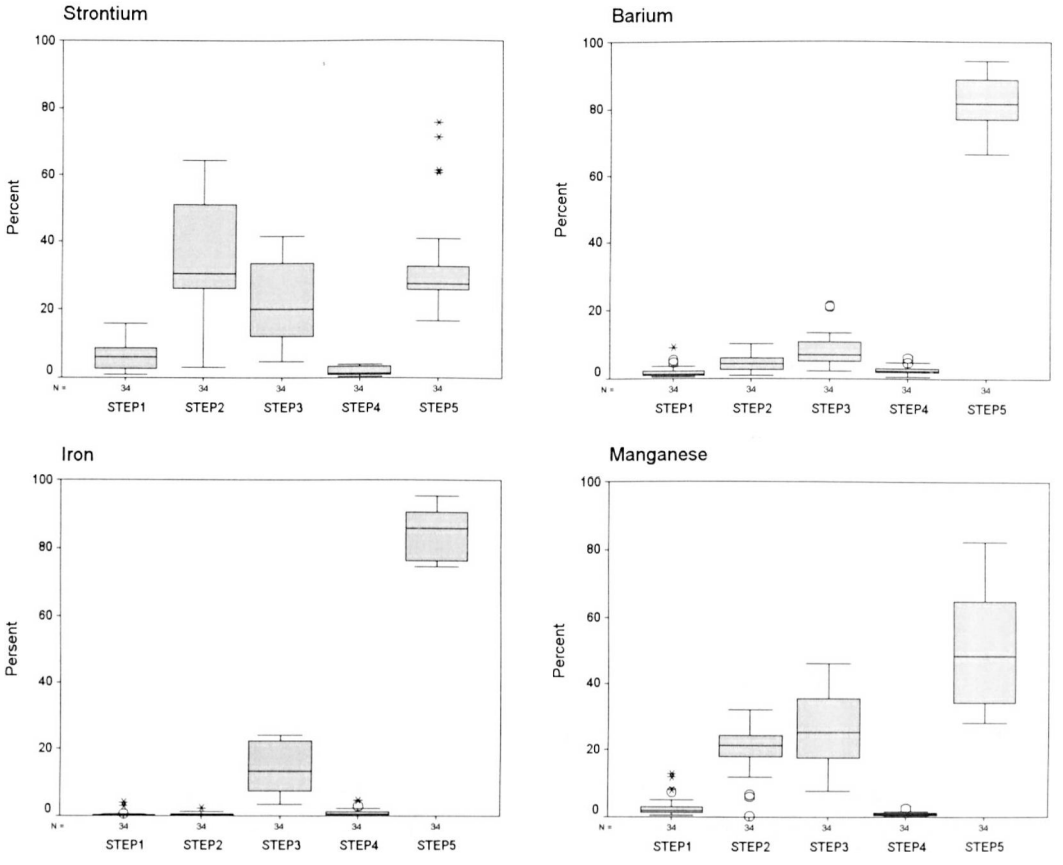


Figure 6.21 Box plot diagrams illustrating the partitioning of the trace elements Sr, Ba, Fe and Mn in street dusts across a five step sequential extraction procedure. Results in percentage of total value.

Figure 6.21 shows the partitioning of the trace elements Sr, Ba, Fe and Mn. Strontium is partitioned more evenly across the 5 steps as opposed to other elements. It is partitioned mainly into steps 2 and 5. It is partitioned in the following order 2>5>3>1>4. Barium is partitioned largely into step 5 followed by steps 3 and 2. It was partitioned in the following order 5>3>2>4>1. Iron was mainly partitioned into step 5 (82%) followed by steps 3 and 2. It partitioned in the following order 5>3>2>4>1.

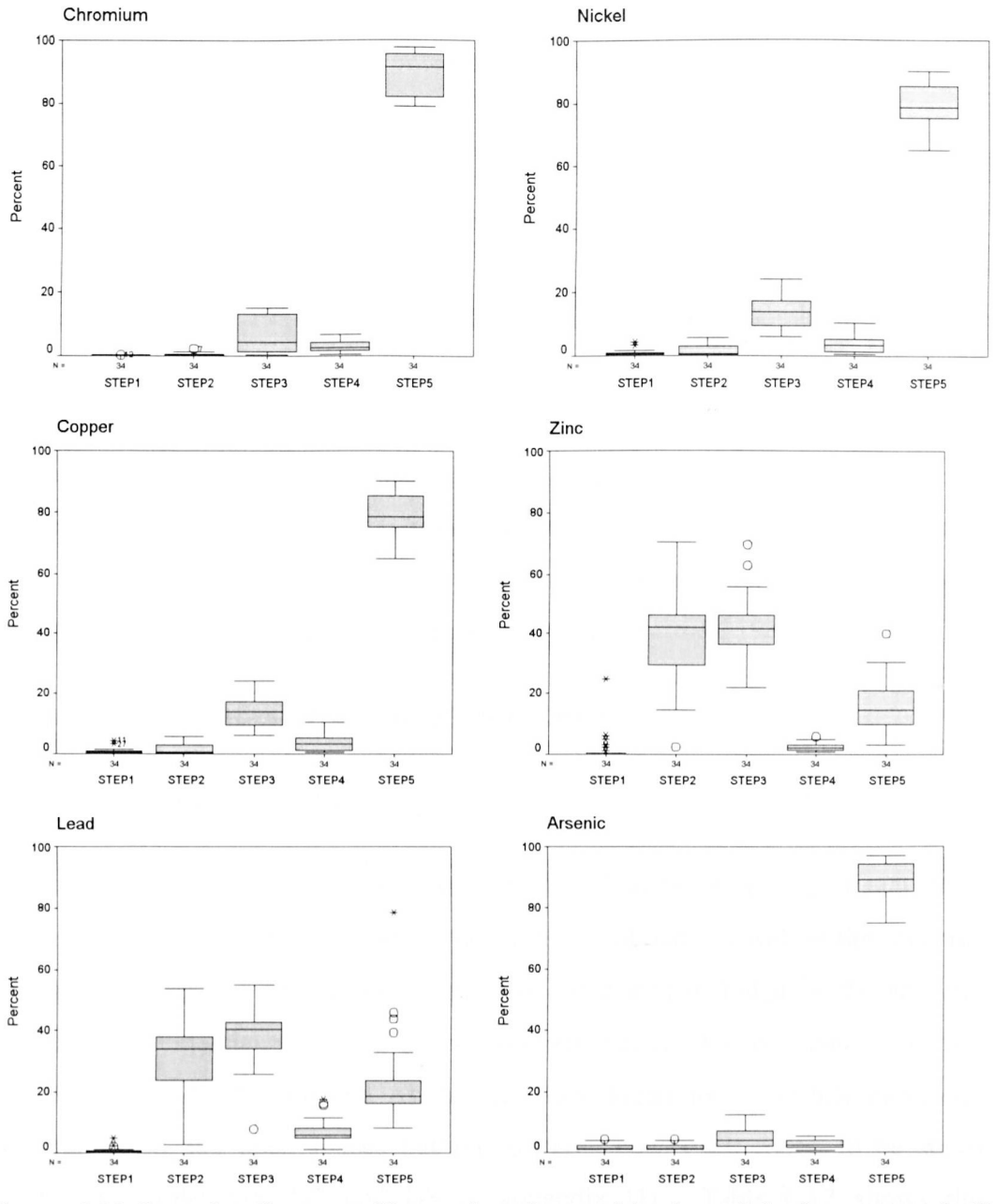


Figure 6.22 Box plot diagrams illustrating the partitioning of the heavy metals Cr, Ni, Cu, Zn, Pb and As in street dusts across a 5 step sequential extraction procedure. Results in percentage of total value.

Figure 6.22 displays the partitioning of the heavy metals Cr, Ni, Cu, Zn, Pb and As. The majority of Cr was partitioned into step 5 (89%) with the other 4 steps being of minor importance. It was partitioned in the following order 5>3>4>2>1. Nickel as in soils was also largely partitioned into step 5 (79%) with step 3 being of secondary importance. Nickel partitioned in the following step order 5>3>4>2>1. The majority of Cu is partitioned between steps 4 and 5. Copper is partitioned in the following order 5>4>3>2>1. A large portion of Zn is partitioned into steps 3 and 2. Zinc was partitioned

in the following order 3>2>5>4>1. Lead was partitioned into the following step order 3>2>5>4>1. The majority of As, was partitioned into step 5 with the other 4 steps being of minor importance. It was partitioned in the following order 5>3>4>1>2.

Environmental and health effects of trace and heavy metal contaminants in dusts are concerned with the mobility and availability of the elements within the dust matrices (Gibson and Farmer, 1984). Calcium, S, Zn and Pb were predominantly partitioned in steps 2 and 3. These elements are more mobile and more potentially bioavailable than elements which were largely partitioned into steps 4 and 5. While trace element mobility and availability are of less obvious significance as regards uptake by plants. They do reflect however, differences between soil and street dust which are attributable to variations in physical (e.g. grain size) and chemical characteristics as well as distance from sources of contamination (e.g. cars) (Gibson and Farmer, 1984).

6.6 Secondary statistical treatment of the datasets

6.6.1 Analysis of variance (ANOVA)

ANOVA analysis was carried out to test whether there were any significant differences between the element concentrations in the various land uses, as well as the varying parent geological materials. The different land use categories included in the analysis were residential, commercial, industrial areas and open spaces. The concentrations of Cr, Ni, Cu, Zn Cd, Ca, K, Na, Fe and As in soils were found to be slightly elevated in the industrial areas and open spaces but this difference was not found to be statistically significant (Tables D6, D7 and D8 in appendix D). Table 6.17 shows the only statistically significant differences (at the 95% level of significance) for elements in soils which have been categorised according to land use. It is interesting to note that concentrations of Pb and Ba, which indicate a traffic source, are significantly different in samples taken from open spaces and residential areas, to other areas. The main open space in Gibraltar is the upper rock nature reserve (URNR). The topography of the area (very steep cliffs and slopes) meant that many samples were taken within a few metres from the road. This area has a considerable traffic flow in the form of private vehicles, coaches and taxis. The majority of taxis and coaches in Gibraltar operate on diesel fuel which is known to have Pb and Ba additives (Mielkie, 1991).

Table 6.17 ANOVA results for statistically significant differences between different geological parent materials.

Element	Geological associations
Li	Catalan sands **Vs** limestone dolomite, interbedded limestone dolomite Fill made ground **Vs** limestone dolomite, interbedded limestone dolomite
K	Catalan sands **Vs** pale grey dolomite, limestone dolomite, interbedded limestone dolomite
Ba	Catalan sands **Vs** fill made ground, limestone dolomite, interbedded limestone dolomite
Al	Catalan sands **Vs** pale grey dolomite, limestone dolomite, interbedded limestone dolomite
La	Catalan sands **Vs** fill made ground, pale grey dolomite, dark grey dolomite, limestone dolomite, interbedded limestone dolomite
Ti	Catalan sands **Vs** limestone dolomite, interbedded limestone dolomite, dark grey dolomite, recent beach sands
Mn	Catalan sands **Vs** limestone dolomite
Na	Catalan sands **Vs** fill made ground, scree breccias, pale grey dolomite, limestone dolomite, interbedded limestone dolomite, recent beach sands
Mg	Catalan sand **Vs** fill made ground, pale grey dolomite, dark grey dolomite, limestone, interbedded limestone dolomite
V	Catalan sands **Vs** pale grey dolomite, interbedded limestone dolomite
Cu	Catalan sands **Vs** fill made ground, limestone dolomite, interbedded limestone dolomite
Cd	Catalan sands **Vs** limestone dolomite, interbedded limestone dolomite Fill made ground **Vs** limestone dolomite
Pb	Catalan sands **Vs** fill made ground, scree breccias, pale grey dolomite, dark grey dolomite, limestone dolomite, interbedded limestone dolomite
P	Catalan sands **Vs** limestone dolomite, interbedded limestone dolomite, Limestone dolomite **Vs** recent beach sands
S	Catalan sands **Vs** fill made ground, pale grey dolomite, dark grey dolomite, limestone dolomite, interbedded limestone dolomite

Vs = versus

Table 6.18 ANOVA results for statistically significant differences between different land use categories.

Element	Land use associations
Ba	Open spaces **Vs** residential
Pb	Open spaces **Vs** residential

Vs = versus

Certain sites in close proximity to industrial areas as well as open spaces with a former history of industrial use did display elevated concentrations as related to the rest of the dataset. Tables 6.17, 6.18 and 6.19 show the significant differences found for elements in soils between the different geological, land use and sample type categories. Soil samples taken from indigenous soil or exposed outcrops were classified according to the underlying parent geological material. Samples taken on the Catalan sands (table 3.3)

have a statistically significant difference in concentrations of Li, K, Ba, Al, La, Ti, Mn, Na, Mg, V, Cu, Cd, Pb, P and S to samples taken on other geological materials.

The Catalan sands consist of medium grained sands with well rounded grains. These grains show a high percentage of quartz rather than limestones indicating that they have been derived from a source outside Gibraltar, as Gibraltar rocks have almost no quartz bearing strata (Rose and Rosenbaum, 1990). Additionally they are found on the east side of Gibraltar in an area where there is less traffic than on the busier western side and are situated at the base of the old catchments, (now sand slopes) over one hundred metres above sea level. Therefore the impact of traffic and industry on the Catalan sands is minimised.

The soil samples were also classified according to sample type. Soil samples high in fly ash and shot blasting sand content, soil and wind blown sand samples (the latter includes the Catalan sands) all have concentrations of Li, Na, K, Ba, Al, La, Ti, Mn, Fe, Co, Cu, Zn, Cd, Cd, Pb, P, S, As, Mg, Ca, Sr, V and Ag which are significantly different to concentrations found in other sample types. Furthermore, the anthropogenically related elements like Ba, Fe, Co, Cu, Zn, Cd, Pb, P, S, As, Mg, Sr and Ag all list samples with high fly ash content as having concentrations that are significantly different to concentrations of at least one other sample type for example soil, beach sands, cave sediments etc.

T-tests were carried out to assess significant differences between element concentrations in soils taken from civilian and military sites and similarly between natural and garden soils. The difference noticed between these two groups was found to be statistically significant for the elements Ba, Ti and Cr in planted verses natural soils. The GM concentrations of Li, K, Be, Ba, Al, La and As were found to be higher in soils than in house and street dusts. Those of sodium, Sr, Ti, Ni, Cu, Ag, Zn, Cd, P and S were higher in house dusts and those of Mg, Ca, V, Cr, Mn, Fe, Co and Pb were higher in street dusts (section 6.9).

ANOVA analyses were also carried out on the street dust and house dust datasets. The results showed that there were no significant differences between the two sets in the concentrations of the twenty six elements analysed. In the house dust dataset, the results from the questionnaire (Appendix B) issued at each home, was incorporated into the

statistical tests. ANOVA and t-tests were carried out but no statistically significant differences were found between the questionnaire results and the element concentrations.

Table 6.19 ANOVA results for statistically significant differences between different sample type categories.

Element	Sample type associations
Li	Soil **Vs** WBS, red sands, fly ash
Na	WBS **Vs** soil, raised beaches, fly ash, beach sands
	Soil **Vs** red sands, fly ash
	Red sands **Vs** raised beaches, fly ash, beach sands, cave sediments
K	Soil **Vs** WBS, red sands
Ba	WBS **Vs** soil, fly ash
	Red sands **Vs** soil, fly ash
Al	Soil **Vs** WBS, red sands
La	Soil **Vs** WBS, beach sands
Ti	Soil **Vs** WBS, red sands
Mn	Soil **Vs** WBS, red sands
Fe	Soil **Vs** WBS, red sands
	Fly ash **Vs** WBS, soil, red sands, beach sand, cave sediments
Co	Soil **Vs** WBS, red sands
	Fly ash **Vs** soil, red sands, raised beaches, beach sands, cave sediments
Cu	Fly ash **Vs** WBS, soil, raised beaches, beach sands, red sands
	Red sands **Vs** soil, cave sediment
	WBS **Vs** soil, cave sediments
Zn	Soil **Vs** red sands, fly ash, beach sand
	Fly ash **Vs** WBS, beach sands, red sands
	Red sands **Vs** raised beaches,
Cd	WBS **Vs** soil, fly ash
Pb	WBS **Vs** soil, raised beaches, fly ash,
	Soil **Vs** red sands, beach sands
	Red sands **Vs** raised beaches, fly ash
	Fly ash **Vs** beach sand
P	Soil **Vs** WBS, beach sand, cave sediments, red sands
	WBS **Vs** cave sediments
	Red sands **Vs** raised beaches, fly ash, cave sediments
	Cave sediments **Vs** fly ash, beach sands
S	Soil **Vs** WBS, red sands, fly ash, cave sediments
	WBS **Vs** fly ash, cave sediments
	Red sands **Vs** raised beaches, fly ash, beach sand, cave sediments
	Cave sediments **Vs** raised beaches, beach sands
	Fly ash **Vs** beach sand
As	Fly ash **Vs** WBS, soil, red sands, beach sands
Mg	WBS **Vs** soil, fly ash, beach sands
	Red sands **Vs** soil, beach sands
Ca	WB S **Vs** soil
	Red sands **Vs** soil, raised beaches, beach sands
Sr	WBS **Vs** soil, fly ash
	Red sands **Vs** soil, raised beaches, fly ash, beach sands
V	WBS **Vs** soil, red sands
	Soil **Vs** red sands
Ag	WBS **Vs** soil, fly ash

WBS = wind blown sands; **Vs** = versus; fly ash = samples high in fly ash and shot blasting sand content

6.6.2 Correlation Analysis of Soils from Gibraltar

A Pearson correlation coefficient (R^2) has been used to measure the linear association between two variables, if the relationship is significant (at the 0.01 level or $P < 0.01$), a strong linear correlation is assumed. A positive or negative value indicates the direction of the relationship. The correlation has been performed on lognormal data (Table 6.20). The elements Li, Na, K, Be, Ca, Sr, Ba, La, Ti, V Cr, Mn, Fe and Co were significant positively correlated ($R^2 > 0.55$ $P < 0.01$). The abundance of these elements in soils is lithogenically controlled. The elements Na, Be, Ca, Sr, V, Cr, Mn, Fe and Co have a strong positive correlation with the trace metals Ni, Cu, Zn Cd and the non-metals P and S ($P<0.01$).

The elements Ni, Cu, Zn, Cd, Pb and P, S and As were found to have a strong positive correlation at the 0.01 significance level. The elevated concentrations in soils is attributed to anthropogenic additions. However, naturally elevated metal concentrations can occur in soils naturally derived from the parent material and overlying clay rich soils. Lead was found to have fewer strong correlations than the other elements. It was only significantly correlated with Ca, Fe, Cu, Zn, Cd, P, S and As. Additionally, Cd was found to be correlated with Zn, Cu was highly correlated with Zn and Cd, and Pb was correlated with Fe and Cd. Magnesium has not been included in table 6.20, as it did not have any significant correlations with any of the trace elements. This could be due to different factors responsible for controlling the variance of these elements in the soil matrix, such as different parent geological materials. The data were found to be highly correlated and therefore appropriate for multivariate analysis. In the soil data, *n* equals 238 as opposed to the 245 soil samples taken, in order to eliminate the influence of very high outlying values. Correlations are significant at the 0.05 (95%) if Sig. value is <0.05. Correlations that are significant at the 0.01 level, Sig. value <0.01 (99% confidence) are highlighted in bold and are in blue.

6.6.3 Correlation analysis of house dust samples from Gibraltar

A Pearson's correlation analysis of house dust samples was performed on logarithmically transformed data (table 6.21). In contrast to elements in soil, there were fewer significant correlations between elements in the house dust dataset. However, multivariate analysis may reveal underlying trends and be a valuable tool to assist with source apportionment.

Iron has a significant correlation with Li, Be, La, Ti, V, Mn, Co, Ni, Zn, Cd, Pb and As ($P < 0.01$). The elements K, Be, Ba, Sr and S had few significant correlations and Na, Mg, Ca and P have no significant correlation with any other element. Soil, airborne dust, wear and tear of household furnishings and paint all contribute to the concentration of elements in house dust (Thornton *et al.*, 1990). Therefore, there are several sources of metal in urban house dust.

6.6.4 Multivariate statistics: Factor analysis

A successful multivariate analysis extracts a few factors that define the majority of the variability in the dataset (section 5.1). The factors are interpreted by the elements that have a high loading or correlation to the extracted factor. The purpose of a factor analysis is to reduce firstly a large multivariate dataset into a smaller number of factors which summarises the majority of the variance and secondly to identify a sample or variable that has a distinct variability from the rest of the data. In this way the method reveals outliers or discriminate groups within the data which can be helpful with the interpretation of geochemical anomalies.

6.6.4.1 *Application of multivariate statistics to geochemical datasets for Gibraltar soils*

Factor analysis- Preliminary analysis

The first factor analysis was performed on 24 elements from 238 soil samples. Elements with a poor percentage recovery or unacceptable bias i.e. Ag and Al were removed. This is because the purpose of the analysis is the grouping of elements which reflect the different processes in operation within the Gibraltar environment. The outcome of any multivariate analysis is specific to the input data. A preliminary analysis determines the suitability of the data for multivariate analysis and identifies discriminate cases or variables. A single variable or sample that contributes to the majority of the variation in the dataset hides the latent structure of the remaining data therefore it would be removed as an outlier. The input parameters of the first factor analysis are given in Table 6.22.

Table 6.20 Pearson correlation coefficient of logarithmic transformed elements in Gibraltar surface (0-15 cms) soils (n=238)

		Na	K	Be	Ca	Sr	Ba	La	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	S	As
Li	R^2	.70	.89	.69	.22	.57	.56	.66	.75	.91	.56	.32	.44	.65	.52	.28	.09	.28	-.14	.02	.44	.39
	Sig.	*.00*	*.00*	*.00*	*.22*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.07*	*.01*	*.00*	*.00*	*.13*	*.64*	*.12*	*.45*	*.92*	*.01*	*.03*
Na	R^2		.62	.83	.68	.82	.56	.71	.82	.79	.68	.70	.78	.85	.79	.58	.47	.53	.23	.19	.63	.56
	Sig.		*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.01*	*.00*	*.21*	*.30*	*.00*	*.00*
K	R^2			.46	.15	.38	.51	.59	.60	.78	.51	.24	.38	.54	.40	.07	-.08	.17	-.33	-.05	.18	.28
	Sig.			*.01*	*.43*	*.03*	*.00*	*.00*	*.00*	*.00*	*.00*	*.19*	*.03*	*.00*	*.02*	*.72*	*.68*	*.37*	*.07*	*.77*	*.34*	*.12*
Be	R^2				.59	.86	.46	.62	.75	.84	.57	.76	.79	.88	.77	.67	.52	.57	.41	.34	.78	.67
	Sig.				*.00*	*.00*	*.01*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.02*	*.06*	*.00*	*.00*
Ca	R^2					.76	.45	.44	.49	.36	.52	.80	.71	.57	.64	.62	.62	.50	.51	.38	.46	.44
	Sig.					*.00*	*.01*	*.01*	*.00*	*.04*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.03*	*.01*	*.01*
Sr	R^2						.61	.73	.79	.71	.54	.79	.72	.74	.70	.55	.46	.48	.40	.28	.64	.54
	Sig.						*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.01*	*.01*	*.02*	*.12*	*.00*	*.00*
Ba	R^2							.75	.69	.58	.71	.39	.42	.50	.54	.35	.31	.25	.13	.21	.41	.43
	Sig.							*.00*	*.00*	*.00*	*.00*	*.03*	*.02*	*.00*	*.00*	*.05*	*.09*	*.17*	*.48*	*.24*	*.02*	*.01*
La	R^2								.77	.74	.66	.51	.53	.63	.56	.37	.22	.34	.11	.21	.45	.49
	Sig.								*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.04*	*.23*	*.06*	*.56*	*.25*	*.01*	*.00*
Ti	R^2									.80	.60	.56	.53	.67	.57	.43	.31	.33	.14	.14	.54	.41
	Sig.									*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.01*	*.09*	*.07*	*.45*	*.44*	*.00*	*.02*
V	R^2										.70	.58	.69	.84	.72	.52	.33	.56	.13	.27	.67	.68
	Sig.										*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.07*	*.00*	*.48*	*.13*	*.00*	*.00*
Cr	R^2											.56	.72	.74	.84	.68	.60	.64	.28	.50	.67	.76
	Sig.											*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.12*	*.00*	*.00*	*.00*
Mn	R^2												.84	.74	.73	.64	.61	.67	.48	.51	.66	.66
	Sig.												*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.01*	*.00*	*.00*	*.00*
Fe	R^2													.91	.91	.78	.71	.76	.54	.55	.72	.83
	Sig.													*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*	*.00*
Co	R^2														.93	.73	.63	.75	.40	.47	.79	.84
	Sig.														*.00*	*.00*	*.00*	*.00*	*.02*	*.01*	*.00*	*.00*
Ni	R^2															.82	.75	.81	.48	.60	.83	.89
	Sig.															*.00*	*.00*	*.00*	*.01*	*.00*	*.00*	*.00*
Cu	R^2																.89	.81	.75	.68	.80	.82
	Sig.																.00	.00	.00	.00	.00	.00
Zn	R^2																	.76	.85	.73	.69	.74
	Sig.																	*.00*	*.00*	*.00*	*.00*	*.00*
Cd	R^2																		.53	.65	.81	.85
	Sig.																		*.00*	*.00*	*.00*	*.00*
Pb	R^2																			.63	.49	.58
	Sig.																			*.00*	*.00*	*.00*
P	R^2																				.47	.74
	Sig.																				*.01*	*.00*
S	R^2																					.83
	Sig.																					*.00*

Correlations significant at the 0.01 level (99%) are highlighted in **bold and blue** (Sig. <0.01), correlations are significant at the 0.05 (95%) if Sig. <0.05

Table 6.21 Pearson correlation coefficient of logarithmic transformed elements from urban house dusts from Gibraltar (n=80)

		Na	K	Be	Mg	Ca	Sr	Ba	La	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	P	S	As
Li	R^2	-.18	**.47**	.29	.36	-.12	.36	-.10	.38	**.67**	**.53**	.02	**.42**	**.56**	.32	.07	-.03	.13	.18	.26	.25	.17	**.66**
	Sig.	*.21*	*.00*	*.04*	*.01*	*.40*	*.01*	*.51*	*.01*	*.00*	*.00*	*.87*	*.00*	*.00*	*.03*	*.64*	*.86*	*.36*	*.23*	*.07*	*.09*	*.26*	*.00*
Na	R^2		.06	-.22	-.16	-.18	-.30	.02	.23	-.06	-.07	.24	.02	-.11	-.02	.21	-.01	-.01	-.15	-.15	.33	.05	-.18
	Sig.		*.71*	*.14*	*.27*	*.21*	*.04*	*.88*	*.11*	*.70*	*.65*	*.10*	*.92*	*.46*	*.87*	*.15*	*.97*	*.94*	*.30*	*.31*	*.02*	*.75*	*.21*
K	R^2			.29	.24	-.17	.09	-.08	**.43**	.36	**.41**	-.10	.33	.24	-.12	-.12	-.13	-.07	-.04	.15	.39	.21	.19
	Sig.			*.04*	*.09*	*.25*	*.53*	*.59*	*.00*	*.01*	*.00*	*.49*	*.02*	*.09*	*.39*	*.39*	*.38*	*.62*	*.79*	*.29*	*.01*	*.16*	*.19*
Be	R^2				-.10	.07	.23	-.03	.05	.22	.51	.18	**.40**	**.49**	.26	.27	.14	.17	.03	.23	.06	.09	.09
	Sig.				*.48*	*.64*	*.12*	*.84*	*.76*	*.13*	*.00*	*.23*	*.00*	*.00*	*.08*	*.06*	*.35*	*.25*	*.83*	*.12*	*.69*	*.52*	*.56*
Mg	R^2					.16	.39	-.15	.15	.37	-.12	-.09	.17	.03	-.09	-.19	-.12	.08	-.13	.10	-.01	.12	.12
	Sig.					*.29*	*.01*	*.29*	*.29*	*.01*	*.43*	*.56*	*.25*	*.85*	*.51*	*.18*	*.43*	*.59*	*.37*	*.49*	*.95*	*.42*	*.46*
Ca	R^2						.63	-.28	-.09	-.18	-.26	-.25	-.18	-.13	-.29	-.16	-.05	.17	-.07	-.13	-.20	.13	-.27
	Sig.						*.00*	*.05*	*.55*	*.22*	*.08*	*.08*	*.21*	*.38*	*.04*	*.26*	*.73*	*.24*	*.64*	*.37*	*.17*	*.37*	*.06*
Sr	R^2							**-.62**	-.04	.29	-.06	-.19	-.07	.14	.05	-.09	.01	.15	.01	.04	.05	**.63**	.05
	Sig.							*.00*	*.80*	*.04*	*.67*	*.19*	*.62*	*.33*	*.76*	*.54*	*.93*	*.30*	*.97*	*.81*	*.76*	*.00*	*.72*
Ba	R^2								.19	-.06	.21	-.02	.20	.19	-.03	.03	.11	-.01	.17	.21	-.03	**-.84**	.33
	Sig.								*.20*	*.67*	*.16*	*.88*	*.16*	*.19*	*.84*	*.85*	*.45*	*.97*	*.23*	*.14*	*.82*	*.00*	*.02*
La	R^2									.36	**.46**	.10	**.54**	**.48**	-.04	.14	-.12	.07	.08	.14	.37	-.09	.35
	Sig.									*.01*	*.00*	*.48*	*.00*	*.00*	*.78*	*.33*	*.40*	*.64*	*.56*	*.32*	*.01*	*.54*	*.02*
Ti	R^2										.37	-.01	.32	**.46**	.20	.10	.20	.24	.30	.23	.31	.24	**.41**
	Sig.										*.01*	*.95*	*.03*	*.00*	*.16*	*.48*	*.18*	*.09*	*.03*	*.11*	*.03*	*.09*	*.00*
V	R^2											.39	**.59**	**.64**	.18	.38	-.01	-.09	.16	.19	.22	-.11	**.42**
	Sig.											*.01*	*.00*	*.00*	*.23*	*.01*	*.94*	*.53*	*.27*	*.18*	*.13*	*.47*	*.00*
Cr	R^2												.34	.32	**.41**	**.79**	.16	.13	.07	.01	-.05	.06	.04
	Sig.												*.02*	*.02*	*.00*	*.00*	*.28*	*.37*	*.65*	*.95*	*.74*	*.68*	*.80*
Mn	R^2													**.61**	.21	.32	.07	.17	.11	.27	.09	-.23	.36
	Sig.													*.00*	*.15*	*.02*	*.64*	*.24*	*.46*	*.06*	*.54*	*.11*	*.01*
Fe	R^2														**.57**	**.58**	.39	**.49**	**.48**	**.44**	.02	-.14	**.59**
	Sig.														*.00*	*.00*	*.01*	*.00*	*.00*	*.00*	*.90*	*.35*	*.00*
Co	R^2															**.61**	.45	**.43**	**.42**	.38	-.14	.09	.39
	Sig.															*.00*	*.01*	*.00*	*.00*	*.03*	*.34*	*.52*	*.01*
Ni	R^2																**.53**	**.49**	.37	.22	-.12	.00	.15
	Sig.																*.00*	*.00*	*.01*	*.12*	*.42*	*.98*	*.31*
Cu	R^2																	**.75**	**.45**	.22	-.13	-.03	.25
	Sig.																	*.00*	*.00*	*.13*	*.36*	*.82*	*.08*
Zn	R^2																		**.54**	.29	-.11	-.06	.26
	Sig.																		*.00*	*.04*	*.46*	*.69*	*.07*
Cd	R^2																			**.49**	-.06	-.13	**.40**
	Sig.																			*.00*	*.69*	*.38*	*.00*
Pb	R^2																				.03	-.14	.34
	Sig.																				*.85*	*.35*	*.02*
P	R^2																					.23	.17
	Sig.																					*.12*	*.26*
S	R^2																						-.22
	Sig.																						*.14*

Correlations significant at the 0.01 level (99%) highlighted in **bold and blue** (Sig. <0.01), correlations are significant at the 0.05 (95%) if Sig. <0.05

A factor analysis (FA) was performed on a correlation matrix as opposed to a covariance matrix. A covariance matrix is used when variables are measured on different scales as the input data have been logarithmically transformed (Facchinelli *et al.*, 2001; Reimann *et al.*, 2002; Manly, 1994). Therefore a correlation matrix was calculated and provided the starting point for factor analysis.

Table 6.22 Parameters of the Factor Analysis (FA)

Input parameters		***Comments***
Variables	Li, Na, K, Be, Mg, Ca, Sr, Ba, La, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, P, S and As	Elements > analytical detection limit with acceptable quality control and recovery
Cases	N =238	East side reclamation samples where the land use has changed were removed
FA Parameters		
Descriptive	Extract: Correlation matrix at P < 0.01, KMO-Bartlett's test	KMO-Bartlett's test determine if a correlation matrix is suitable for matrix manipulation
Extraction	Method: PCA Analyse: correlation matrix Display: unrotated factor score and scree plot Extract:4 factors	The number of Eigenvalues extracted is determined after a number of preliminary analysis
Rotation	Method: Varimax Display: rotated solutions and loading plots	
Scores	Save as new variables	
Missing values		Replaced with the analytical detection limit

The results of the preliminary factor analysis are given in Table 6.23. The Kaiser-Meyer-Olkin (KMO) (Kinnear and Gray, 2001) measure of sampling adequacy and Bartlett's test of sphericity (Kinnear and Gray, 2001) are options within the statistics package SPSS v11 that test if the data are appropriate for a factor analysis. A high value for the KMO indicates that a high proportion of the variance in an element is a common to all elements. A significance value (<0.05) for Bartlett's test indicates a significant relationship between the variables.

The variance of individual elements accounted for by the extracted factors is given by their communalities (Table 6.23). A factor analysis extracts only the principal components that explain the majority of the variation in the dataset. Components that describe only a minor amount of variance are removed. A high communality (>0.6) indicates that the majority of the variance was accounted for by the extracted factors. A

low communality means that the variance has not been explained by a component or factor. In this analysis all the variables have a high communality (>0.7) with the exception of Na, La, Cr and Ni. It is concluded that the majority of the variance in these elements has been accounted for in the four extracted factors. An element with a low communality and low loading score on the extracted factors has no relationship to the majority of the dataset and is removed as an outlier.

Table 6.23 Results of factor analysis for Gibraltar surface (0-15 cms) soils

Test of analysis	Kaiser-Meyer-Olkin measure of sampling adequacy	0.887
	Bartlett's test of sphericity. significance	0.000
Communalities of extracted factors	Element	Communalities
	Li	0.89
	Na	0.69
	K	0.85
	Be	0.85
	Ca	0.80
	Mg	0.92
	Sr	0.78
	Ba	0.85
	La	0.48
	Ti	0.85
	V	0.87
	Cr	0.57
	Mn	0.87
	Fe	0.91
	Co	0.94
	Ni	0.68
	Cu	0.87
	Zn	0.78
	Cd	0.60
	Pb	0.72
	P	0.78
	S	0.81
	As	0.89
Summary of factors		
Factor	**Variables highly correlated with factor >0.7**	
F1	Li, K, Be, Ca, Al, Ti, V, Cr, Ni	
F2	Co, Cu, Zn, Cd, Pb, S, Ba, As	
F3	Mg, Ca, Sr	
F4	Na, Ba, Fe, Co, P	

In this first example four factors were extracted representing 77% of the total variance in the data matrix. The first factor (F1) had an eigenvalue of 14 and represents 55% of the total variance, the second factor (F2) had an eigenvalue of 2 and represents 10% of the total variance, the third factor (F3) had an eigenvalue of 2 and represents 8% of the total variance, and the fourth factor (F4) had an eigenvalue of 1 and represents 4% of the total variance in the data matrix. The elements with a high loading (>0.6) on these factors have been summarised in Table 6.24 and in the rotated component matrix. Elements with a loading exceeding 0.6 are used to interpret that factor.

The first three factors explain 77% of the total variance, they all have an eigenvalue >1. A scree plot (figure 6.23) shows a marked change in gradient after the fourth factor and illustrates a method used to decide how many factors are important to the dataset. The other factors were not regarded as important and can be referred to as noise (Davies *et al.*, 1992). In this example the number of factors were chosen after a number of repeated analysis and a through examination of the outcome.

The four factors extracted are summarised and labelled below:

F1 Li, K, Be, Ca, Al, Fe, Ti, V, Cr, Ni *(Lithogenic/pedogenic)*
F2 Fe, Mn, Co, Cu, Zn, Cd, Pb, S, Ba, As *(Anthropogenic)*
F3 Mg, Ca, Sr *(geologically related factor)*
F4 Na, Ba, Fe, Co, P

If an element has a low factor loading on all factors and a low communality it is removed as an independent variable. This analysis was carried out on the entire dataset and then subsequently on civilian and military soils as well as the different land use categories mentioned in section 6.7.1.

The first three factors (F1, F2 and F3) were extracted each time regardless of the smaller number of samples in the test and the varying land uses. The original samples have a coefficient with the new factors saved as a factor score in the dataset. Factor scores are typically plotted as a scatter diagram and labelled by their sample number (figure 6.24). In a plot of the factor scores for F1 and F2 samples contributing highly to the variance in F1, included sites which are discussed in section 7.3. These sites are identified as range outliers. The majority of the total variation of the dataset was attributed to F1. Samples with a high loading on F2 refer to specific sites with Gibraltar (section 7.3). These sites were then removed from the analysis as outliers which allowed the variation in the remaining dataset to be examined.

The subsequent outputs of the runs where the samples were divided into land use classes were all comparable to the first factor analysis. The same key three factors were extracted each time regardless of land use category, these are; F1 the lithogenic/pedogenic factor, F2 the anthropogenic factor, and F3, the geologically related factor. An important feature of a FA is that the factors are independent and uncorrelated. An element with a high loading on two factors has variance reflected by both factors

which are themselves uncorrelated. Loading plots and the loading scores were used here to clarify with which factor the element was associated.

Table 6.24 Rotated component matrix for the preliminary analysis of soils

Variable	Component			
	1	2	3	4
Ln Li	.860	.242	.270	-.147
Ln Na	.192	.375	.443	.570
Ln K	.775	.183	.401	.240
Ln Be	.799	.354	-.023	-.306
Ln Mg	.200	.068	.851	.176
Ln Ca	.076	.186	.938	-.006
Ln Sr	.268	.397	.742	.065
Ln Ba	.494	.452	.497	.400
Ln La	.634	.198	.097	.183
Ln Ti	.794	.123	.272	.368
Ln V	.826	.377	.196	-.127
Ln Cr	.726	.226	-.020	.026
Ln Mn	.714	.335	.483	.138
Ln Fe	.637	.552	.203	.406
Ln Co	.520	.662	-.011	.485
Ln Ni	.775	.148	.137	.212
Ln Cu	.211	.833	.250	.268
Ln Zn	.161	.814	.233	.203
Ln Cd	.187	.737	.168	-.037
Ln Pb	.217	.750	.335	-.005
Ln P	.474	.515	.490	-.220
Ln S	.239	.719	.484	-.026
Ln As	.578	.610	-.048	.297

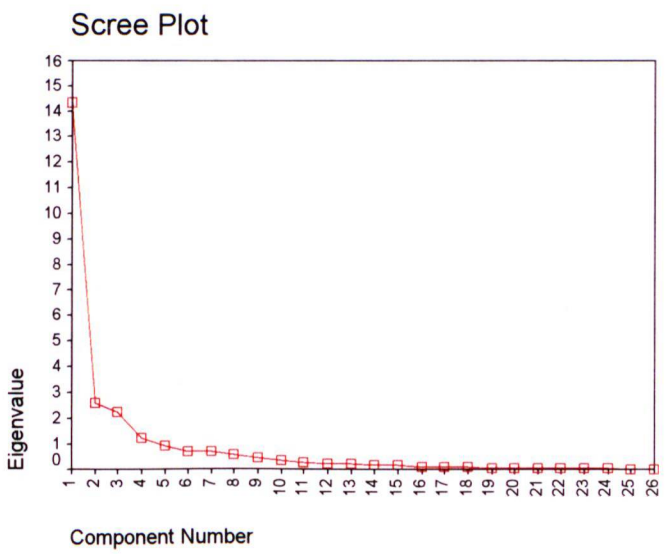


Figure 6.23 Scree plot for factor analysis on Gibraltar surface (0-15 cms) soils.

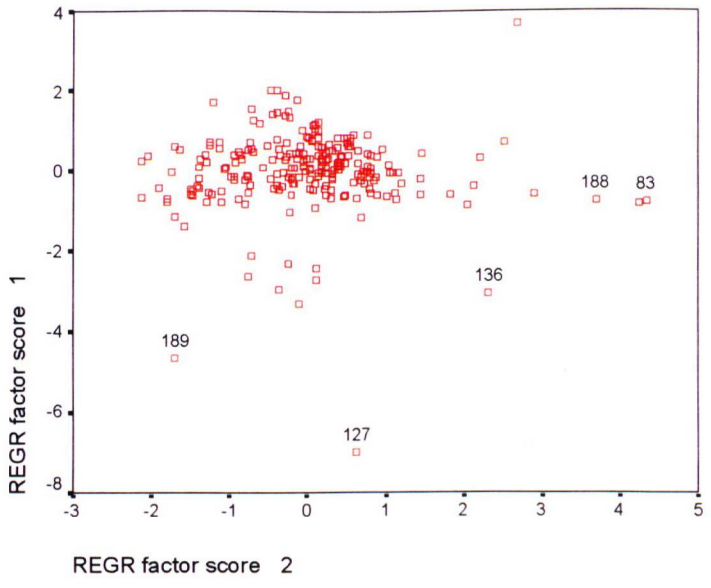


Figure 6.24 Scatter diagram of factors scores F1 and F2.

Factor 1. The lithogenic/pedogenic factor

Factor 1 represents 55% of the total variation and had high loadings on the elements Li, K, Be, Ca, Al, Fe, Ti, V, Cr, Ni. These elements are typically found within the soil matrix and relate to the soil parent material and the soil-forming process. The concentration of these elements in soil was to some extent inherited from the parent material. The alkali element K is an important constituent of the alkali feldspars (albite-orthoclase). Potassium becomes mobile in soil during weathering (Chapter 2). Lithium can be substituted into the aluminosilicates crystal lattice; it is highly mobile in soils becoming strongly bound to the clay fraction. The concentration of Li and K reflects the underlying geological material and redistribution into secondary soil phases during weathering. Titanium, V, and Cr are first row transition elements. Titanium occurs as resistant oxides or illminite in soils, its concentration is controlled by underlying geology. Vanadium replaces Ti, Al and Si in the primary crystal lattice. Its concentration in soil is primarily geologically controlled with minor input from the combustion of V rich coal and the disposal of the associated fly ash (Leep *et al.*, 1995; Kabata-Pendias and Pendias, 2001). Chromium naturally occurs as the resistant mineral chromite ($FeCr_2O_4$). It is not known if this mineral is present in Gibraltar, the geological setting makes it unlikely.

Factor 2. The anthropogenic factor

The second factor accounts for 10% of the total variation in the dataset. It has high loading scores on the anthropogenic elements Ba, Fe, Mn Co, Cu, Zn, Cd, Pb, S and As.

The metals Co, Cu, Zn, Cd and Pb can be largely introduced to soil by anthropogenic processes. The combination of Pb and Ba is often regarded as a traffic factor as these two elements are known additives to diesel fuel (Harrison *et al., 1981*; Farago, personal communication). Harrison *et al.* (1981) collected 30 (× 48 hour) samples alongside a busy road in the City of Birmingham, UK, during the winter of 2000/2001. Several of the trace metals studied (Cu Zn, Cd, Ba) were thought to derive mainly from brake, tire, and road wear. They suggest that changes in fuel technologies would have relatively little impact on concentrations of these trace metals. Average metal concentrations found in used gasoline engine oil in a 1994 study are Ba at 2.73 mg/kg, Be at <0.02 mg/kg, Cd at <1.51 mg/kg, Cr at 3.19 mg/kg, Pb at 47.23 mg/kg, Ni at <1.40 mg/kg, and Zn at 1161 mg/kg (Vermont Agency of Natural Resources, 1994). Levels of Ba however, have decreased dramatically in recent years because barium is no longer is a component in lubricant dispersants (Harrison *et al.*, 1981).

Industrial activities that release metals into urban soil include metal manufacturing, electroplating, manufacture of batteries, pigments, paints and dyes and pesticides, disposal of sewage sludge, landfill and fly ash and the generation of dust from scrap yards (Thornton, 1991). Some of these industrial activities are present in Gibraltar. A summary of industrial and urban activities releasing metals into the environment is given in sections 2.5.1 and 2.5.2 Tables 2.4 to 2.6. Not all the activities listed will however be applicable to Gibraltar as shown in table 2.4. The * in table 2.4 indicates the industrial sources which can be found in Gibraltar and neighbouring Spain. The uses listed in table 2.6 which are in blue font, are found in Gibraltar.

Iron and Mn are widely distributed in the soil profile. They occur in primary minerals, clay, are associated with organic matter and form amorphous oxides and hydroxides. The latter is an important phase in the scavenging and fixing of metals and other cations in soil (Hawkes and Webb, 1962). The occurrence of Fe and Mn with metals in the anthropogenic factor (F2) has been accredited to strong metal associations and Fe-Mn oxides in soil. In soils the chemistry of Co resembles that of Mn and Fe. Cobalt had a high loading F2. Thus the conclusion is the concentration of Co was influenced by anthropogenic input resulting in secondary associations with Fe-Mn oxides. Sulphur is also associated with the anthropogenic factor. Sulphur is strongly associated with organic matter in soil (Lindsay, 1979); its association with the anthropogenic elements may be a reflection of the strong organo-metal complexes that fix metals in urban soil.

Anthropogenic sources of As into soil come from industrial processes such as metal processing and chemical works. Arsenic can have a high concentration in coal released during combustion (as occurs in the coal processing plant in the industrial complex in neighbouring Spain) or enriched in fly ash which is disposed of in landfill sites (as was done when in the East side reclamation project. The reclamation site was used as a landfill for the fly ash and bottom ash of the incineration process). Associations with Fe oxides, clay and organic matter control As associations in soils. Arsenic commonly appears as the arsenate ion in the form $H_2AsO_4^-$ species with a high affinity for Fe oxides under normal pH ranges (Thornton and Farago, 1997).

Factor 3. The geologically related factor

Factor 3 showed a high loading on the elements Ca, Sr and Mg. The parent material of an area controls the occurrence of Sr and Mg in soils and their cation size is similar to Ca^{2+} therefore substituting for Ca in minerals (Kabata-Pendias and Pendias, 2001). Factor 3 can be interpreted as the geologically related factor. The association of these three elements reflects the underlying geology of Gibraltar. The Gibraltar limestone is formed from the mineral calcite ($CaCO_3$), with dolomite or dolostone composed in significant proportions of the mineral dolomite ($CaMg(CO_3)_2$) (Rose and Hardman, 1995). Magnesium is widely distributed in nature in a variety of compounds: as carbonate in magnesite, $MgCO_3$, and dolomite. Strontium can be used as an analogue for calcium. These ions have similar chemical structure and behave similarly in the soil and in the plant. Strontium concentrations in soil may also be increased by human activities such as the disposal of coal ash and incinerator ash as well as industrial wastes.

Factor 4. Unidentified factor

The elements in this factor (Na, Ba, Fe, Co, P) could arise from a combination of lithogenic and anthropogenic factors. Iron is widely distributed in the soil profile. As already stated it occurs in primary minerals, clay and is associated with organic matter and forms amorphous oxides and hydroxides. It is an important phase in the scavenging and fixing of metals and other cations in soil (Hawkes and Webb, 1962). The anthropogenic addition of bioavailable P into soil as a fertiliser is important in public gardens and open spaces. Phosphorous occurs in the orthophosphate form in soils ($H_2PO_4^{2-}$), (Lindsay, 1979). Sodium is an important constituent of the alkali feldspars (albite-orthoclase). Sodium becomes mobile in soil during weathering. The concentration of Na reflects the underlying geological material and redistribution into

secondary soil phases during weathering (Lindsay, 1979). In Gibraltar, the content of Na in soils and dusts in probably a reflection of sea spray. In soils Co resembles the chemistry of Mn and Fe. Cobalt is also associated with the anthropogenic factor F2. As stated above, the concentrations of Co could be influenced by anthropogenic input resulting in secondary associations with Fe-Mn oxides. The inclusion of Ba in this could result from an anthropogenic input (associated with F2) as well as the parent materials in the soil.

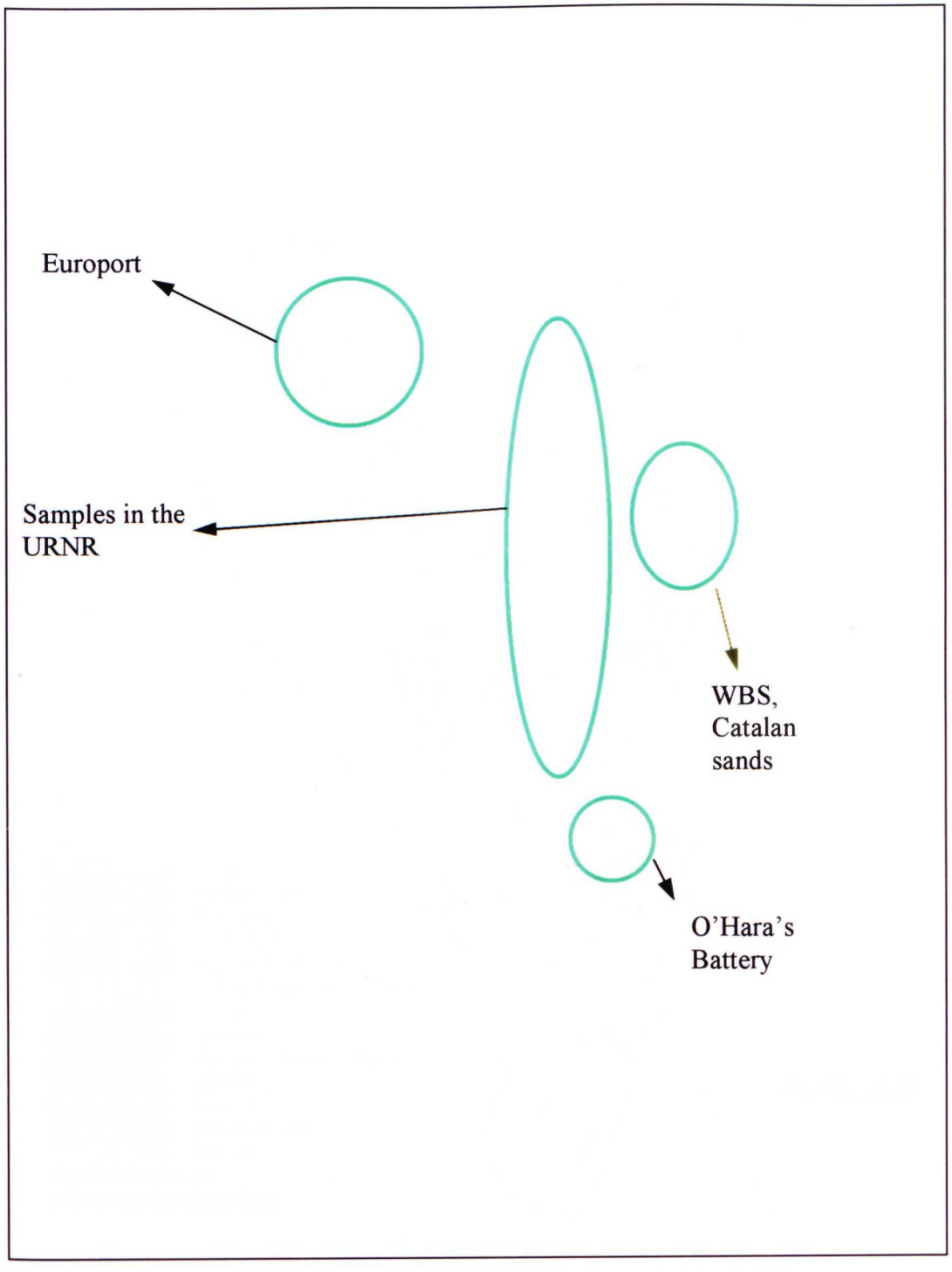
Three main factors were extracted to explain the majority of the variance in the Gibraltar geochemical soil dataset (described above). The factors were saved as new variables into the original dataset. Each soil sample has a coefficiant score for each corresponding factor and this has been plotted as a layer on a GIS. Samples with high loadings in the lithogenic/pedogenic factor (F1) and the geologically related factor (F3) corresponded sites in the Upper Rock Nature Reserve (URNR), open spaces and sites of exposed soil outcrops (figure 6.25, 6.26). These sites are discussed in section 7.3. Samples with a high loading in F2, the anthropogenic factor are displayed in figure 6.27.

Additional factor analysis of anthropogenic elements in soils

In order to find the underlying relationships between the anthropogenic elements the samples with a high score on F1 (exceeding >0.6) were selected for a further factor analysis. These variables are Fe, Mn, Co, Cu, Zn, Cd, Pb, S, Ba and As. Three factors were extracted and summarised below:

F1: Cu, Zn, S, Cd, As (*industrial factor-1)* *(70% of total variance)*
F2: Co, Fe, Mn (*industrial factor-2)* *(9% of total variance)*
F3: Pb, Ba (*traffic factor)* *(7% of total variance)*

Factors 1 and 2 illustrate a mixed industrial factor. The possible sources include electroplating, chemical industry, paints, pigments, dyes and contamination resulting from landfill material, sewage sludge and fly ash. Factor 3 was interpreted as the traffic factor. Barium is a component of motor oil and has been reported as a better indicator of vehicle pollution than Pb (Vazquez-Duhalt, 1989; Monaci and Bargagli, 1997; DeMiguel *et al.*, 1997). Lead has been removed from petrol in many countries, however leaded petrol is still used in Gibraltar. Lead additives in petrol are declining but still in use. Soil acts as a sink for Pb due to the formation of stable compounds (Davies, 1994).


Europort
Samples in the URNR
WBS, Catalan sands
O'Hara's Battery

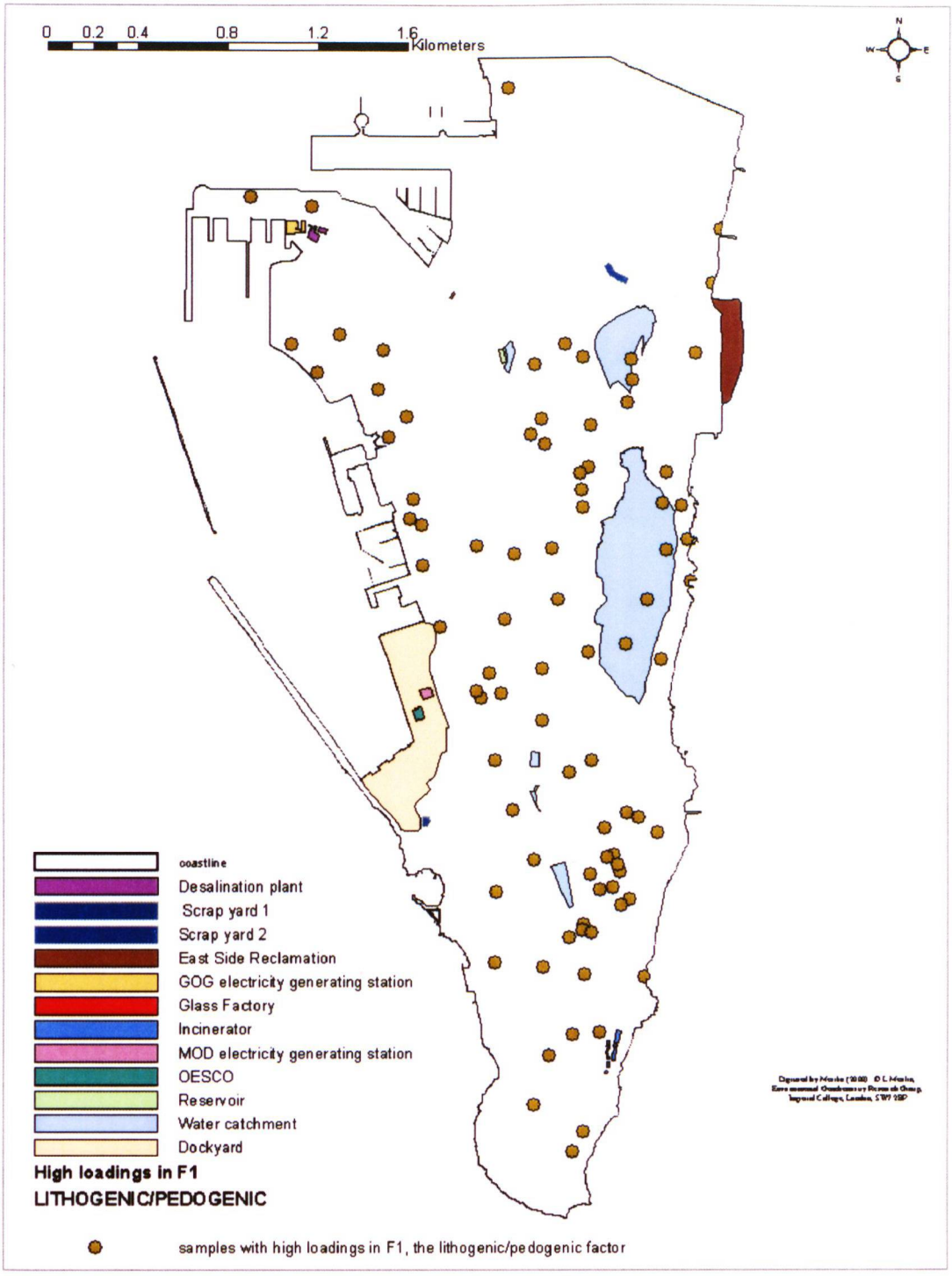


Figure 6.25 Soil surface (0-15 cms) samples with high loadings on F1, the lithogenic/pedogenic factor.

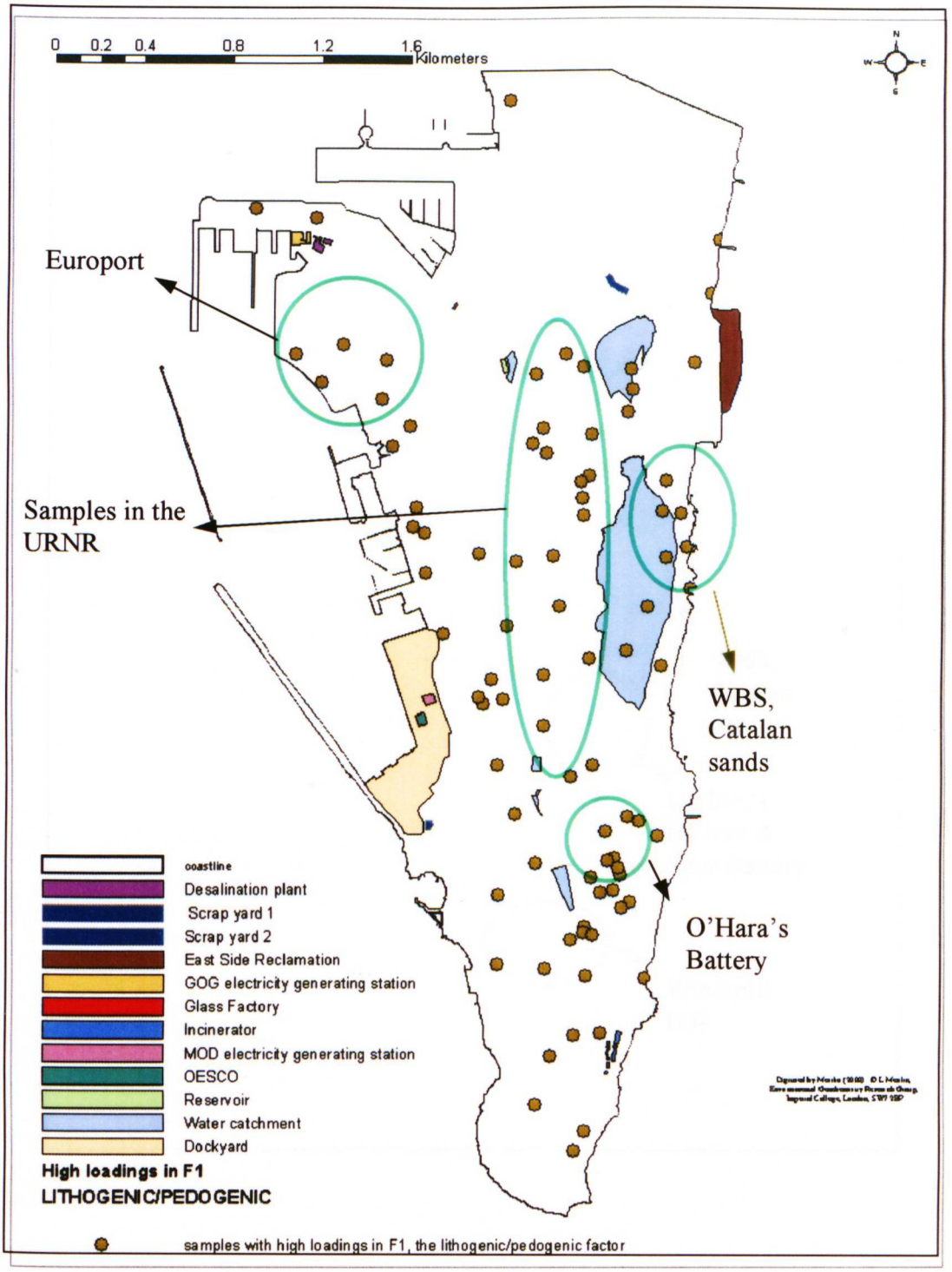
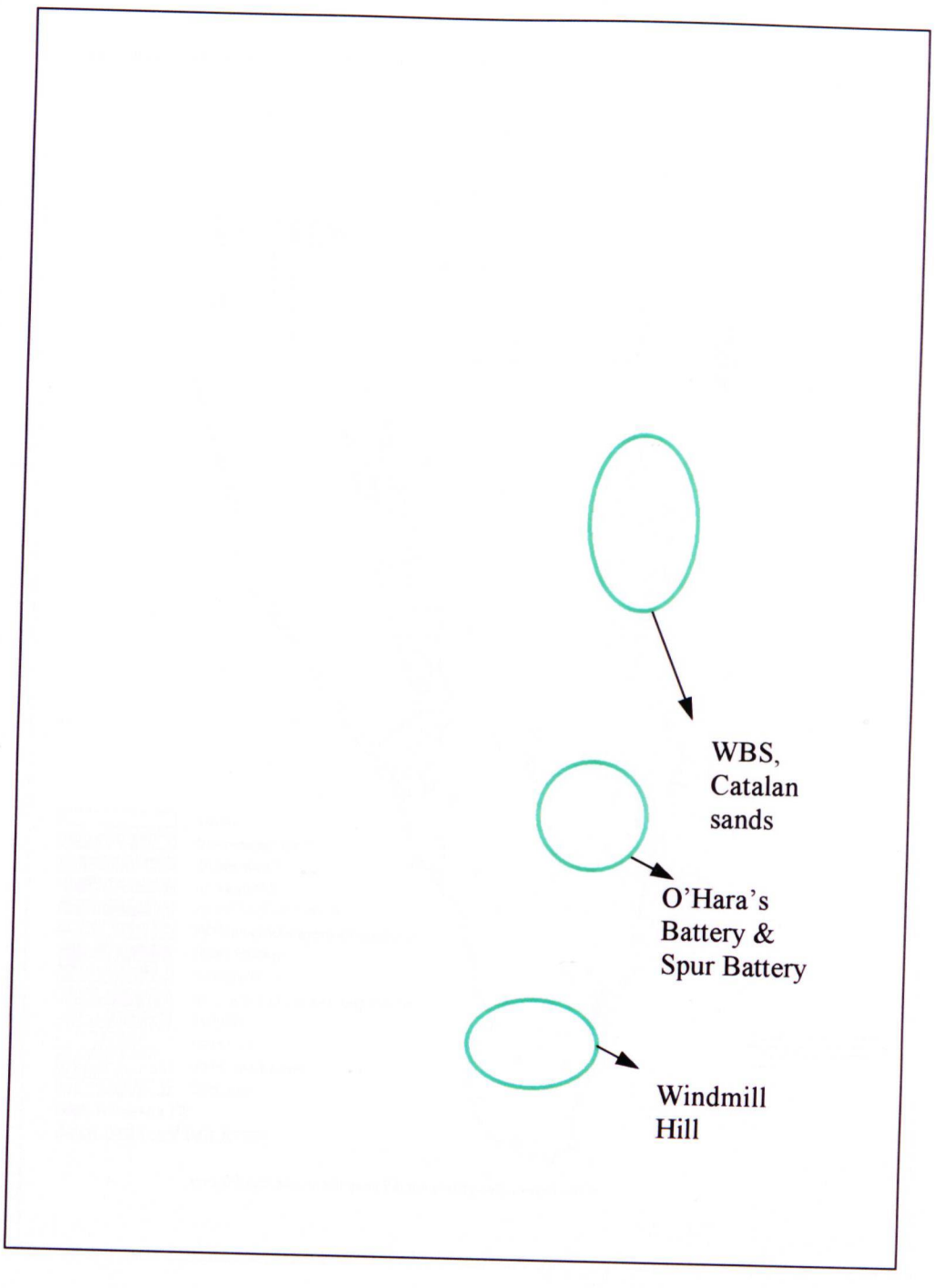


Figure 6.25 Soil surface (0-15 cms) samples with high loadings on F1, the lithogenic/pedogenic factor.


WBS,
Catalan
sands
O'Hara's
Battery &
Spur Battery
Windmill
Hill

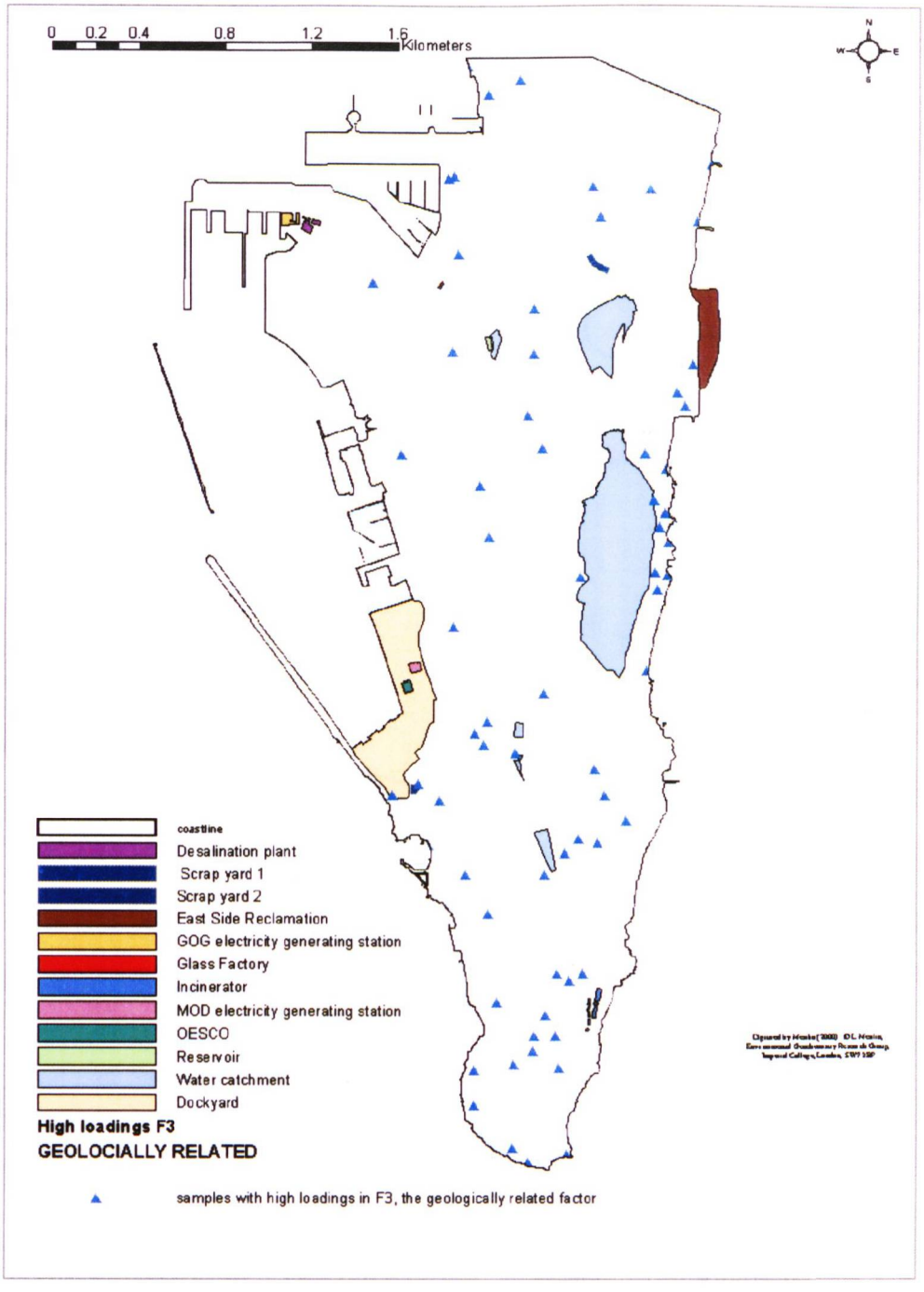


Figure 6.26 Soil surface (0-15 cms) samples with high loadings on F3, the geologically related factor.

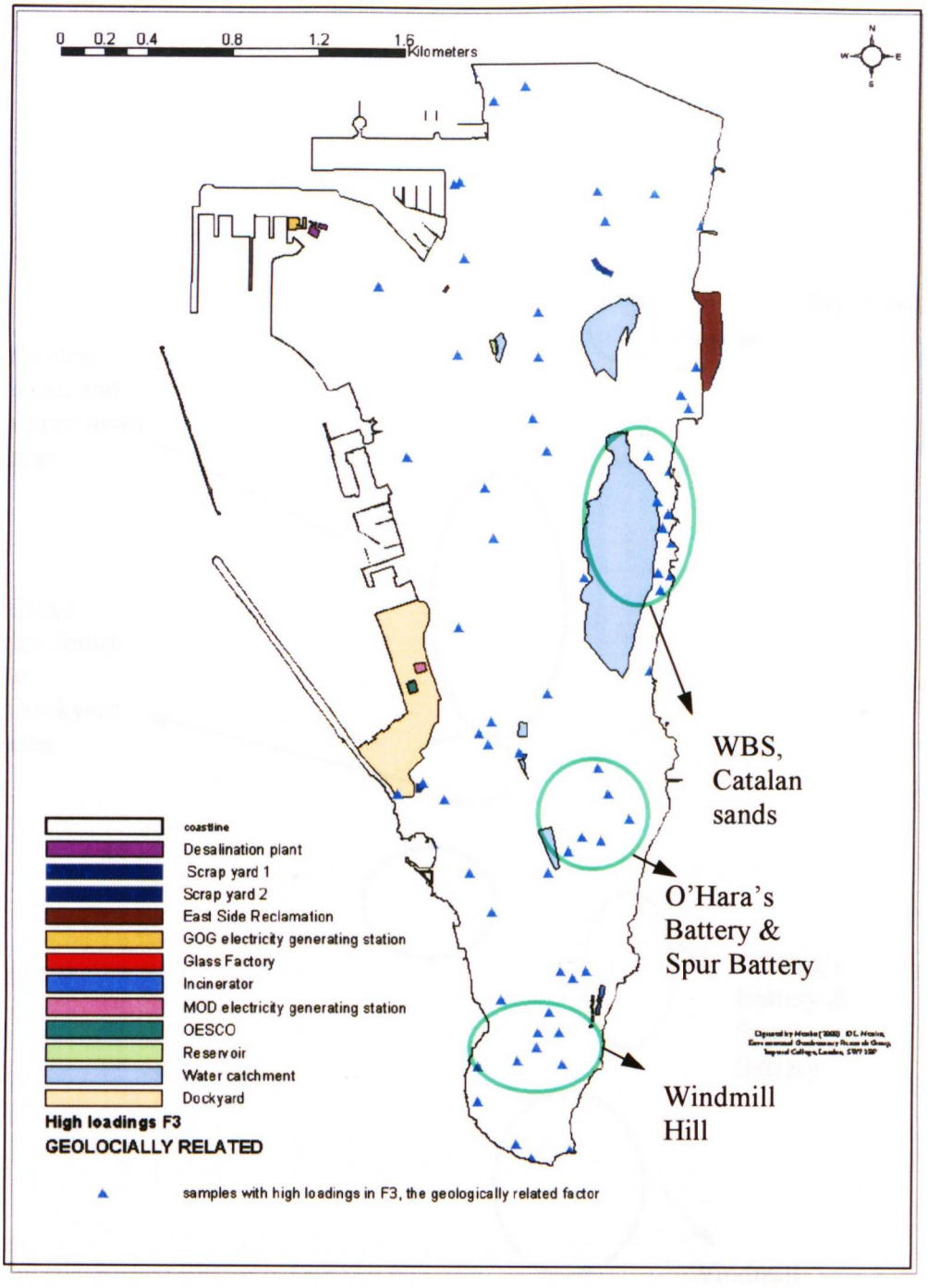
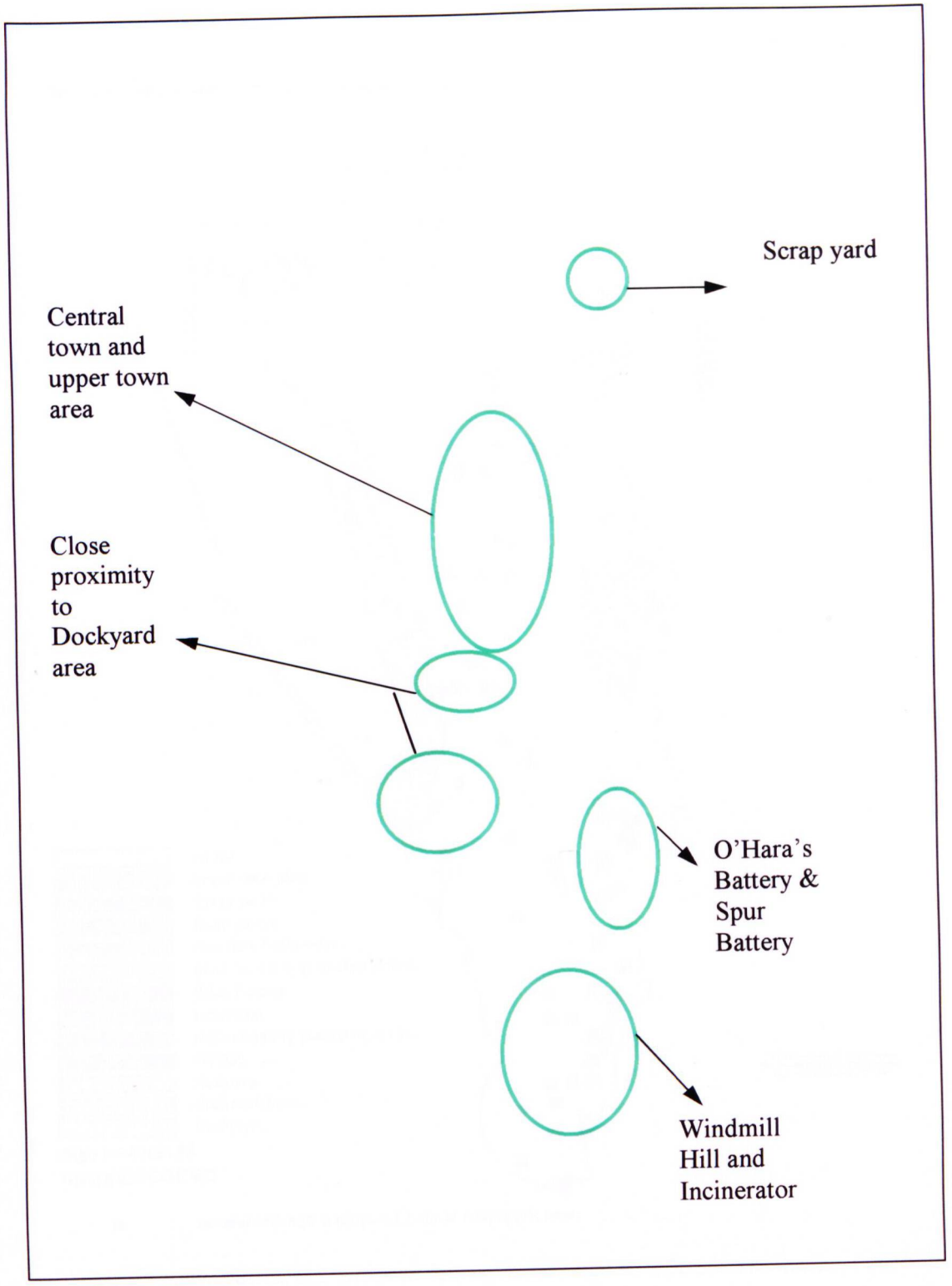


Figure 6.26 Soil surface (0-15 cms) samples with high loadings on F3, the geologically related factor.


Scrap yard
Central town and upper town area
Close proximity to Dockyard area
O'Hara's Battery & Spur Battery
Windmill Hill and Incinerator

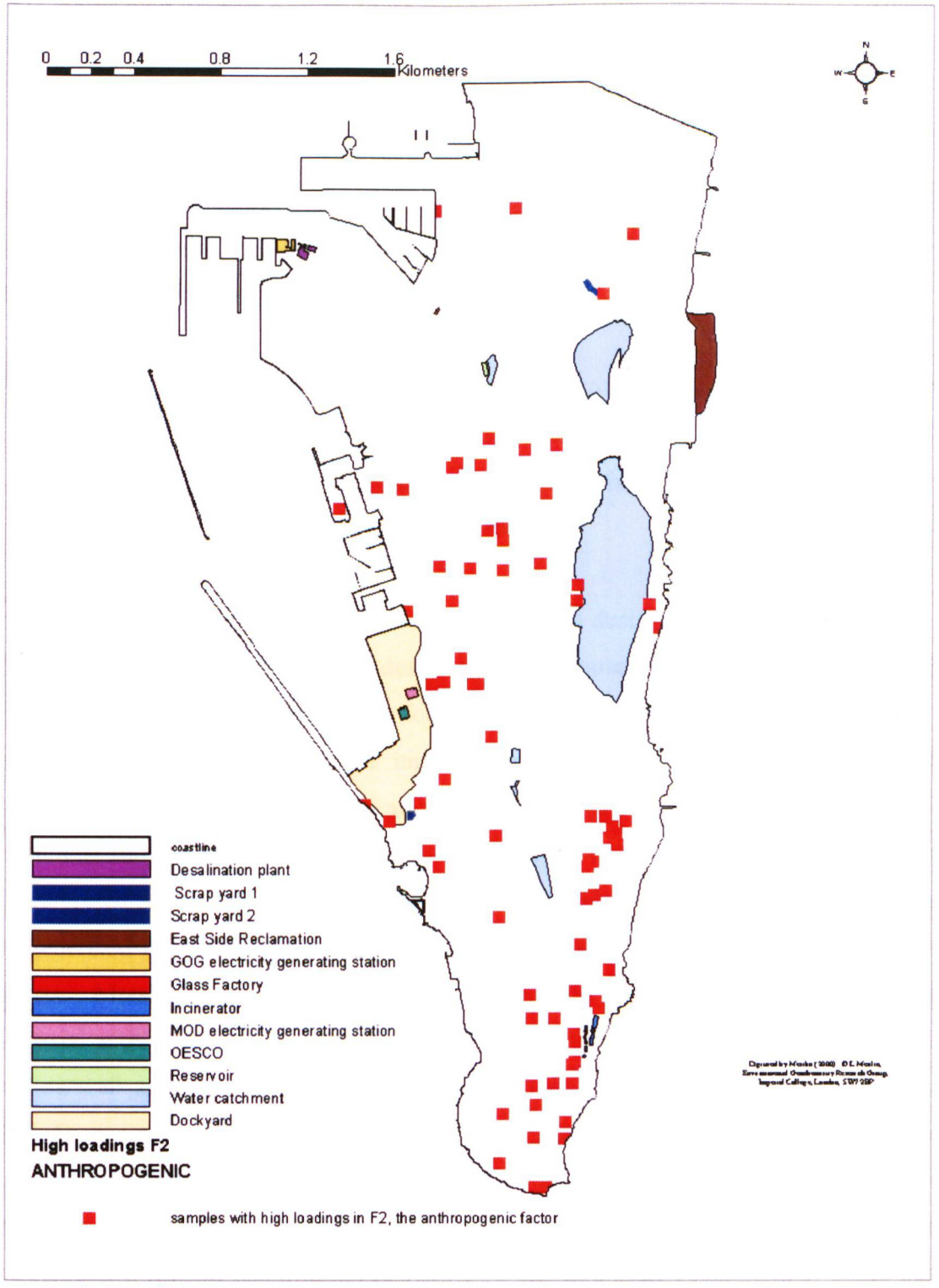


Figure 6.27 Soil surface (0-15 cms) samples with high loadings on F2, the anthropogenic factor.

The anthropogenic trace metals Cr, Ni, Cu, Zn, Cd and Pb and the elements Ba, Mn, Fe, S and P have been plotted on a GIS. Sites with a high factor score (>0.5) have been plotted as a layer in the GIS. The sites with the highest loadings for these factors (figure

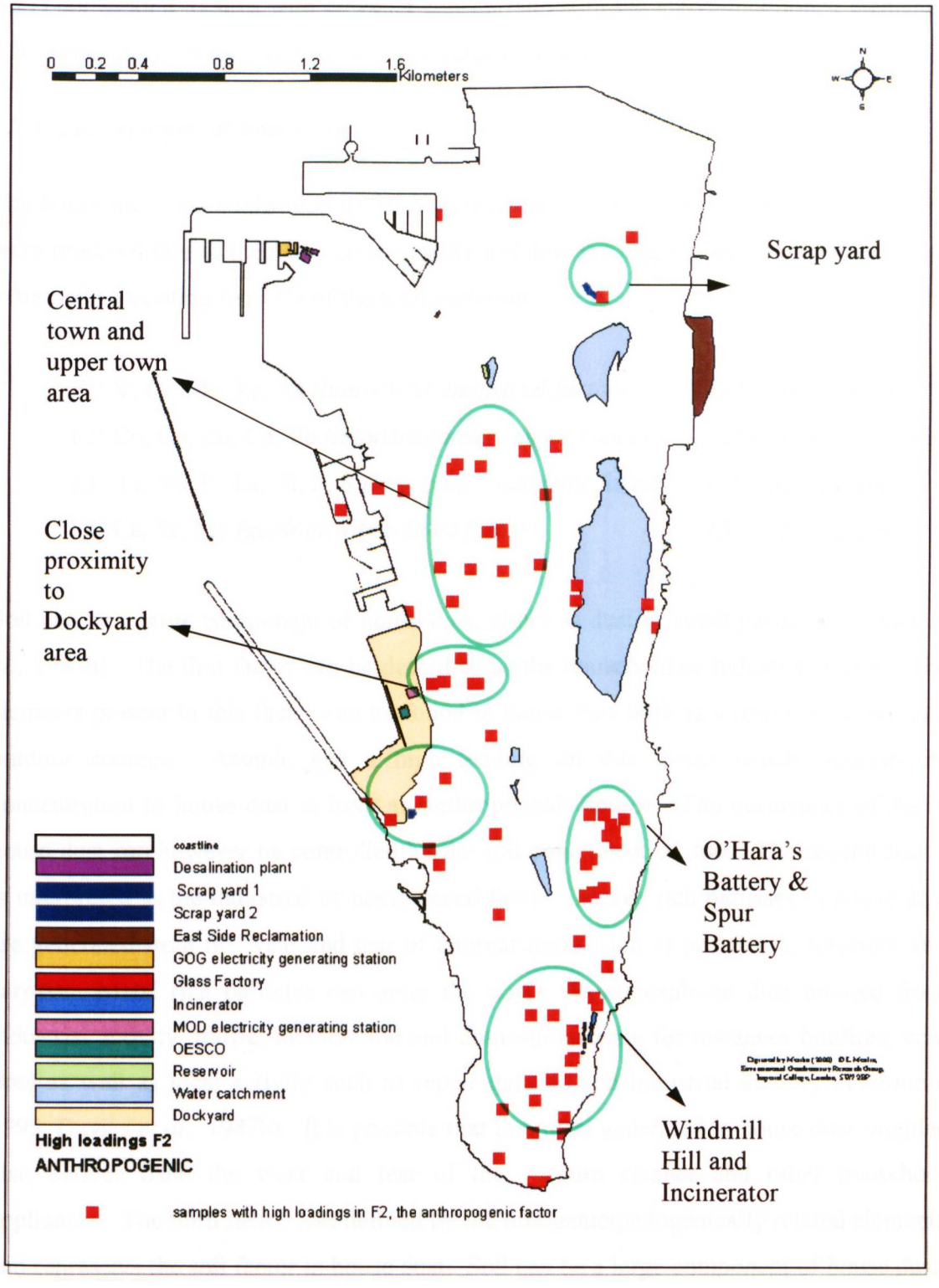


Figure 6.27 Soil surface (0-15 cms) samples with high loadings on F2, the anthropogenic factor.

The anthropogenic trace metals Cr, Ni, Cu, Zn, Cd and Pb and the elements Ba, Mn, Fe, S and P have been plotted on a GIS. Sites with a high factor score (>0.5) have been plotted as a layer in the GIS. The sites with the highest loadings for these factors (figure

6.27) correspond to sites with elevated concentrations in the above-mentioned elements. These sites have been classed as outlying values for this dataset (section 7.3).

6.7 Factor analysis of house dust

The house dust data conformed to the requirements necessary for FA. Silver, Al and Be were removed due to their low communality and low loading scores. Four factors were extracted accounting for 77% of the total variation.

F1: V, Cr, Mn, Fe, As *(household/ industrial factor)* *(54% total variance)*
F2: Co, Cu, Zn, Cd, Pb *(industrial/heavy metal factor)* *(21% total variance)*
F3: Li, Na, K, La, Ti, P, S *(lithogenic/pedogenic factor)* *(8% total variance)*
F4: Ca, Sr, Mg *(geologically related factor)* *(5% total variance)*

Soil can be a large component of house dust, either as dust or small particles (Davies *et al.*, 1987b). The first factor can be described as the household or industrial factor. The elements present in this factor can be found in house dust both as a result of indoor and outdoor sources. Arsenic had a high loading on this factor which suggests its concentration in house dust is from an anthropogenic source. The occurrence of As in house dust can however be controlled by the soil component of dust. The second factor is interpreted as the industrial or heavy metal factor. Metals rich particles in house dust are generated from the wear and tear of internal items such as paintwork, furniture and carpets. Metal rich particles can enter the home via atmospheric dust emitted from industrial activity, traffic, incineration and domestic activity for instances bonfires, coal fires as well as local activity such as repair garages and industrial activity (Thornton, 1995; Davies *et al.*, 1987b). It is possible that the metal generated in house dust samples also derives from the wear and tear of the vacuum cleaner and other household appliances. The third factor was defined by the lithogenic/pedogenically related elements and represents the soil factor in house dust. Soil can be a large component of house dust, either as dust or small particles (Davies *et al.*, 1987b). The fourth factor is identified as the geologically related factor and possibly illustrates the influence of the geology of Gibraltar on the composition of house dusts.

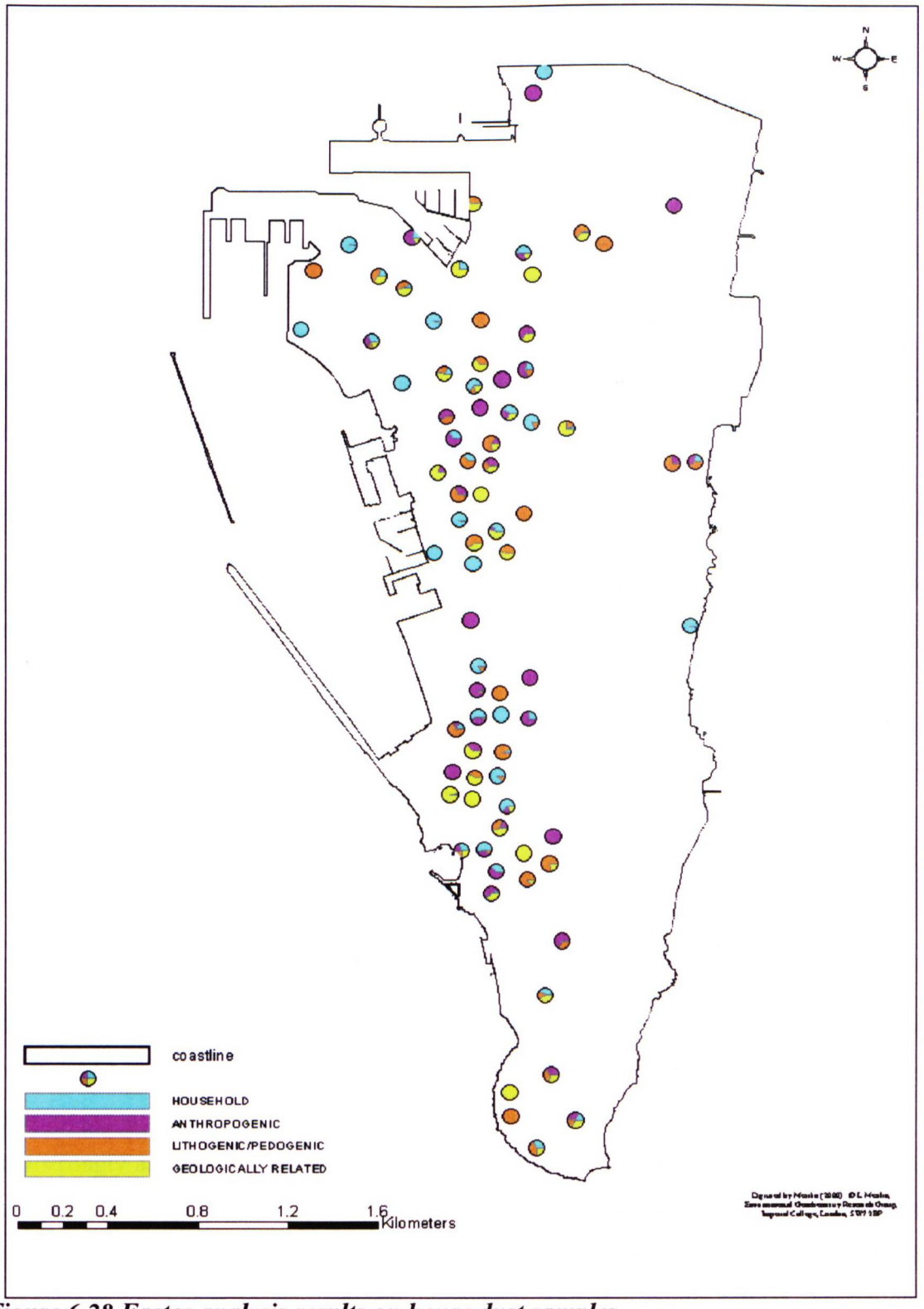


Figure 6.28 Factor analysis results on house dust samples.
Every pie chart illustrates the respective contribution of each of the main factors identified (F1, F2, F3 and F4) towards the total composition of that house dust sample.

Figure 6.28 shows the results of the FA on the house dust data. Each pie corresponds to an individual sample. Every pie illustrates the respective contribution of each of the main factors identified (F1, F2, F3 and F4) towards the total composition of that house dust

sample. The samples identified with high scores for the anthropogenic and household/metal factors correspond to the samples described as outlying sites discussed in section 7.4. Figure 6.28 does not show any immediately discernible spatial pattern as regards the geographic distribution of the four factors found for house dusts across Gibraltar. Sites with high loadings in the household and anthropogenic factors (F1 and F2) are identified and discussed in section 7.4 but they are not always necessarily found in close proximity to industrial areas. Spatially related patterns are found in section 7.4 as regards elevated concentrations of a variety of elements in house dusts across different areas of Gibraltar. These patterns however are not portrayed with the factor maps produced.

6.8 Factor analysis of street dusts

The FA on the street dusts data revealed four factors which accounted for 87% of the total variance in the dataset.

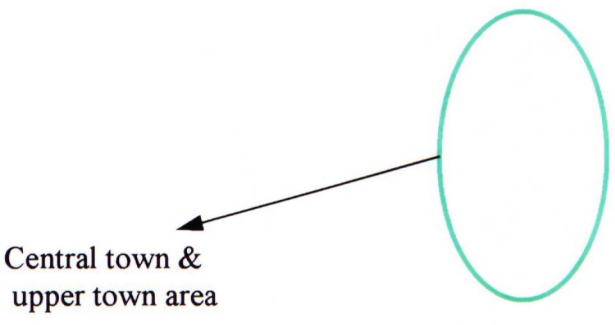
F1: Na, Ca, Sr, Mg, Mn, Ni, Cu, Ag, and S *(soil related/anthropogenic factor)* *(59% total variance)*

F2: Li, K, Be, Al, La, V, P, As (*lithogenic/pedogenic factor)* *(12% total variance)*

F3: Pb, Ba *(traffic factor)* *(6% total variance)*

F4: Co, Cu, Cd, Ti *(industrial factor)* *(5% total variance)*

The first factor has a combination of elements related to the underling geology such as Ca, Sr and Mg (Factor 3, the geologically related factor,) as well as elements relating to anthropogenic inputs. In the results of the sequential extractions on street dusts, Ca is very strongly associated with the carbonate phase (step 2). This indicates (as with soils) the strong influence of the carbonate phase on heavy metal chemical forms in street dusts as calcite ($CaCO_3$), (Li *et al.*, 2001) which is a primary mineral in the geology and soils in Gibraltar. Calcium is also present in cement and this could reflect the building /demolition processes operating within the urban environment. The latter factor includes the elements Mn, Cu, Ag and S.


Central town &
upper town area

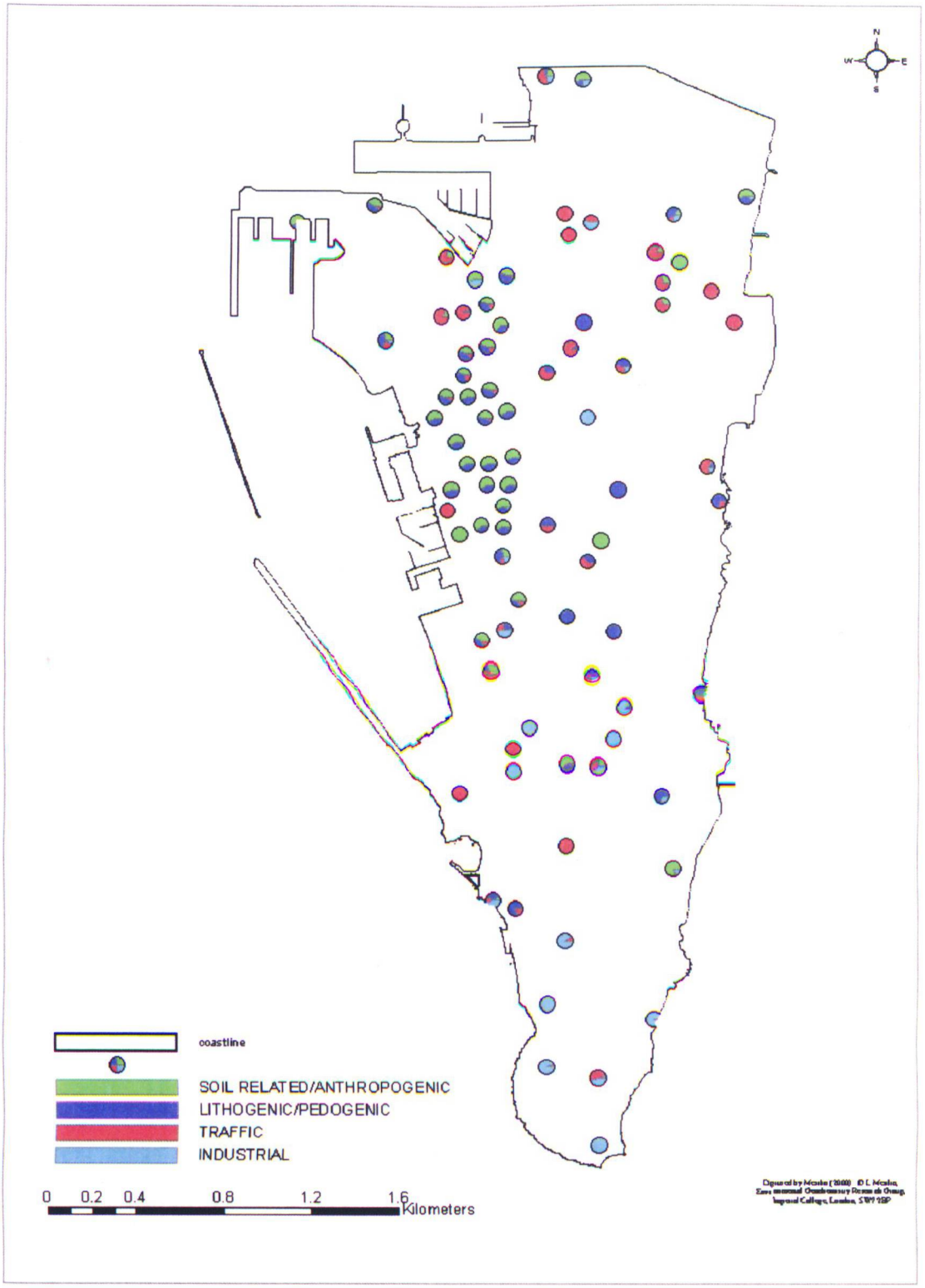
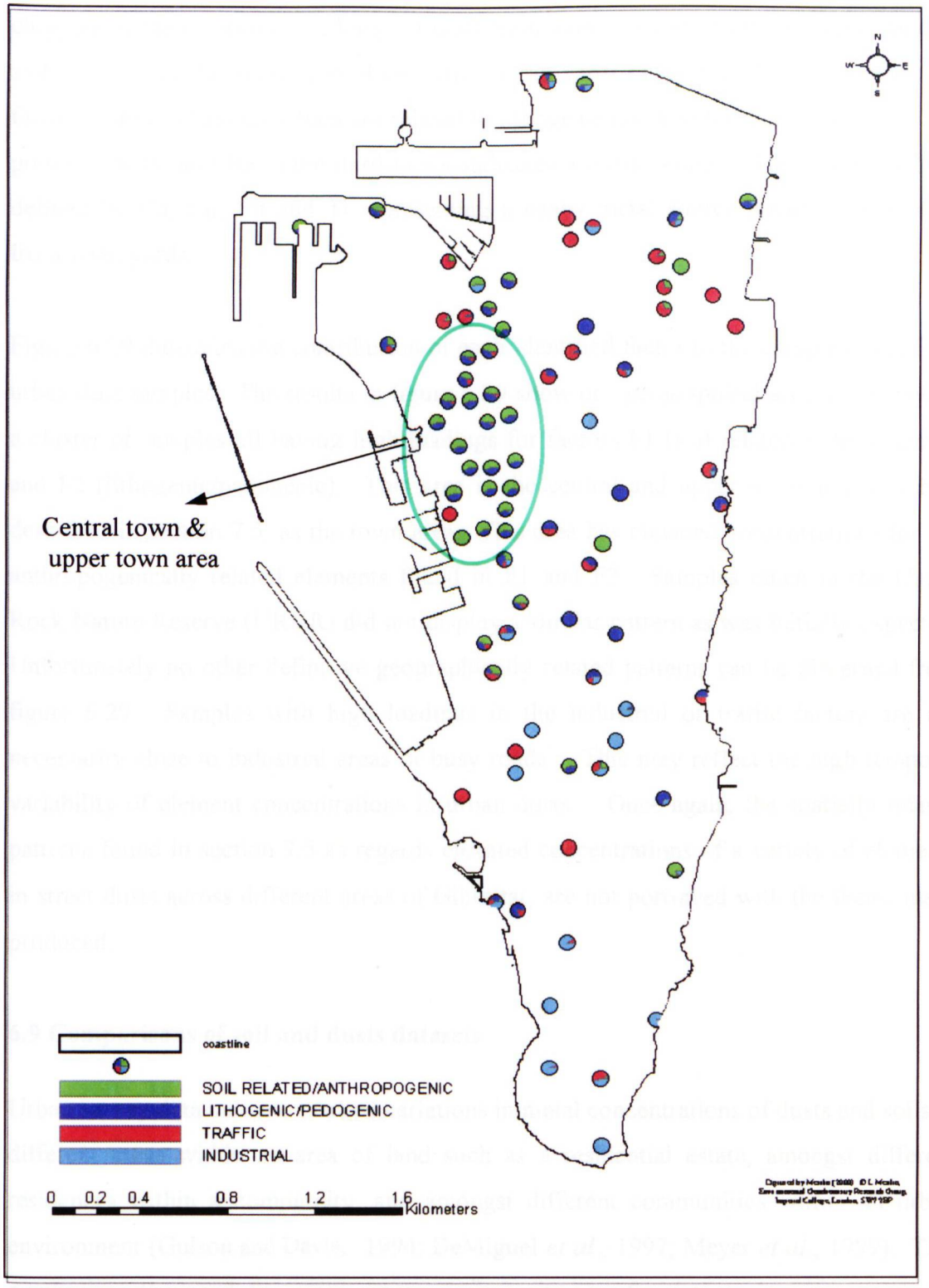


Figure 6.29 Factor analysis results on street dust samples.
Every pie chart illustrates the respective contribution of each of the main factors identified (F1, F2, F3 and F4), towards the total composition of that street dust sample.

A number of distinct metal associations have been extracted from the anthropogenic elements that represent different metal sources within dusts. Industrial activities that release metals into urban dusts include metal manufacturing, electroplating, paint



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chipping of the exterior of buildings, runoff from guttering and roofing material, landfill and fly ash and the generation of dust from scrap yards (Thornton, 1991). The second factor contains elements which are related to lithogenic and soil forming processes. The presence of Pb and Ba in the third factor indicates a traffic source. The fourth factor is defined by Co, Cu, Cd and Ti representing a heavy metal source possibly originating from scrap yards.

Figure 6.29 illustrates the contribution of each identified factor to the composition of the urban dust samples. The results in figure 6.29 show one geographical area as displaying a cluster of samples all having high loadings for factors F1 (soil related/anthropogenic) and F2 (lithogenic/pedogenic). This area is the central and upper town area which is described in section 7.5, as the town area. This area has elevated concentrations for the anthropogenically related elements found in F1 and F2. Samples taken in the Upper Rock Nature Reserve (URNR) did not display a similar pattern as was initially expected. Unfortunately no other definitive geographically related patterns can be discerned from figure 6.29. Samples with high loadings in the industrial or traffic factors are not necessarily close to industrial areas or busy roads. This may reflect the high temporal variability of element concentrations in urban dusts. Once again, the spatially related patterns found in section 7.5 as regards elevated concentrations of a variety of elements in street dusts across different areas of Gibraltar, are not portrayed with the factor maps produced.

6.9 Comparisons of soil and dusts datasets

Urban survey data indicate marked variations in metal concentrations of dusts and soils in different areas within an area of land such as a residential estate, amongst different residences within a community, and amongst different communities within an urban environment (Gulson and Davis, 1994; DeMiguel *et al.*, 1997; Meyer *et al.*, 1999). This emphasises the need for more representative, site-specific data to improve upon the current understanding of indoor and outdoor exposure assessments. A key question for example is the extent to which the metal content of house dust originates from the transport of outdoor dusts and soil into the interior of a home. The results presented in this study do not permit any firm or definitive conclusions to be made on the exact nature of indoor sources of contamination. They do indicate however that dusts generated within the house itself can be an important source of exposure for certain elements. It is

important to note that indoor/outdoor concentration ratios vary widely from one element to another and from one residence to another within an area (Rasmussen *et al*, 2001). These variations when compared to exterior soil and dusts in Gibraltar (or any other urban environment), combined with the distinct multi-element signature of house dust can make it difficult to accurately predict the contribution that each of these factors have towards exposure assessment studies.

Table 6.25 Descriptive statistics for soil, house dust (HD) and street dust (SD) datasets from Gibraltar. (mg/kg)

	Soil GM (n = 238)	HD GM (n = 80)	SD GM (n = 83)	Soil median	HD median	SD median	Soil 95th percentile	HD 95th percentile	SD 95th percentile
Li	13	7.5	10	14	7.7	13	49	16	20
Na	348	6381	680	353	7200	482	1330	18420	2610
K	3909	3138	2777	4360	3230	2731	13800	5545	5707
Be	0.67	0.3	0.4	0.72	0.3	0.4	2	0.6	0.8
Mg	6760	6509	12847	7360	6730	15400	24700	13470	25710
Ca	29930	50213	76845	44403	48800	79700	125000	172800	131800
Sr	63	99	98	74	98	90	173	265	205
Ba	122	57	107	145	57	110	503	139	196
Al	16188	8332	11266	18418	8510	14500	50300	19620	21480
La	11	11	8.1	14	9.5	9.1	26	58	18
Ti	409	495	473	465	523	496	864	1107	1296
V	34	29	41	36	32	45	109	99	128
Cr	87	81	132	113	70	153	259	421	350
Mn	274	142	338	317	153	327	668	365	608
Fe	15321	9545	22954	17100	9050	28200	48300	29080	44306
Co	6	6.6	6.8	7	5.9	7.8	16	31	13
Ni	37	79	57	39	76	52	81	312	130
Cu	30	232	168	38	214	211	411	1395	781
Ag	0.23	2.8	0.4	0.3	2.9	0.3	1	27	3.1
Zn	153	1025	528	168	957	484	1500	6134	1608
Cd	0.2	3.1	0.48	1	2.8	0.7	4	14	2.5
Pb	86	300	433	131	246	392	1680	2323	2190
P	678	1224	715	926	1190	680	3300	3667	1850
S	463	10469	1830	657	11000	1380	2290	32840	7254
As	9	6	7.4	9	5.6	8.4	49	22	16

GM = geometric mean, HD = house dust, SD = street dust (Please note Cd and Co had samples below the IDL. Concentrations below 2 mg/kg to be assessed with caution)

Table 6.25 shows some descriptive statistics for the three datasets in Gibraltar. It was not possible to run AVOVA analysis, correlation analysis or regression analysis or make

direct comparisons between the house dust data and garden soil data because very few homes (<5) had gardens (83 house dust samples, 5 garden soil samples).

The high GM and 95th percentile values of Cu, Cd, Pb and Zn in house dust compared with soils and street dust possibly reflects factors associated with metal deposition such as the location of the residence within Gibraltar, the level of traffic near the home, and the use of lead-based paint, solders and plumbing materials within the home. Also factors to be considered are the type of heating, the housing characteristics, for example whether the home is damp, the number of persons occupying the premises, the proximity to an industrial site, whether the residence is a flat and on which floor above street level the premises are located.

The elements Na, Sr, Ti, Ni, Cu, Ag, Zn, Cd, P and S all have higher median and mean values in house dust than in the soil or street dust samples collected. The identification of the sites with elevated concentrations for these elements can be found in section 7.4. The high concentrations of Sr, Ti, Ni, Cu, Ag, Zn and Cd within the home environment possibly results from ceramics, Ni-Cd batteries, wire and cable, plumbing pipes, roofing and brass and bronze alloys. In addition, electronics, disinfectants, jewellery, electrical goods, household appliances, brass or bronze items, tableware and coinage can contribute to higher concentrations of the these elements within the home, and most, if not all, of these are often present. Section 2.5.2 describes the different anthropogenic sources of element concentrations found with an urban environment.

The high values of heavy metal concentrations including Cu, Pb, and Zn in house dust as opposed to the associated soil and street dust could be attributed to internal enrichment factors (Thornton, 1995). Cadmium, Cu, Pb and Zn are good indicators of contamination in soils because they appear in gasoline, car components, oil lubricants, industrial and incinerator emissions (Adriano, 2001; Alloway, 1995), which can enter the home environment through atmospheric deposition. The Mediterranean climate experienced in Gibraltar means that most homes have their windows open for several hours on a daily basis. This, when combined with the close proximity of certain homes to industrial activities, helps to identify possible sources for the high concentrations found within such areas (section 7.4). The soil dataset displayed higher median and mean values for the concentrations of the following elements: Li, K, Be, Ba, Al, La and As. This is likely to

be due to the longer residence time of these elements in the soil matrix, to factors relating to the underlying geology or to the anthropogenic addition of these elements to soil.

Table 6.25 shows that street dusts displayed higher median and mean concentrations for eight out of the twenty-six elements analysed. These elements include Mg, Ca, V, Cr, Mn, Fe, Co and Pb. High element values in street dusts as compared to roadside soils reflect the short-term contamination of dusts from vehicle exhaust emissions and component wearing. The high Mg and Ca concentrations could reflect the geology as well as anthropogenic factors such as cement. Refractory bricks, leaded petrol, roofing, guttering, pipe work and plating of car parts are probable sources of Cr, Mn, Fe, Co and Pb. On occasions for elements such as Cr, Mn, Fe and Co the 95th percentile value was higher in soils or house dusts even if the median and mean concentrations were higher in street dusts. Possible explanations of this are: the longer residence time of these elements in soils: losses of soluble species from street dust by run-off during municipal street cleaning, greater attenuation in garden soils due to the higher organic matter content of the soil matrix, wash-off of settled dust, paint chips, other particulate matter from houses, and leaching of soluble species from exterior walls and roof materials.

6.10 Chapter conclusions

Exploratory statistical tools have been used to present the results of soils, street dust and house dust geochemical datasets. These included descriptive statistical and graphical summaries consisting of histograms and box plots. The latter were used to assess the distribution of the data. A Kolmogorov-Smirnov test was used to determine if the data displayed to a normal distribution. Most elements displayed a lognormal distribution, and so are therefore suitable to undergo multivariate statistical analysis. The complex nature of the element concentrations in soils and dusts does not automatically fit the requirements of the numerical analysis models. Because of this, additional numerical analysis techniques were employed to transform the information into a numerically meaningful set of variables. However, even after further statistical treatment and the use of multivariate statistics the information gained is descriptive and the most useful information regarding the geographic distribution and the sources or reasoning behind high or low values is still hidden. The application of GIS will aid in further interpretation.

The elements Li, V, La, Ti and Co were highly partitioned in step 5, the residual fraction. Elements associated that are mostly partitioned in this fraction occur in stable phases, they are bound to the primary rock forming minerals, ore minerals and organic matter and are not normally bioaccessible. The soil data were classified according to the following land use categories; residential, commercial, industrial areas and open spaces. The concentrations of Cr, Ni, Cu, Zn Cd, Ca, K, Na, Fe and As in soils, were found to be slightly elevated in the industrial areas and open spaces but this difference was not found to be statistically significant. Certain sites in close proximity to industrial areas as well as open spaces with a former history of industrial use did display elevated concentrations as related to the rest of the dataset. The ANOVA analysis showed that there are significant differences between some of the element concentrations in the varying land use categories (table 6.18). Additionally significant differences were found between the element concentrations in the different geological parent materials.

Baseline values were calculated for soils for the years 2001 and 2003. The soil data were then compared to the 2003 baseline range. Calcium, Ba, Al, La, Ti and Mn are the only elements with maximum concentrations below the upper baseline value. The maximum concentrations for the remaining elements exceed this calculated value. Multivariate factor analysis was used to extract factors explaining the majority of the variance in the dataset. Three main factors were extracted; anthropogenic, lithogenic/pedogenic and geologically related. Factor 1, the lithogenic/pedogenic factor, represents 55% of the total variation and had high loadings on the elements Li, K, Be, La, Ti, V, Cr and Ni. The second factor, the anthropogenic factor accounts for 10% of the total variation in the dataset. It has high loading scores on the anthropogenic elements Co, Cu, Zn, Cd, Pb, S and As. The third factor, the geologically related factor accounts for 8% of the total variation. It is characterised by the elements Ca, Sr and Mg.

Analysis of the house dust dataset revealed that elements including Na,K, Mg, Ca, Al, Fe, Cu, Zn, Pb, P and S have a very large standard deviation suggesting a large scatter about the arithmetic mean. Once the data underwent logarithmic transformation, a lognormal distribution was achieved. Factor analysis was used to extract four factors accounting for 77% of the total variation. The first factor can be described as the household or industrial factor. It accounted for 54% of the total variance and had high loadings for the elements V, Cr, Mn, Fe and As. The second factor is interpreted as the industrial or heavy metal

factor. It accounted fir 21% of the total variance and displayed high loadings for the elements Co, Cu, Zn, Cd and Pb. The third factor was defined by the lithogenic/pedogenically related elements and represents the soil factor in house dust. It accounted for 8% of the total variance. The fourth factor is identified as the geologically related factor and illustrates the influence of the geology of Gibraltar on the composition of house dusts. The elements associated with this factor were Ca, Sr and Mg and accounted for 5% of the total variance found.

The street dust dataset illustrated some elements such as arsenic as having a normal distribution, other elements including Cu, Zn and Cd (and to a lesser extent Pb) display a normal distribution only when the data underwent logarithmic transformation. The spread of the distribution of elements such as Na, K, P, S, V, Sr, V, Sr, Ni, Zn and Pb clearly indicates a bi modal distribution, meaning that the variance of some of these elements come from two or more populations which would indicate two or more distinct sources, again either geological, anthropogenic or both. The patterns found in street dusts are very similar to those found in soils for the major elements (section 6.5.1). The elements La, Ti, Be, co, V, Ba, Fe, Cr, Ni, Cu, Cd and As are partitioned largely (>50%) into step 5, the residual fraction, and so are presumed to have a low mobility in street dusts.

The FA on the street dust data revealed four factors which accounted for 87% of the total variance in the dataset. The first factor has a combination of elements related to the underling geology such as Ca, Sr and Mg as well as elements relating to anthropogenic inputs. The second factor contains elements which are related to lithogenic and soil forming processes. The presence of Pb and Ba in the third factor indicates a traffic source. The fourth factor is defined by Co, Cu, Cd and Ti representing a heavy metal source, possibly originating from scrap yards.

The mean concentrations of Li, K, Be, Ba, Al, La and As were found to be higher in soils than in house and street dusts. Sodium, Sr, Ti, Ni, Cu, Ag, Zn, Cd, P and S were higher in house dusts and Mg, Ca, V, Cr, Mn, Fe, Co and Pb were higher in street dusts than in soils (section 6.9). The urban environment is affected by a wide variety of anthropogenic activities, which usually tend to increase metal concentrations in soils and dusts. The origin of elevated concentrations within these different media in urban environments is an area of much attention, research and debate. The distribution and concentration of

elements within soils and dusts (both indoor and outdoor) in cities is believed to frequently be a function of geographic influence. The maps produced in this chapter illustrate how results from statistical techniques can be incorporated into a GIS. These maps can be incorporated with data related to geology, land use, transportation techniques etc. This can then allow the identification of sites or areas which require further research, as well as aiding in the verification of hypotheses regarding spatial patterns within the dataset. This is explored further in chapter 7.

CHAPTER 7

Spatial data presentation and discussion

7.1 Introduction

This chapter presents the results of the spatial data analyses for elemental concentrations in soils and in dusts in Gibraltar Geochemical and environmental data tend to show **spatial dependence** (section 5.5). The environment is the outcome of actions and interactions of different processes and factors (natural and anthropogenic), which operate at different scales, ranging from micrometres to thousands of kilometres. Conventional statistical methods consider only the values (in specified units) of element concentrations in an attempt to reveal relationships between them, and to provide a quantitative measure of their properties. These techniques do not capture either the geographic reference of element concentrations or its use as a tool for understanding any natural geochemical variability and any sources of possible contamination.

GIS analysis captures the geographic reference of the data, thereby permitting the numerical analysis of the variables (in this case, element concentrations in soils and dusts) in order to create a geographic pattern of their distribution. This then allows the analytical data to be correlated with secondary data sources in different formats and scales, leading to the communication of the results through a logically organised and effective visualisation system. In this research GIS are used to evaluate and represent both the chemical analysis measurements and the numerical analysis results produced from the application of statistical techniques applied to soils and dusts in Gibraltar.

7.2 Spatial analysis tools and the presentation of geochemical data

In this work, geostatistical methods have been used to assess the spatial distribution of element concentrations across Gibraltar. Different techniques of spatial data analyses were assessed in terms of their applicability and accurate representation of the processes occurring within the environment under investigation.

The basic hypothesis behind geostatistical methods is that: *things* (be it objects or element concentrations in soils) *that are closer together are more alike than things that are further apart* (Webster and Oliver, 2001). The concentrations of elements in soils display spatial dependency and the variance between locations is said to increase with distance (Johnston *et al.*, 2001; Webster and Oliver, 2001). Once this relationship has been modelled, it is used to predict the concentration of an element in unsampled areas. Variograms and kriging (see section 5.4.1) are tools used for this purpose.

The accuracy and validity of this geostatistical hypothesis is increasingly being questioned particularly within urban environments. The main arguments presented against are those stated in section 2.6.2 for geochemical baselines and include: firstly the spatial heterogeneity found within very small distances in urban areas, and also rural areas (due to the presence of mineral deposits and natural geochemical anomalies); and secondly, the temporal variability of element input from anthropogenic sources to the natural environment. The methods of creating smooth surfaces are appropriate to data with a low degree of variability. Figure 7.1a displays a predicted surface using Inverse Distance Weighting (IDW). IDW splits the surface into a series of grids and calculates an average value for each grid from the measurements within and surrounding the grid. Samples that are closer to the predicted area contribute more to the outcome than the samples at a greater distance. The geochemical data for Gibraltar are highly variable due to specific point sources, which contribute to element concentrations which exceed guideline values (DEFRA/EA SGV) and/or world means, this point will be discussed below.

Figure 7.1 below shows two smooth surfaces. The first (Fig 7.1a) was produced using IDW) and the second using ordinary kriging (Fig 7.1b). In Fig 7.1b the spatial

distribution was initially modelled by a semivariogram followed by kriging to create a continuous surface.

Interpolation surfaces are not always suitable tools for predictive modelling. Each site will have certain characteristics, which will not allow the use of such models. Gibraltar is one such location and the reasons are discussed below. There are established limitations to all interpolation methods. However, kriging allows the user to determine the error, thereby evaluating the method (the degree of error is not assessed with IDW). Parameters are set within the variogram to produce the best model describing the autocorrelation of the data. This model assumes a constant unknown mean value and requires the data to be normally distributed which is achieved by logarithmic transformation. The semivariogram cloud models the autocorrelation of the data. Features that are closer together are assumed to be more alike than features that are further apart. The autocorrelation is modelled by fitting the best-fit line (yellow line) from a variety of models (Section 5.4.1.1). The properties of the semivariogram indicate autocorrelation and allow optimum kriging parameters to be set (Figure 5.1). Typically in large heterogeneous datasets the semivariogram values cease to increase gradually with distance and spread out as can be seen from Figure 7.2.

At this point the semivariogram is bounded, values up to this point are autocorrelated and after it are not. Figure 7.2 shows the apparent lack of autocorrelation in the dataset. The range is the distance at which the semivariogram values level off. The data for Gibraltar display a very large range. The nugget value is the semivariogram value at zero distance. In an ideal model this is 0.0. Heterogeneous data such as the soil data for Gibraltar typically have a high nugget size, as seen from Figure 7.2. This is due to micro scale variability or measurement error (Davis, 1973, Webster and Oliver, 2001).

In Kriging the surrounding measured variables are weighted to derive a prediction for an unmeasured location. A *local* weighted averaging procedure is used where the data have different weights according to their positions to the unknown point and to each other (Oliver, 1996).

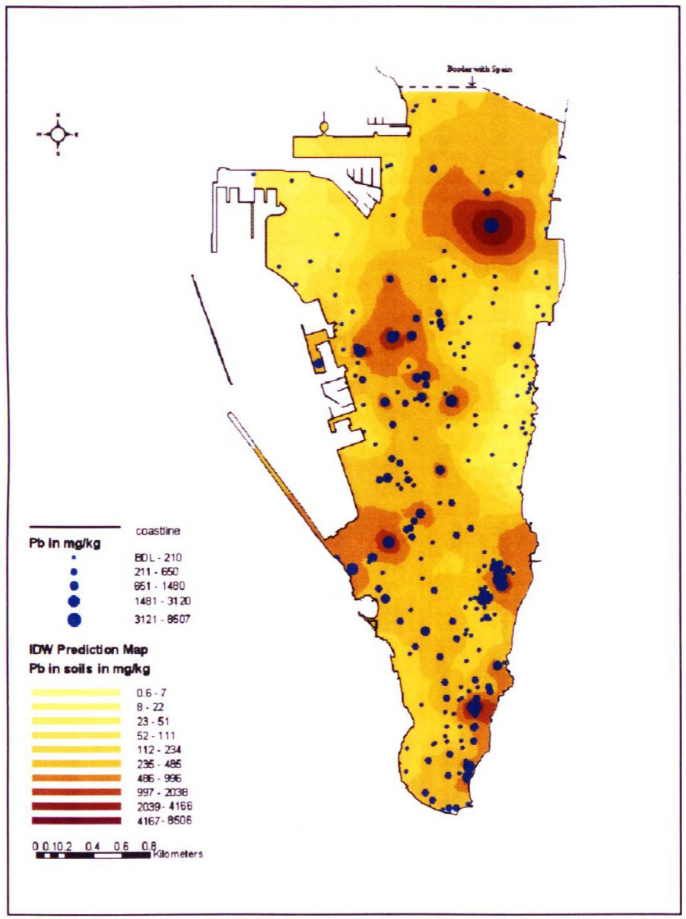


Figure 7.1 (a) Predicted and measured locations of Pb concentrations in soils from Gibraltar, using Inverse Distance Weighting. (n=238)

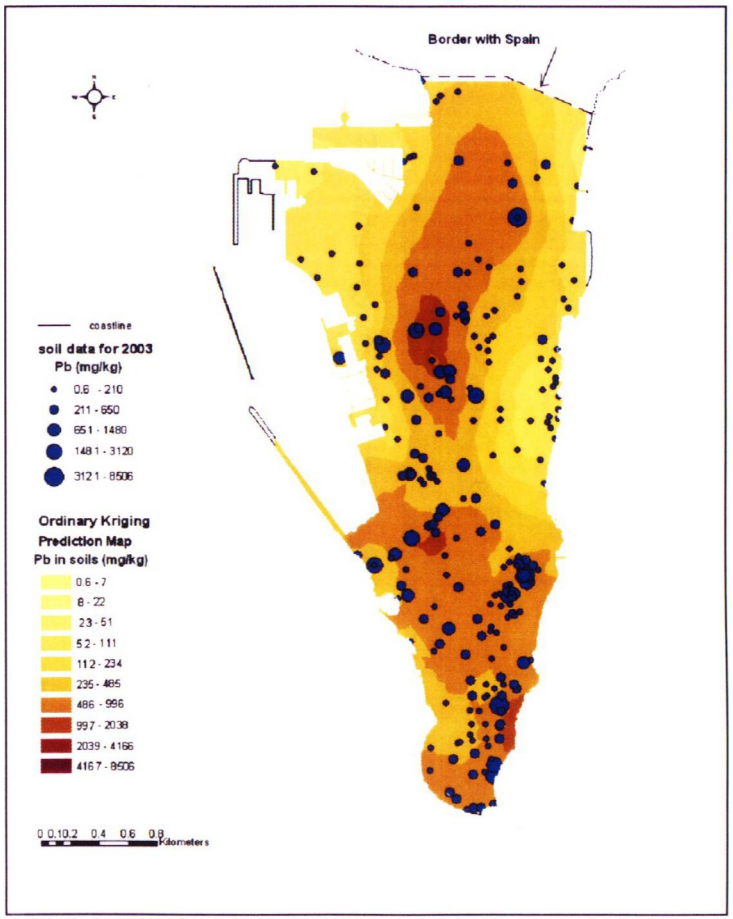


Figure 7.1 (b) Predicted and measured locations of Pb concentrations in soils from Gibraltar using ordinary kriging. (n=238)

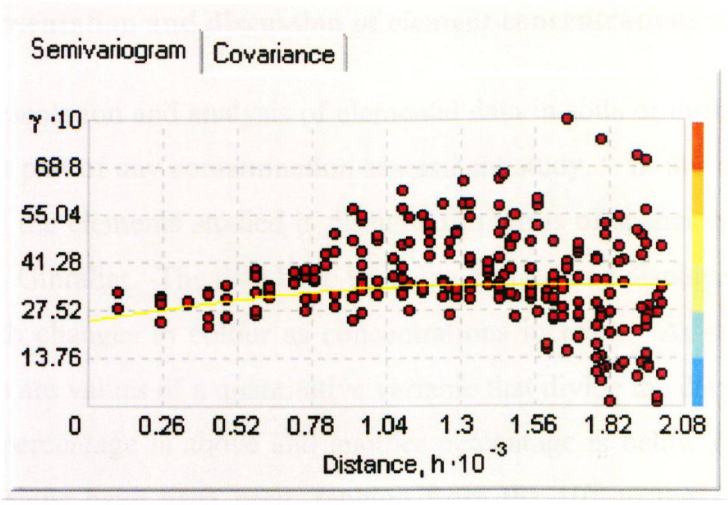


Figure 7.2 Semivariogram of Pb in soils from Gibraltar.

A disadvantage with such methods is that highly variable geochemical data produce a surface with many peaks and troughs and outlying values have a large influence, which often results in surfaces that are misrepresentative (Figure 7.1b). The weights are based on the distance between measured points, the prediction location, and the overall spatial arrangement. In figure 7.1 (a and b) the Pb concentrations at the actual sampling sites have also been displayed on the map to highlight the possible errors of under- and over-estimating high and low values when using such models. The resulting errors, which are clearly visible on the maps, are the result of the clear spatial heterogeneity found within very short distances in Gibraltar and indeed many urban areas. This is a common problem that can lead to the misinterpretation of the data and result in serious consequences for land use management.

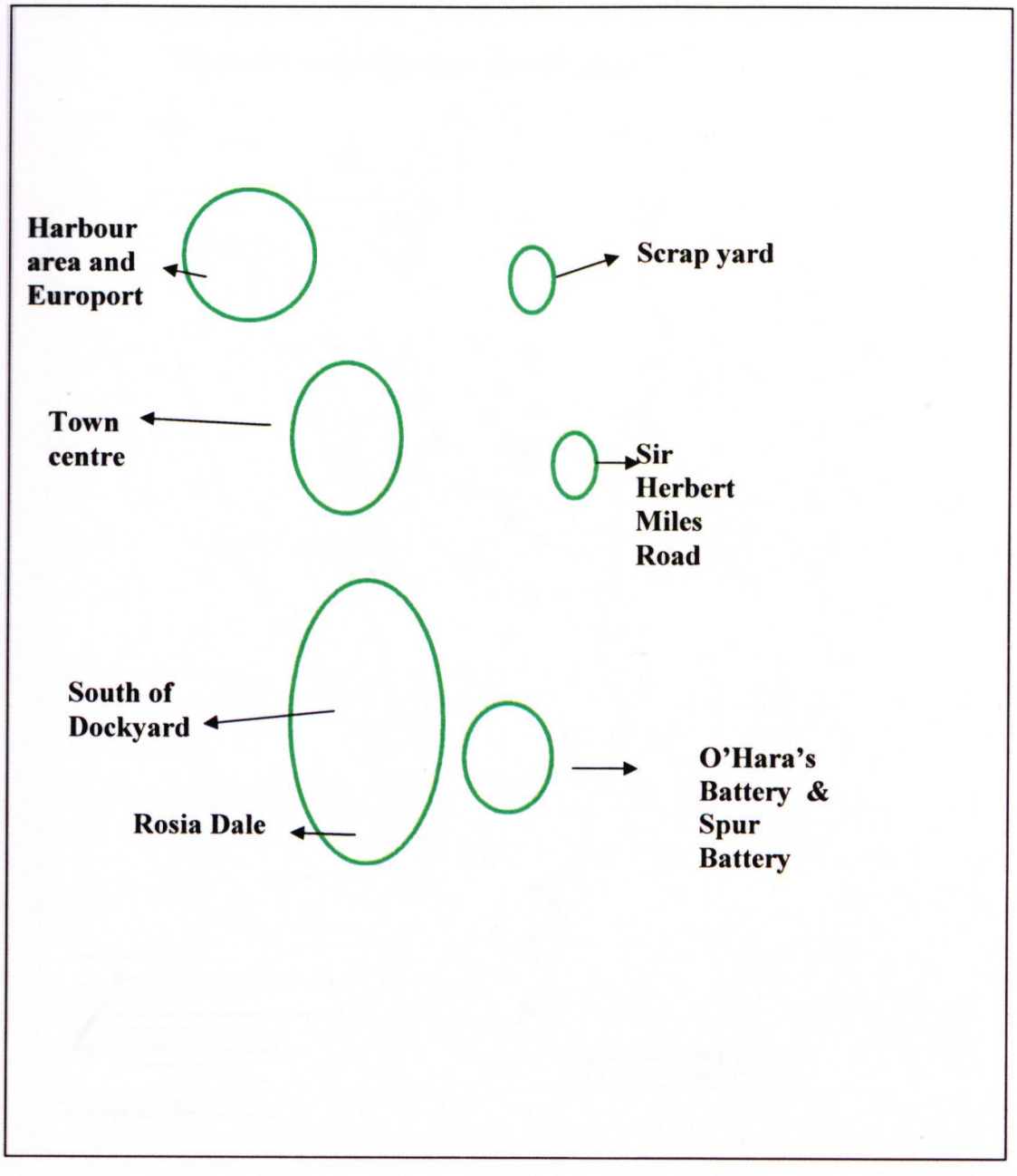
Interpolation techniques are generally not suited to areas with distinctly varying topologies. Ordinary kriging and IDW were used on an area of the southern plateaux in Gibraltar known as Windmill Hill. These methods, (IDW and kriging) although still biased by the presence of discrete point sources of anthropogenic activity, can be acceptable on an individual site basis that has a more homogenous type of topology, but is not applicable on an area as large as Gibraltar with a marked topographical heterogeneity.

7.3 Spatial presentation and discussion of element concentrations in soils

The spatial presentation and analysis of elemental data in soils or dusts is perhaps the most important part of any contamination assessment study. In this sub-section, the analysis for all the elements studied is discussed in terms of spatial distributions and patterns within Gibraltar. The data have been categorised and displayed on maps into percentiles with changes in colour as concentrations increase. As stated in section 6.2, percentiles are values of a quantitative variable that divide the data into groups so that a certain percentage is above and another percentage is below that value. Ten percentile divisions have been used, ranging from the 10^{th} to the 100^{th} percentile. This range of percentile categories has been used to describe the distribution of data within the geochemical maps as a means of categorisation of spatial data, which do not assume a normal distribution. The data has been classed into 10 groups of equal range, as it is felt that this will indicate and allow for a more detailed and in depth view into the spatial distribution of the dataset. These maps (figs 7.4 – 7.27) illustrate the geospatial variability of soils and demonstrate the importance of visualisation in GIS.

The spatial presentation of element concentrations in soils shows that there are certain areas in Gibraltar with concentrations of metals and other elements in either or both of these environmental media that exceed (DEFRA/EA) soil guideline values and/or world means. Figure 7.3 identifies these sites, which are discussed in this chapter. The elements discussed at these sites include: As, Ca, Fe, K, La, Mn, Na, Pb, P, S, Sr, Pb, Cu, Zn, As and V in these media. This type of map allows the identification of sites that require further investigation. It can also aid in the initial identification of possible sources of the elements with concentrations exceeding the guideline values; for example sites with such concentrations can be displayed together with industrial locations, or proximity to major roads. The anthropogenic sources in Gibraltar, which could lead to such concentrations of heavy metals in soils, include the scrap yard, the recent incinerator, traffic, the electricity generating station and the desalination plant, the sand blasting of ships at the dockyard, the rifles ranges and the MOD.

The first site is located to the north east of Gibraltar and is a scrap yard (Photos of these sites can be found in appendix E). *The second site* is Sir Herbert Miles Road.


Harbour area and Europort
Scrap yard
Town centre
Sir Herbert Miles Road
South of Dockyard
Rosia Dale
O'Hara's Battery & Spur Battery

This is a primary road and the location on this road where the soil samples have concentrations exceeding soil guideline values (SGV's) is opposite the Caleta Palace Hotel, adjacent to the fishing village known as Catalan Bay. There is no industrial activity in this area the only possible source resulting in increased element concentrations in soils and dusts would be from traffic.

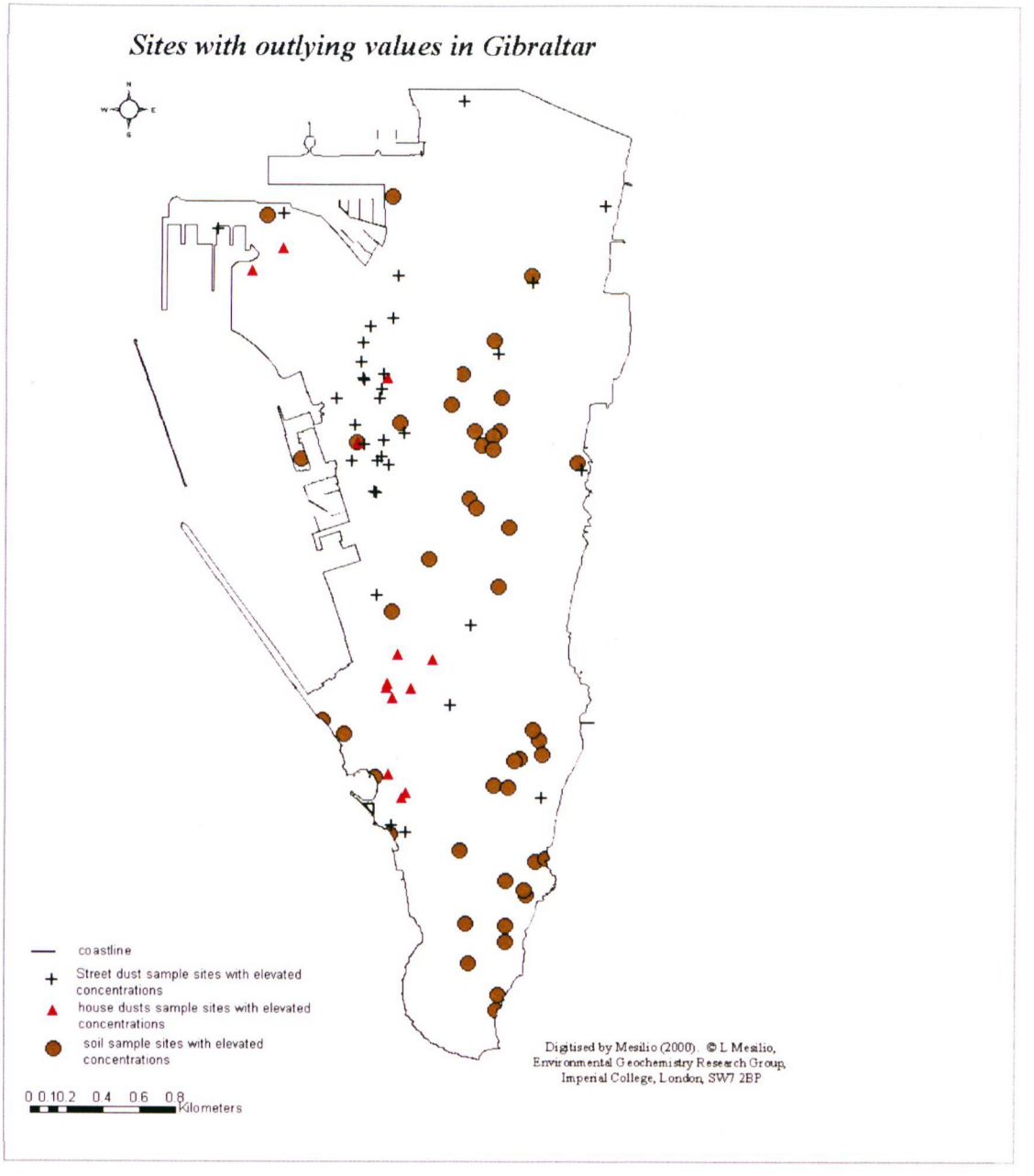


Figure 7.3 Sites with elevated concentrations of Li, K, Ca, Ba, La, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, P, S and As which exceed (where present) guideline values in different environmental media.

This is a primary road and the location on this road where the soil samples have concentrations exceeding soil guideline values (SGV's) is opposite the Caleta Palace Hotel, adjacent to the fishing village known as Catalan Bay. There is no industrial activity in this area the only possible source resulting in increased element concentrations in soils and dusts would be from traffic.

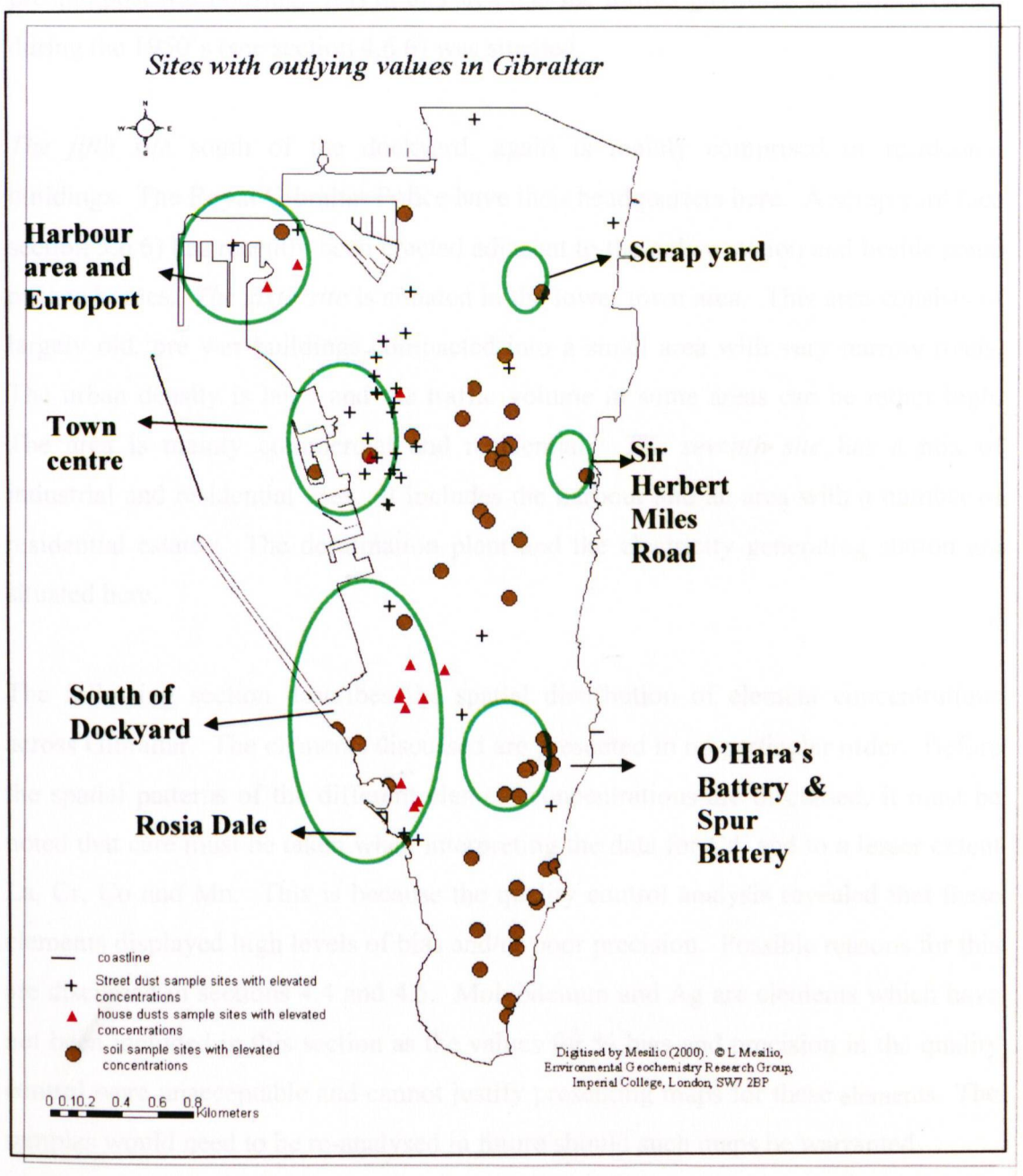


Figure 7.3 Sites with elevated concentrations of Li, K, Ca, Ba, La, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, P, S and As which exceed (where present) guideline values in different environmental media.

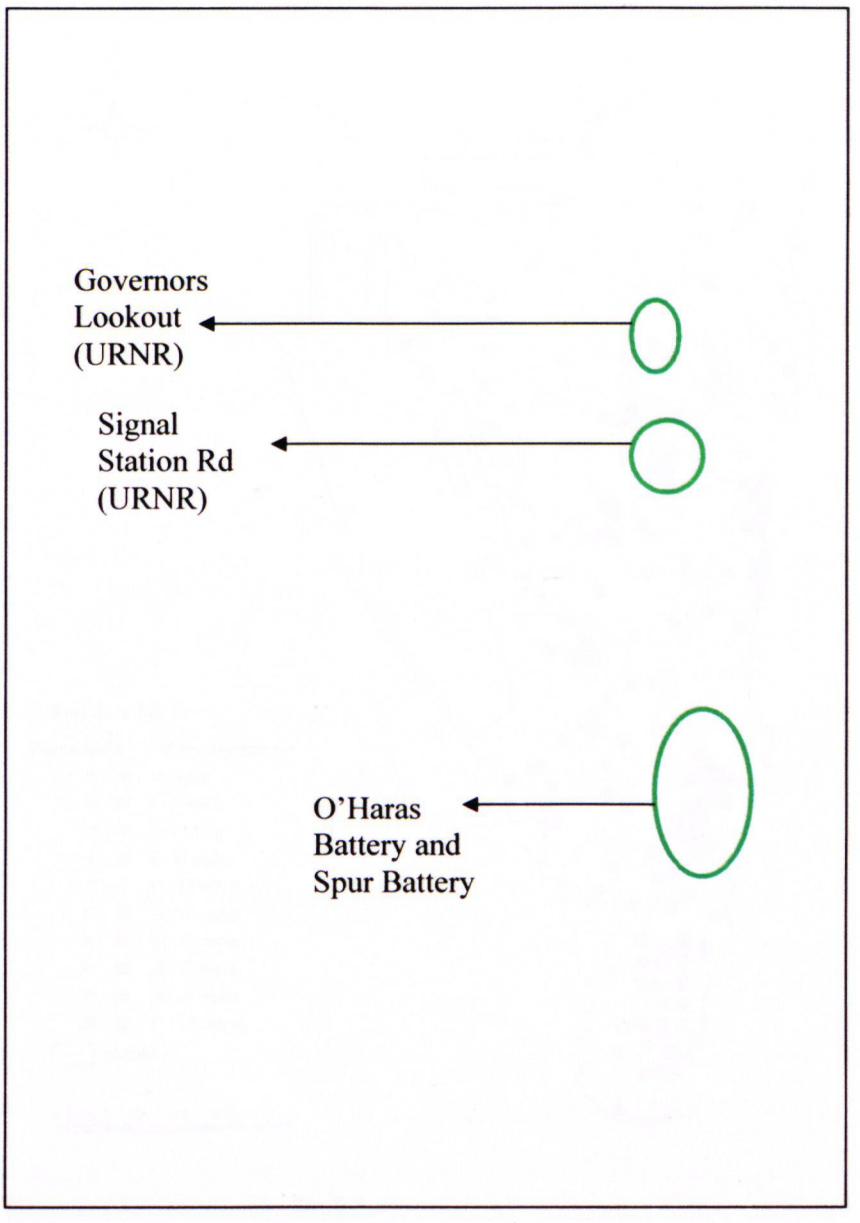
The third site is referred to as O'Haras Battery and Spur Battery. These are World War II guns which are no longer in use. Spur gun was removed in 1981 and transported to a museum in the UK.

The fourth site is known as Rosia Dale. This is now a residential area consisting of pre and post war housing. It is in this area that the former gasworks site which closed during the 1950's (see section 4.6.6) was situated.

The fifth site south of the dockyard, again is mainly comprised of residential buildings. The Royal Gibraltar Police have their headquarters here. A scrap yard (see section 3.6.6) has recently been erected adjacent to the police station and beside some private homes. *The sixth site* is situated in the lower town area. This area consists of largely old, pre war buildings compacted into a small area with very narrow roads. The urban density is large and the traffic volume in some areas can be rather high. The area is mainly commercial and residential. *The seventh site* has a mix of industrial and residential uses. It includes the harbour and an area with a number of residential estates. The desalination plant and the electricity generating station are situated here.

The following section describes the spatial distribution of element concentrations across Gibraltar. The elements discussed are presented in no particular order. Before the spatial patterns of the different element concentrations are discussed, it must be noted that care must be taken when interpreting the data for Cd, and to a lesser extent La, Cr, Co and Mn. This is because the quality control analysis revealed that these elements displayed high levels of bias and/or poor precision. Possible reasons for this are discussed in sections 4.4 and 4.5. Molybdenum and Ag are elements which have not been included in this section as the values for % bias and precision in the quality control were unacceptable and cannot justify presenting maps for these elements. The samples would need to be re-analysed in future should such maps be warranted.

When comparing element concentration values in Gibraltar, soils that have been determined using the nitric/perchloric digestion to literature values (e.g. world means referenced throughout this chapter include values by Alloway (1995), Kabata-Pendias and Pendias (2001), Ure and Berrow (1982)), the effect of incomplete dilution of the


Governors
Lookout
(URNR)
Signal
Station Rd
(URNR)
O'Haras
Battery and
Spur Battery

samples needs to be considered. A significant negative bias (as can be seen from the NIST SRM values in Tables D3 and D4) in some analytical runs suggests a loss of material or incomplete digestion during analysis. This is because complete nebulisation in the ICP-AES may not have been achieved and adsorption of materials onto the glassware can reduce the material available for analysis. Elements where concentrations displayed a negative bias on the reference materials include: Na, k, Mg, Ca, Sr, Ba, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Ca, Zn, Cd, Pb, P, S and As.

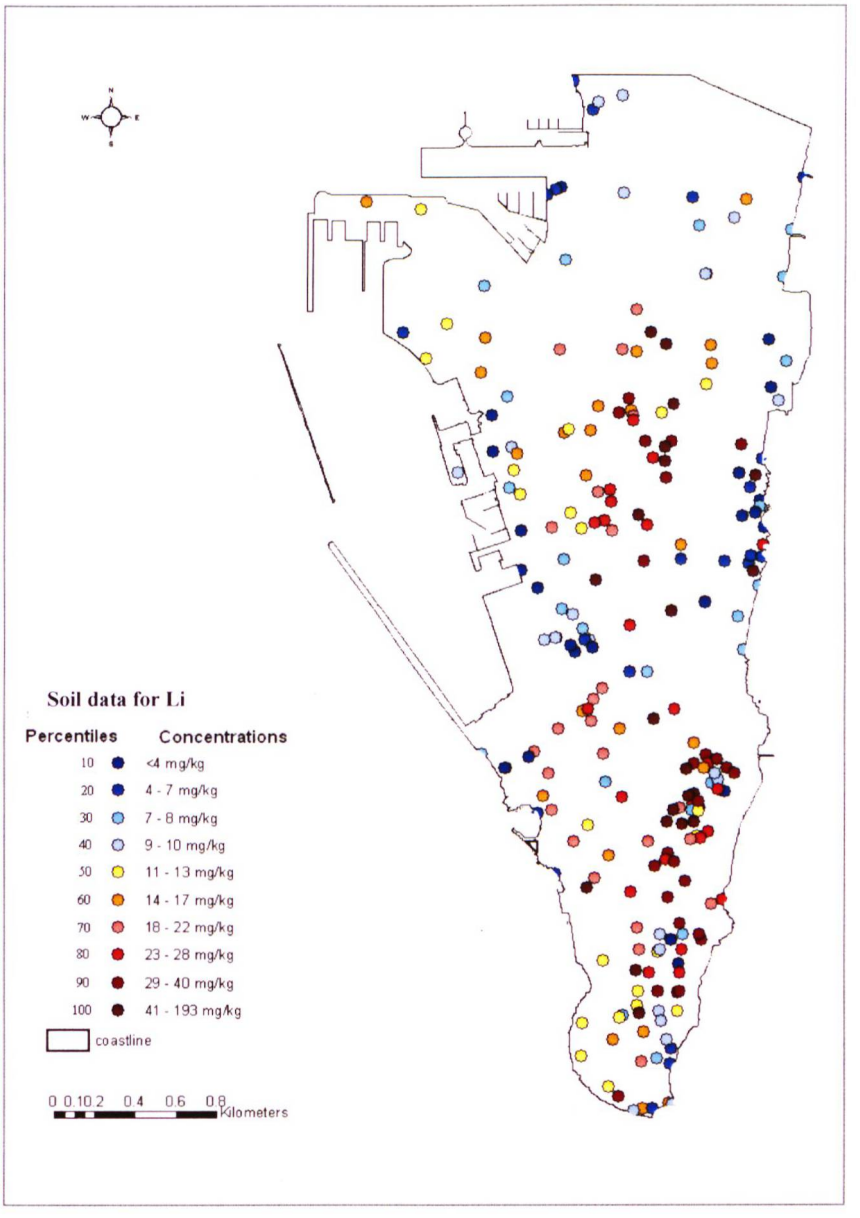


Figure 7.4 Li concentrations in soils (0-15 cms) from Gibraltar. (n=238)

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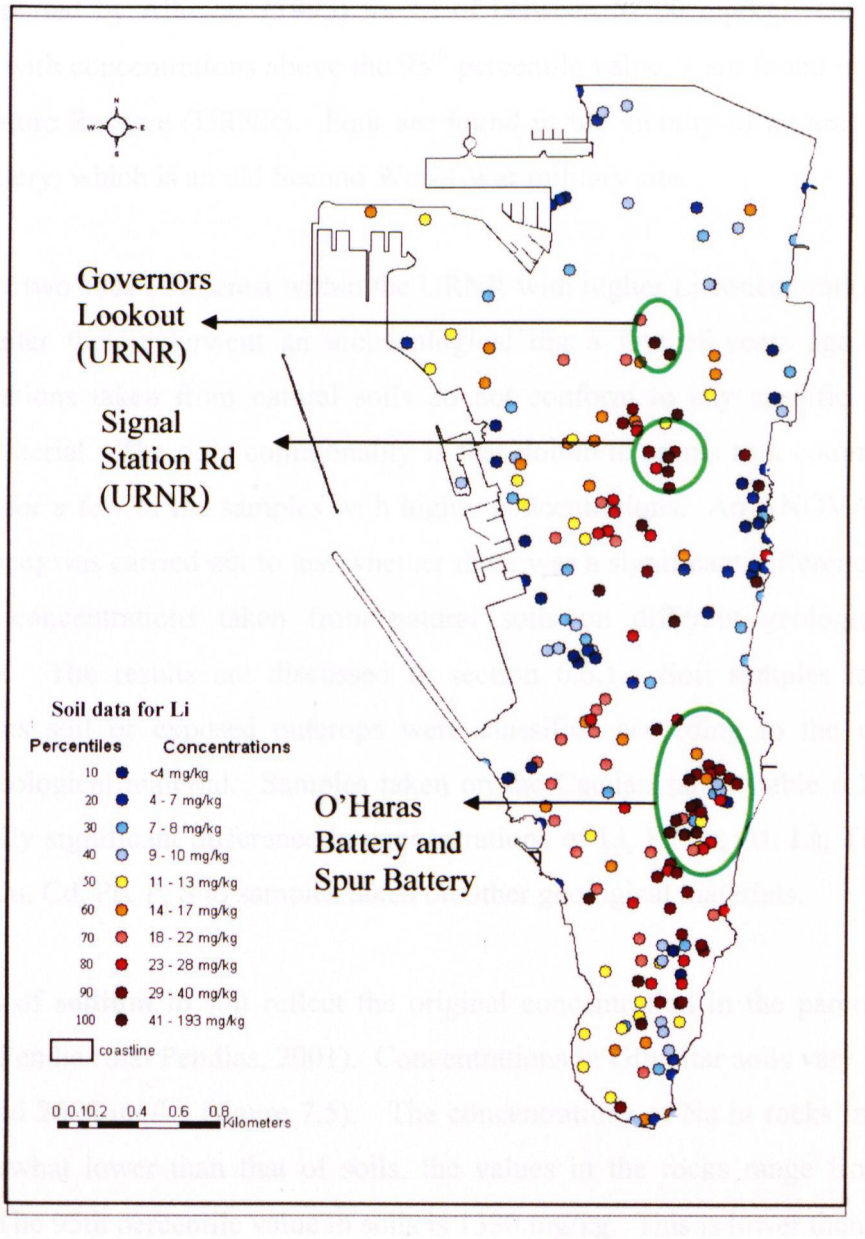


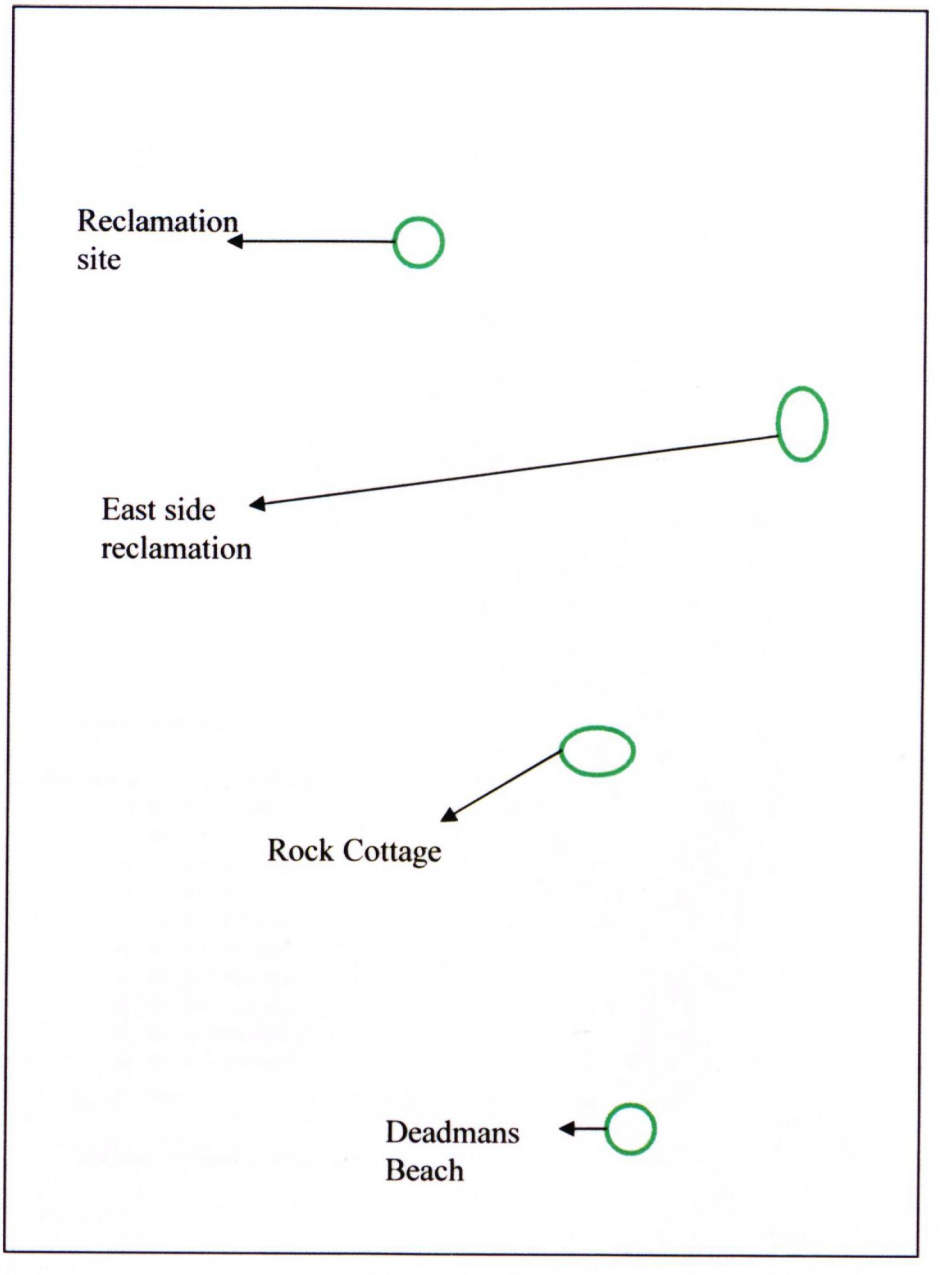
Figure 7.4 Li concentrations in soils (0-15 cms) from Gibraltar. (n=238)

Lithium is an element which is widely distributed throughout the earth's crust. It is usually associated with mica type minerals in the parent rock and can be quite mobile during the initial stages of soil formation but later becomes more stable due to its adsorption onto clay minerals (Kabata-Pendias and Pendias, 2001). The concentrations are reported to vary between 1.3 mg/kg for light organic soils to 56 mg/kg for soils with high carbonate content (Kabata-Pendias *et al.*, 1992). Most of the concentrations in Gibraltar soils (figure 7.4) fall within the levels reported by Kabata Pendias *et al.* (1992). The 95th percentile value is 49 mg/kg, well within the range reported by Alloway (1995) for Li of between 5-200 mg/kg. Out of the 11 samples with concentrations above the 95th percentile value, 7 are found in the Upper Rock Nature Reserve (URNR). Four are found in the vicinity of an area known as Spur Battery, which is an old Second World War military site.

The other two sites of interest within the URNR with higher Li concentrations are at a cave shelter that underwent an archaeological dig a few of years ago. Lithium concentrations taken from natural soils do not conform to any specific geological parent material. The only commonality is that dolomite seems to a common parent material for a few of the samples with higher concentrations. An ANOVA (analysis of variance) was carried out to test whether there was a significant difference between element concentrations taken from natural soils on different geological parent materials. The results are discussed in section 6.6.1. Soil samples taken from indigenous soil or exposed outcrops were classified according to the underlying parent geological material. Samples taken on the Catalan sands (table 6.17) have a statistically significant difference in concentrations of Li, K, Ba, Al, La, Ti, Mn, Na, Mg, V, Cu, Cd, Pb, P, S to samples taken on other geological materials.

Contents of **sodium** in soil reflect the original concentration in the parent material (Kabata Pendias and Pendias, 2001). Concentrations in Gibraltar soils vary between 4 mg/kg and 2608 mg/kg (figure 7.5). The concentrations of Na in rocks in Gibraltar are somewhat lower than that of soils, the values in the rocks range from 42-608 mg/kg. The 95th percentile value in soils is 1330 mg/kg. This is lower than the world means provided by Ure and Berrow (1982) for world means which range from 2730-3160 mg/kg. The site at which this concentration is found (1330 mg/kg) is a land reclamation site on the east side of Gibraltar (see section 3.6.2 and figure 3.3). Three

other sites with Na values above the 95th percentile were also found to be on a former land reclamation site which was in-filled with sand taken from the seabed off the coast of Gibraltar. There does not appear to be however any immediate discernable spatial pattern to the sites with higher Na concentrations as regards the entire dataset. As with the Li concentrations, the only commonality in terms of geology is that the same samples occur on some form of dolomitic material, that is to say, dark grey dolomite, interbedded dolomite and limestone, pale grey dolomite and limestone dolomite. The sites on which these samples were taken do not conform however to any particular land use. Soil samples taken at Rock Cottage, a MOD residential home have a Na concentration of 1170 mg/kg, which, although high when compared with the rest of the dataset, is lower than the means reported by Ure and Berrow (1982). Similarly some of the samples taken at Spur Battery also have concentrations greater than the 95th percentile value, as do samples at Deadmans beach (an abandoned cove) at the extreme south of Gibraltar. One point to take note of is the effect of sea spray on soil concentrations for certain elements. This has not been ascertained in this work, but it must be pointed out that Gibraltar has sea almost all the way around its perimeter, and when this is combined with the small land area, it leads to the assumption that sea spray will have an effect on local soils. Moreover, seawater is used for street washing and other sanitary uses in Gibraltar.


Reclamation site
East side reclamation
Rock Cottage
Deadmans Beach

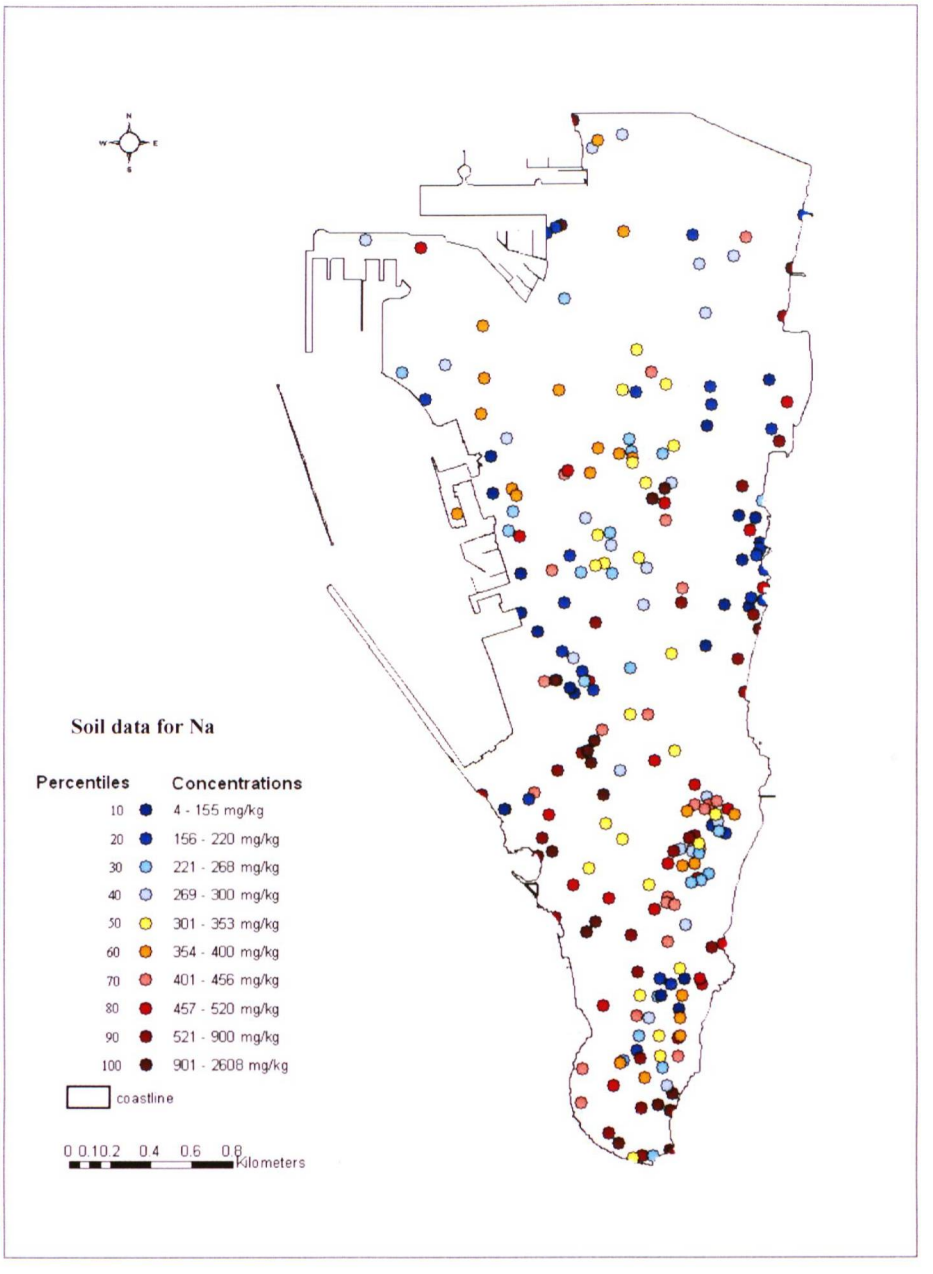


Figure 7.5 Na concentrations in soils (0-15 cm) from Gibraltar. (n=238)

Potassium is an element which is naturally abundant in soils. It is found in fairly high concentrations in most mineral soils except for those of a sandy nature (Kabata-Pendias, 2001). It has a low mobility in soils as potassium cations are adsorbed onto clay minerals, either as part of their structure, or absorbed onto mineral surfaces.

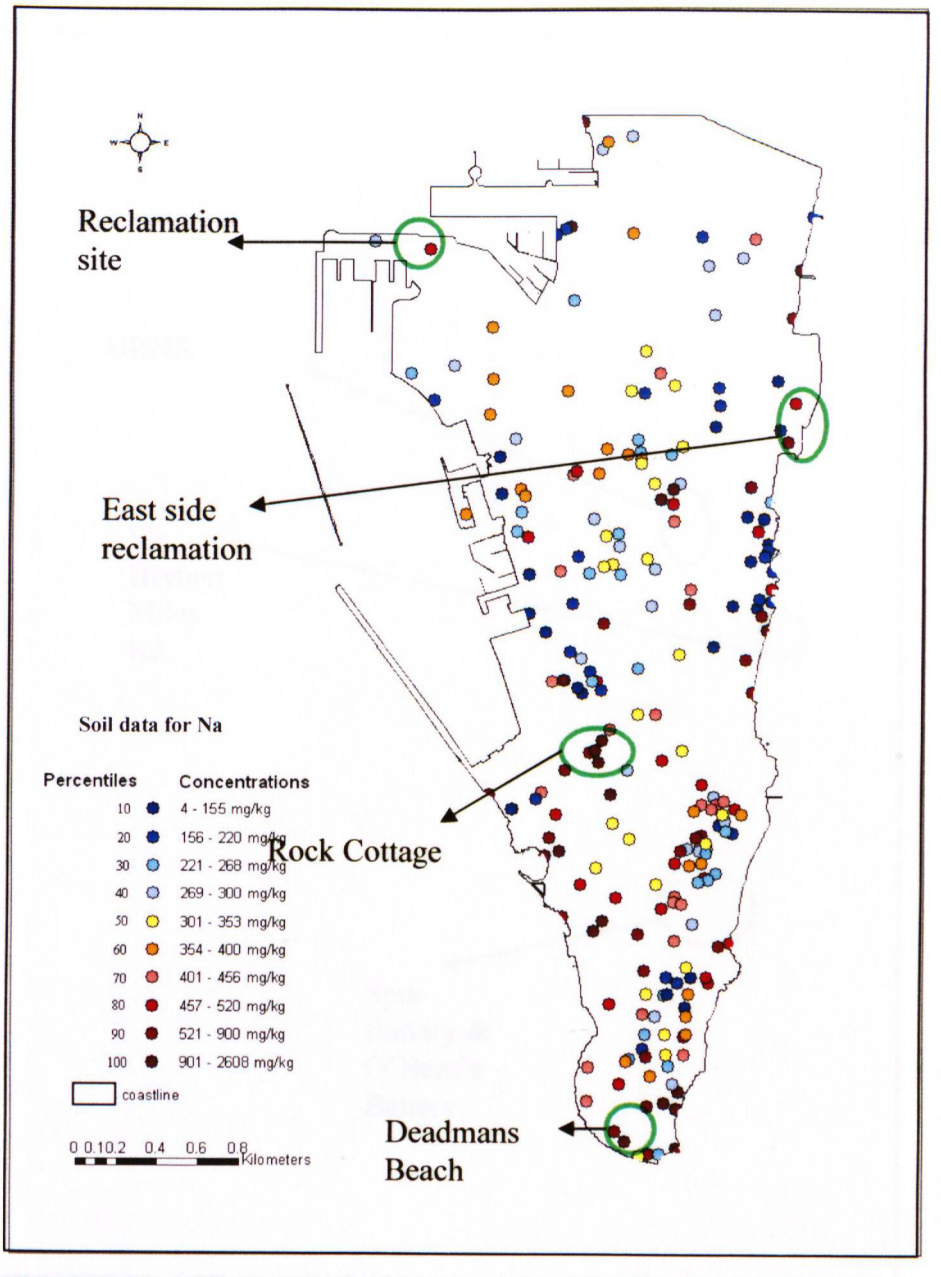


Figure 7.5 Na concentrations in soils (0-15 cm) from Gibraltar. (n=238)

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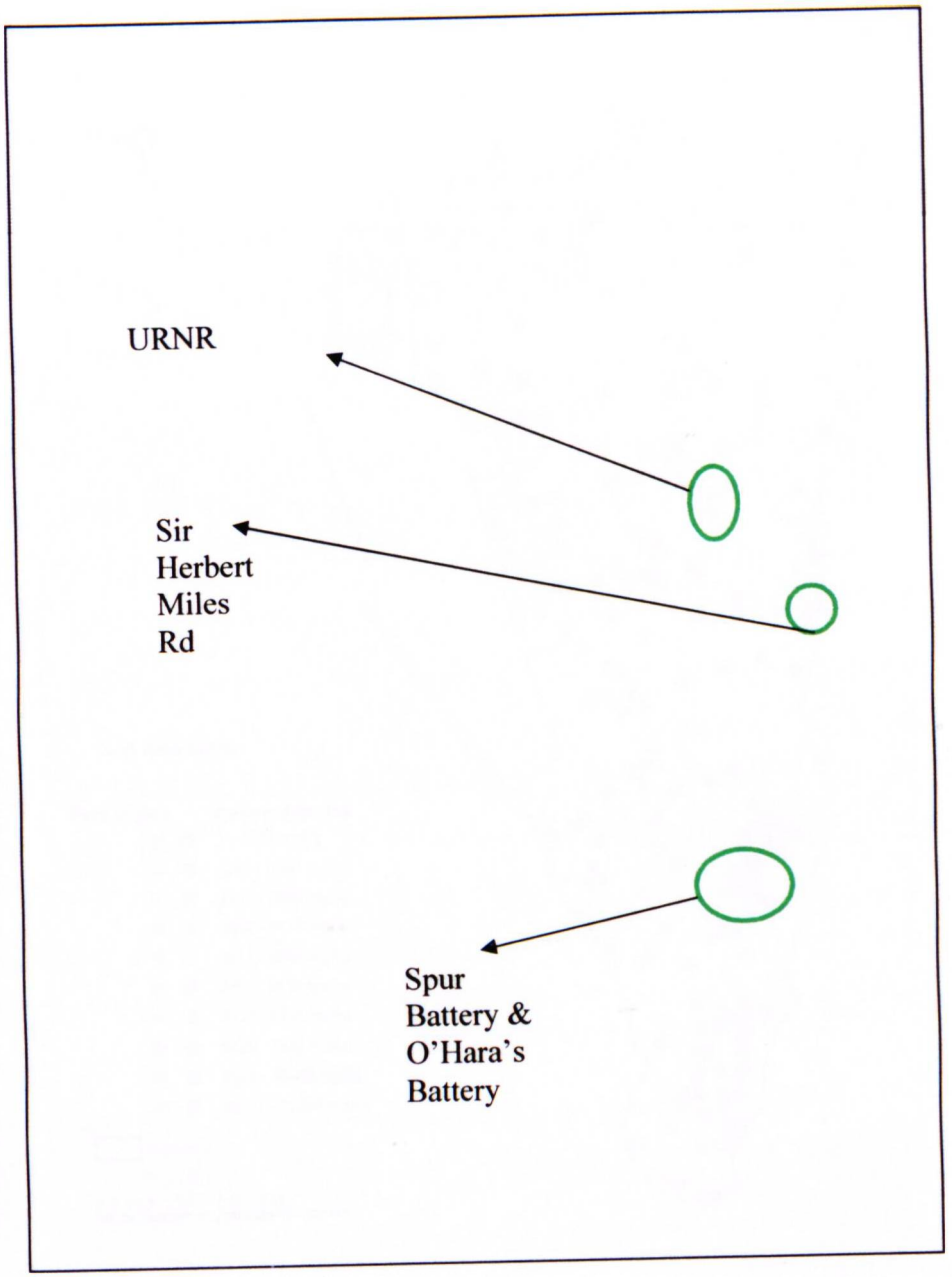

URNR
Sir
Herbert
Miles
Rd
Spur
Battery &
O'Hara's
Battery

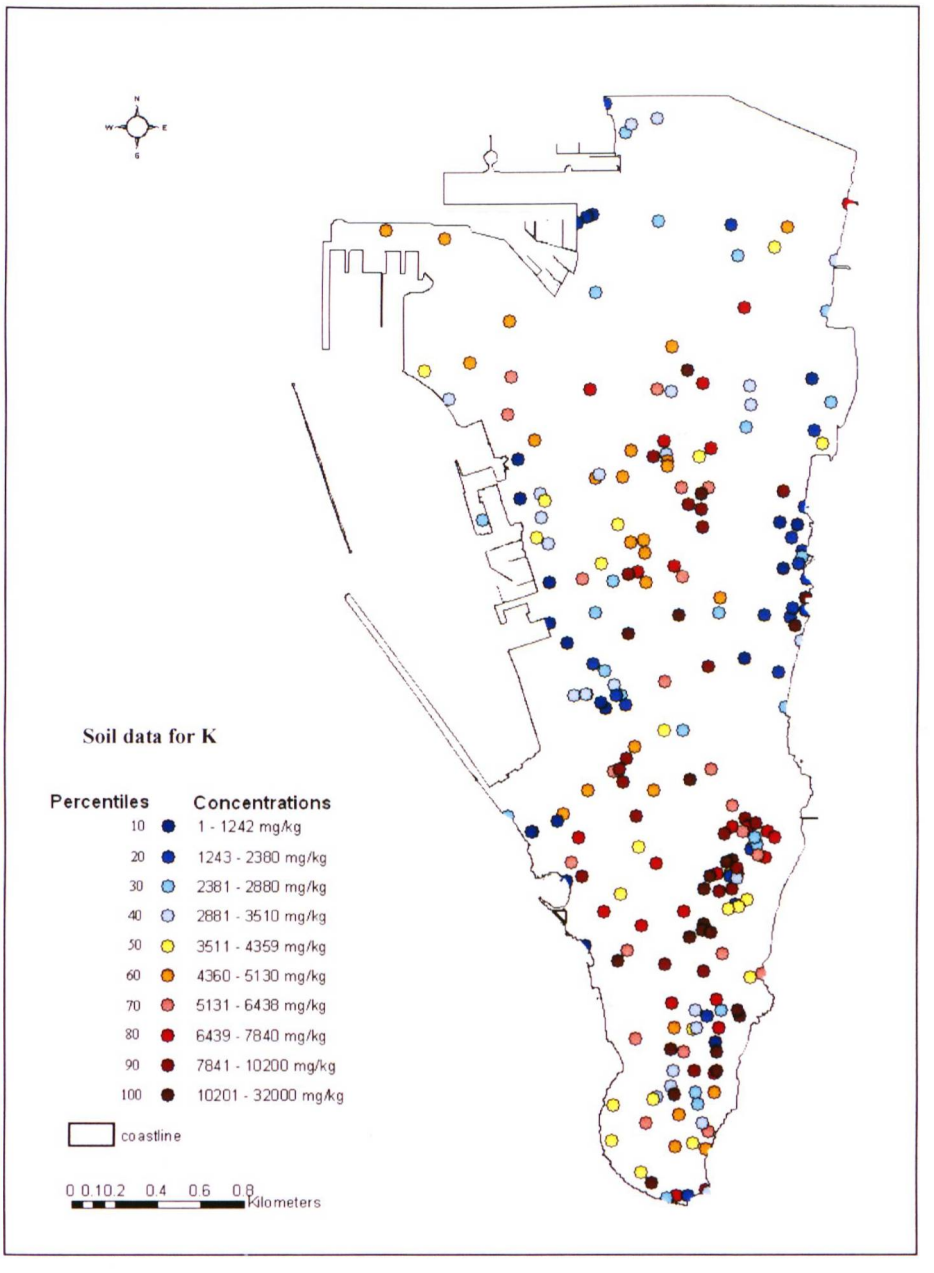
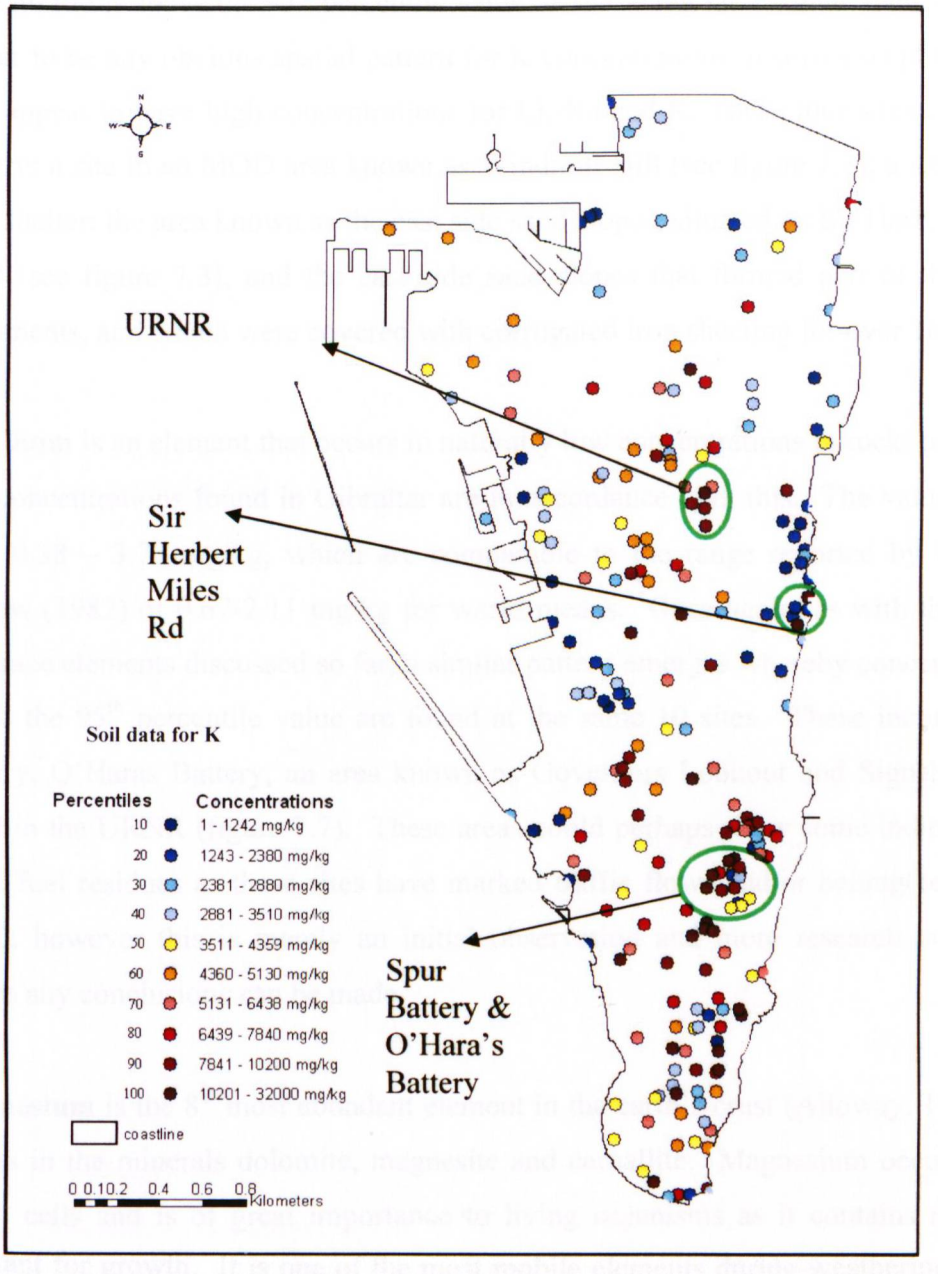


Figure 7.6 K concentrations in soils (0-15 cms) from Gibraltar. (n=238)

The concentrations of K in soils generally reflect the original concentrations in the parent material. The concentrations in soils are found to be much higher than those in the rock samples taken from Gibraltar (27-2170 mg/kg, table 6.9). The concentrations of K in Gibraltar soils are also high compared with the values reported by Ure and Berrow (1982) of 3710-15900 mg/kg for world means. The range in Gibraltar soils is between 1-32000 mg/kg (figure 7.6). The 25th percentile value is 2592 mg/kg and a maximum value of 32000 mg/kg was found at Spur Battery. Ten samples have



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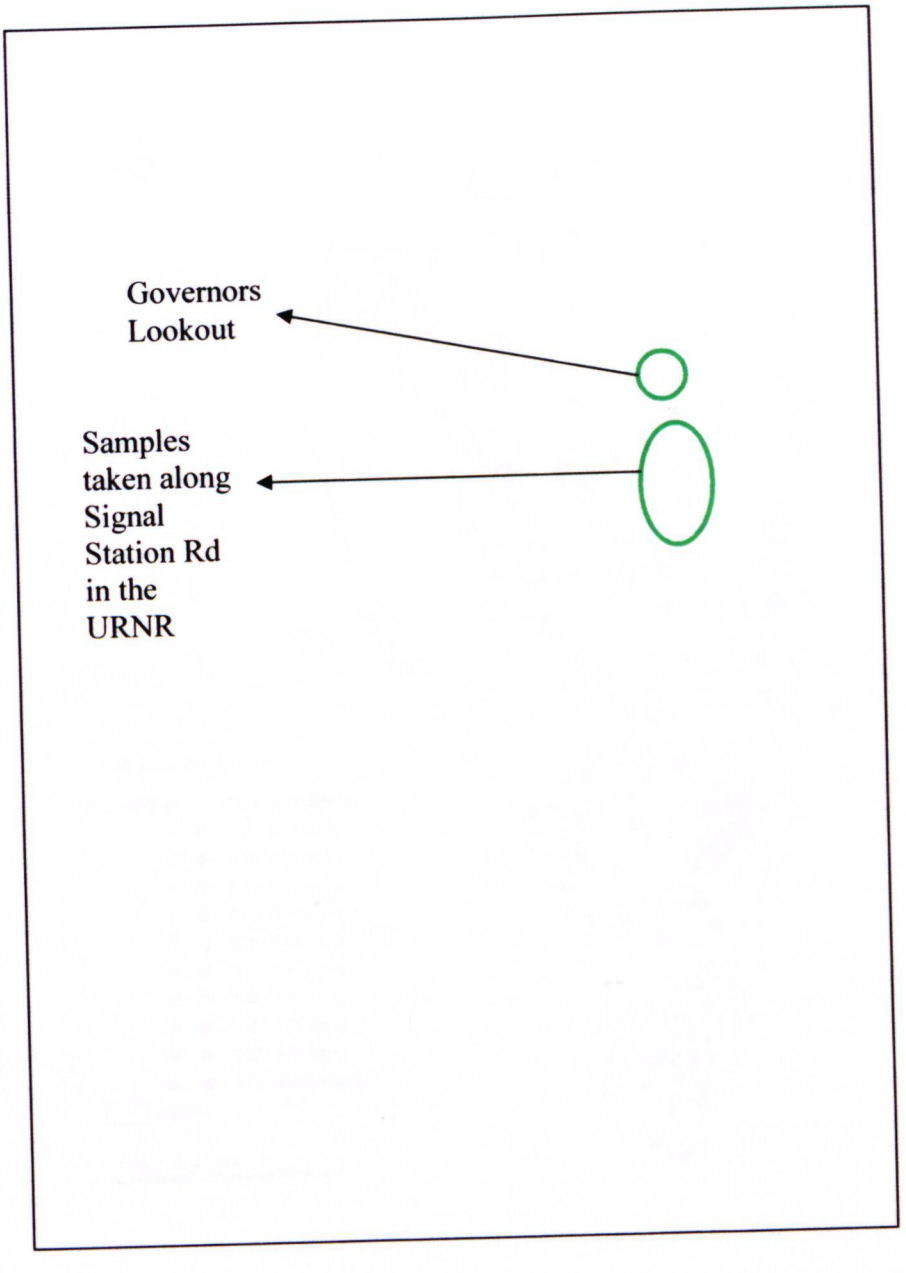
concentrations above the 95th percentile value of 13800 mg/kg. Again, there does not appear to be any obvious spatial pattern for K concentrations in soils except that four sites appear to have high concentrations for Li, Na and K. These four sites are: Spur Battery; a site in an MOD area known as Windmill Hill (see figure 7.3); a site by the cave shelter; the area known as the east side sand slopes, situated on Sir Herbert Miles Road (see figure 7.3); and the east side sand slopes that formed part of the water catchments, and which were covered with corrugated iron sheeting for over 100 years.

Beryllium is an element that occurs in naturally low concentrations in rocks and soils. The concentrations found in Gibraltar are in accordance with this. The values range from 0.38 – 3.73 mg/kg, which are comparable to the range reported by Ure and Berrow (1982) of 0.67-2.11 mg/kg for world means. Once again, as with the major and trace elements discussed so far, a similar pattern emerges whereby concentrations above the 95th percentile value are found at the same 10 sites. These include Spur Battery, O'Haras Battery, an area known as Governors Lookout and Signal Station Road in the URNR (figure 7.7). These areas could perhaps show some indication of fossil fuel residues as these sites have marked traffic flows and/or belong(ed) to the MOD, however this is merely an initial observation and more research is needed before any conclusions can be made.

Magnesium is the 8th most abundant element in the earth's crust (Alloway, 1995). It occurs in the minerals dolomite, magnesite and carnallite. Magnesium occurs in all living cells and is of great importance to living organisms as it contains nutrients important for growth. It is one of the most mobile elements during weathering. Part of the bedrock geology of Gibraltar is composed largely of the mineral dolomite ($CaMg(CO_3)_2$) (Rose and Hardman, 1995). Concentrations in Gibraltar soils range from 2.4 – 114000 mg/kg. The spatial patterns visible from figure 7.8 reflect both the underlying geology as well as anthropogenic activity. The 95th percentile value of 24700 mg/kg compares to the value reported by Alloway (1995) and Wedepohl (1991) of 26000 mg/kg for Mg on limestones (table 2.2). The concentrations found in Gibraltar are higher than the world means reported by Ure and Berrow (1982) of 4820-6910 mg/kg for Mg. The sites of note with concentrations above the 95th percentile value include the cave shelter, Spur battery and the one of the reclamation sites situated close to the airport runway.


Governors
Lookout
Samples
taken along
Signal
Station Rd
in the
URNR

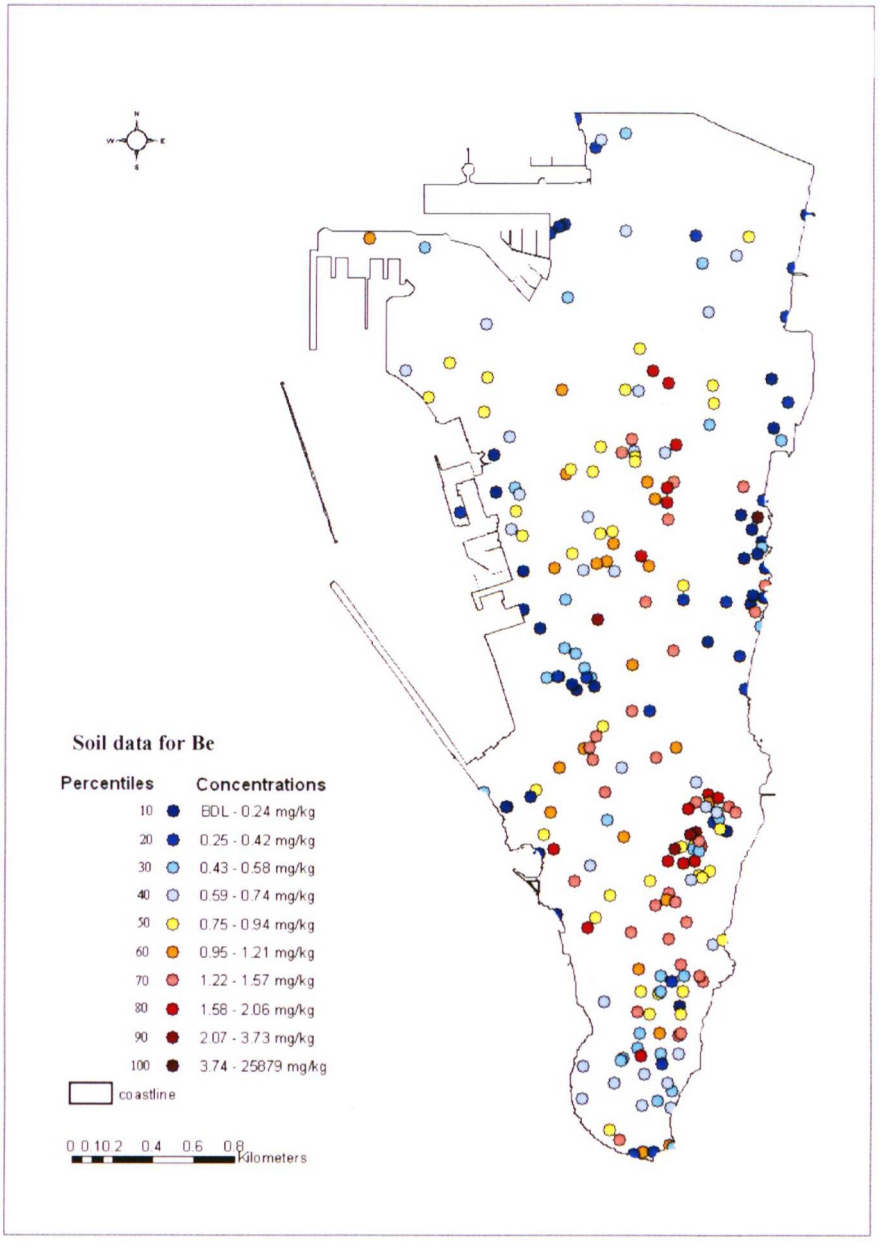
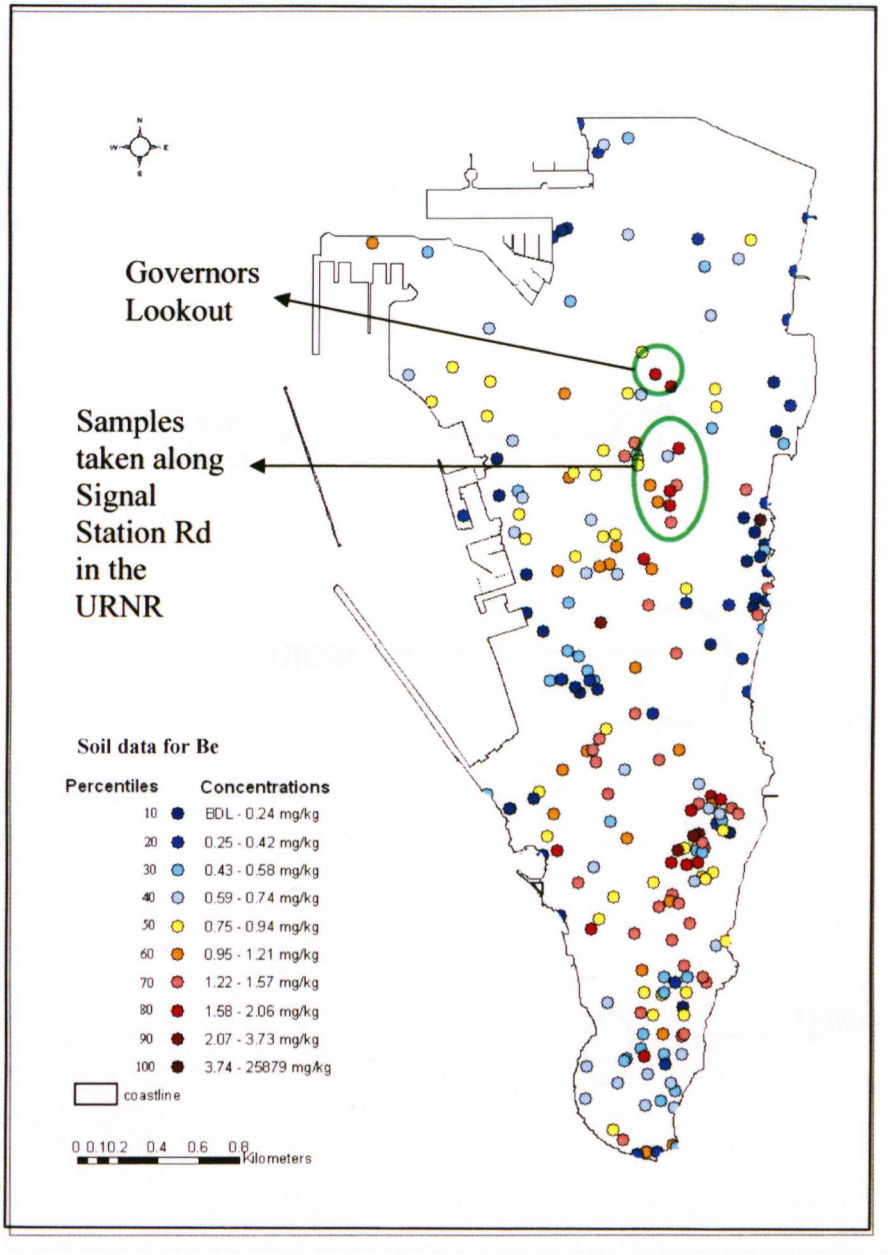


Figure 7.7 Be concentrations in soils (0-15cms) from Gibraltar. (n=238)

The samples taken from the cave shelter and Spur battery are natural soils parent material of which is dolomite. Two samples were taken from each of the beaches situated by the Quarry and both of these samples have Mg concentrations exceeding the 95th percentile value (figure 7.8). The natural geology of Gibraltar has a large influence on the natural concentrations of certain elements within soils and dusts. As expected, concentrations of Magnesium taken from natural soils are higher on areas of dolomite parent material.



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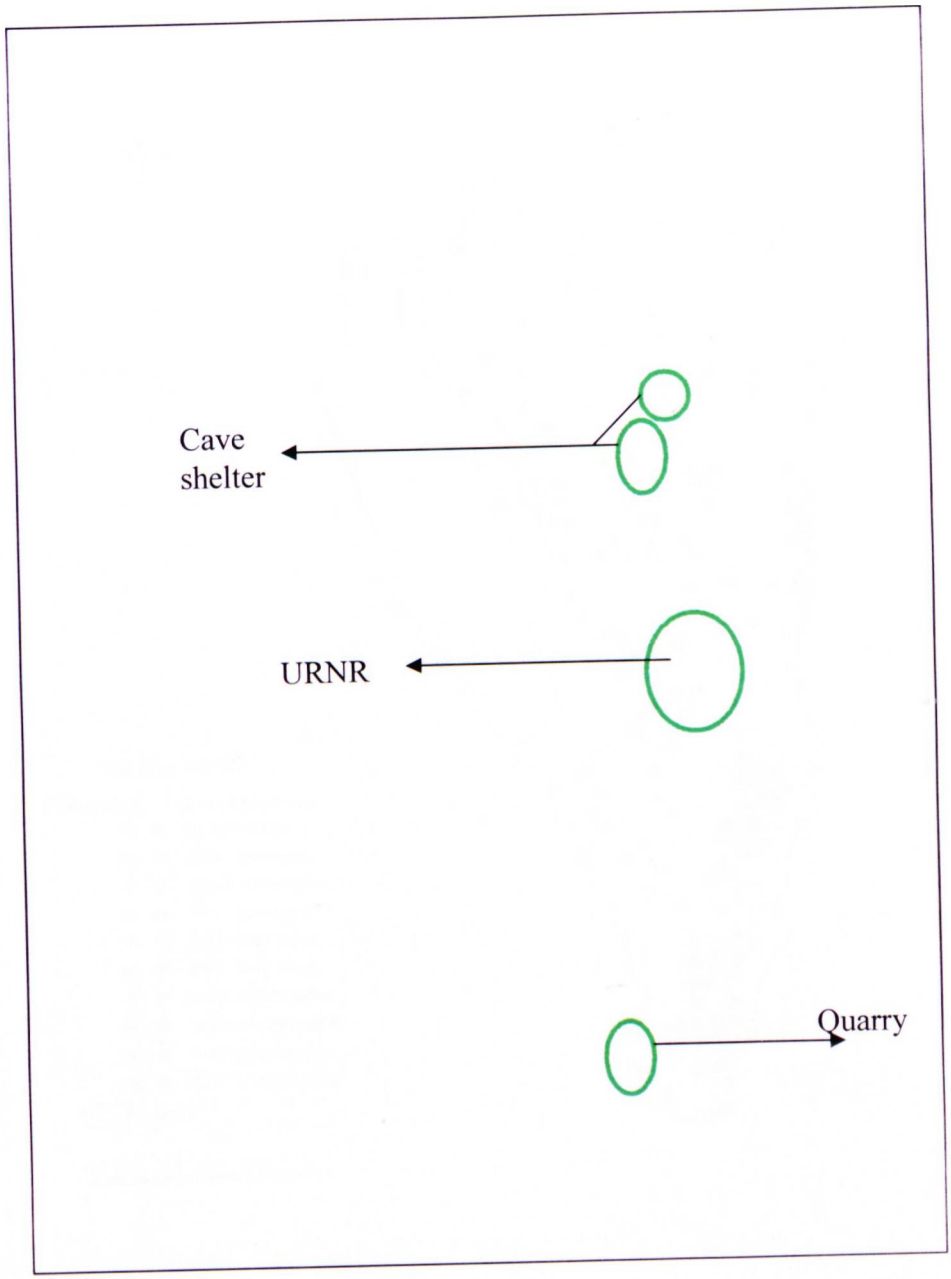

Cave
shelter
URNR
Quarry

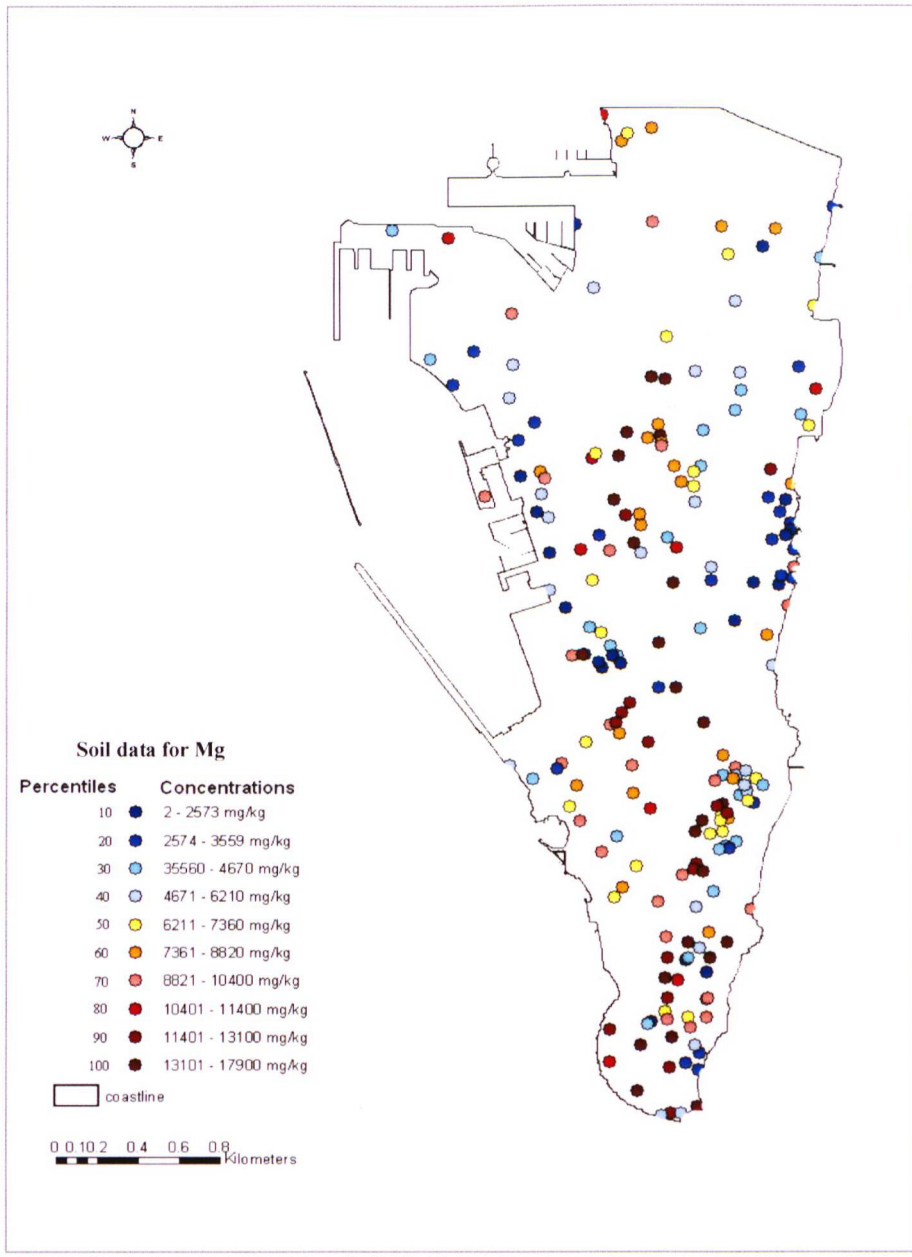
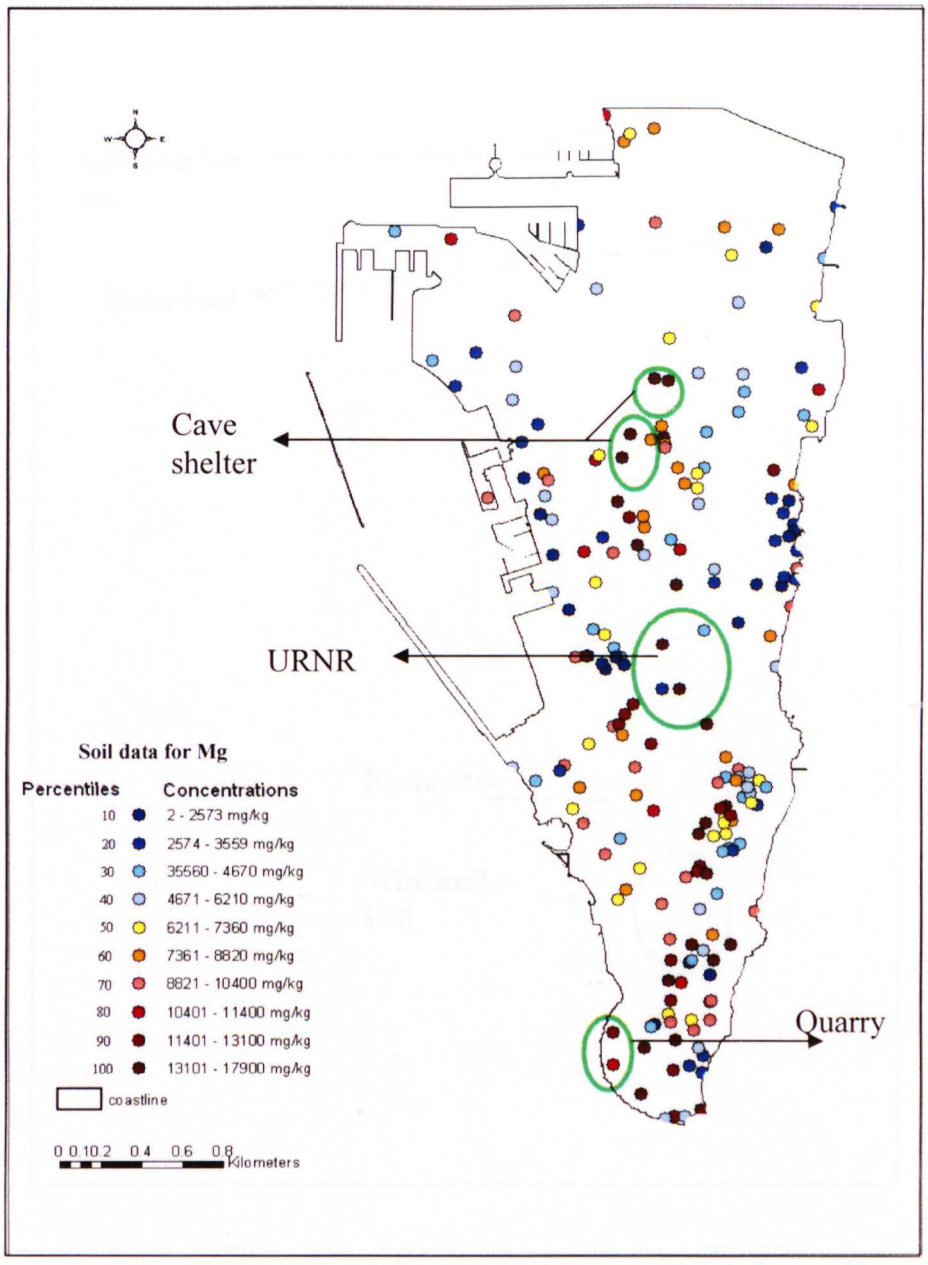


Figure 7.8 Mg concentrations in soils (0-15 cms) from Gibraltar. (n=238)

Calcium is naturally abundant in soils particularly in those on sedimentary bedrock. Limestone is composed mainly of carbonates, predominantly calcite. The Gibraltar limestone is formed from the mineral calcite ($CaCO_3$), with as mentioned above, dolomite or dolostone, composed largely of the mineral dolomite ($CaMg(CO_3)_2$) (Rose and Hardman, 1995) (figure 3.4). The high Ca values obtained throughout reflect both the underlying geology (concentrations in Gibraltar rocks range from 216000-422000 mg/kg, table 6.9) as well as anthropogenic activity (figure 7.9).



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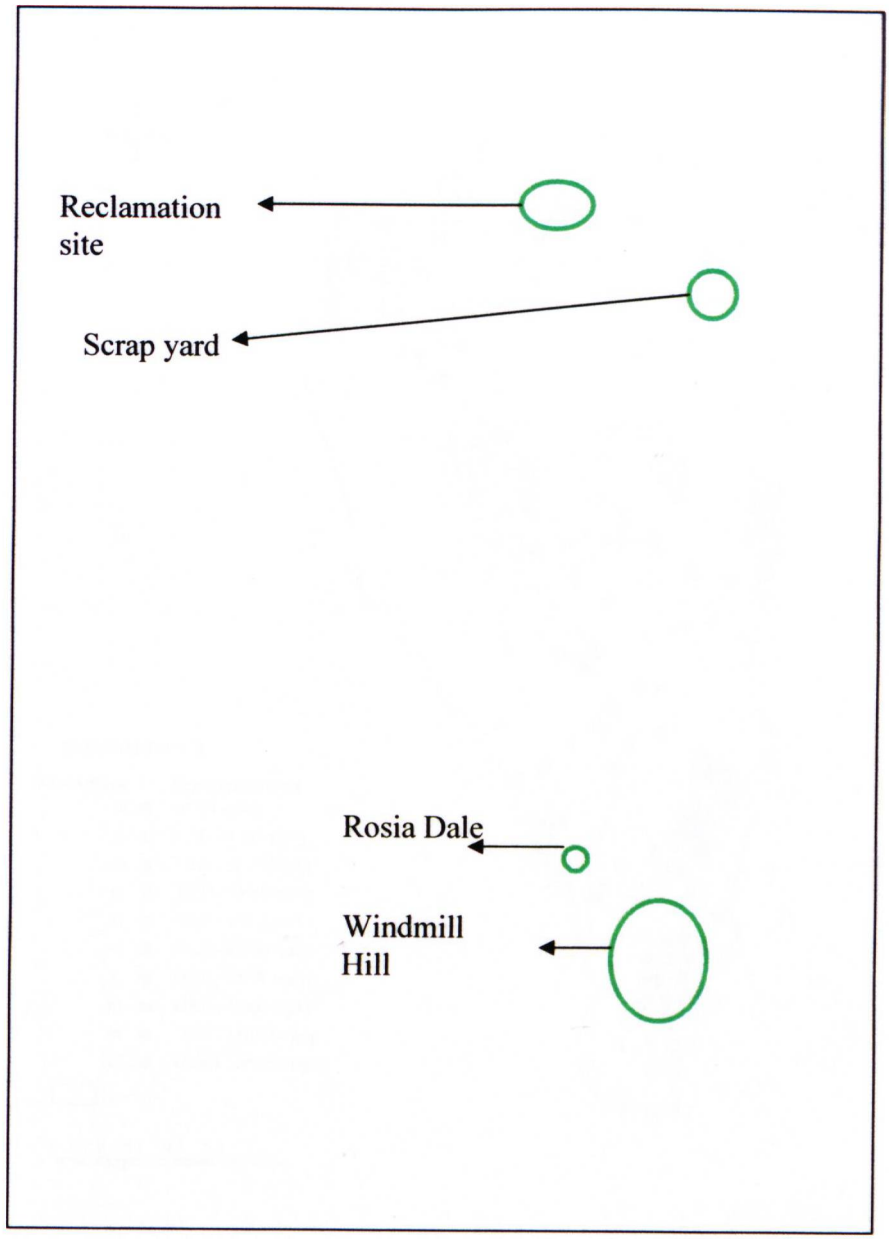

Reclamation site
Scrap yard
Rosia Dale
Windmill Hill

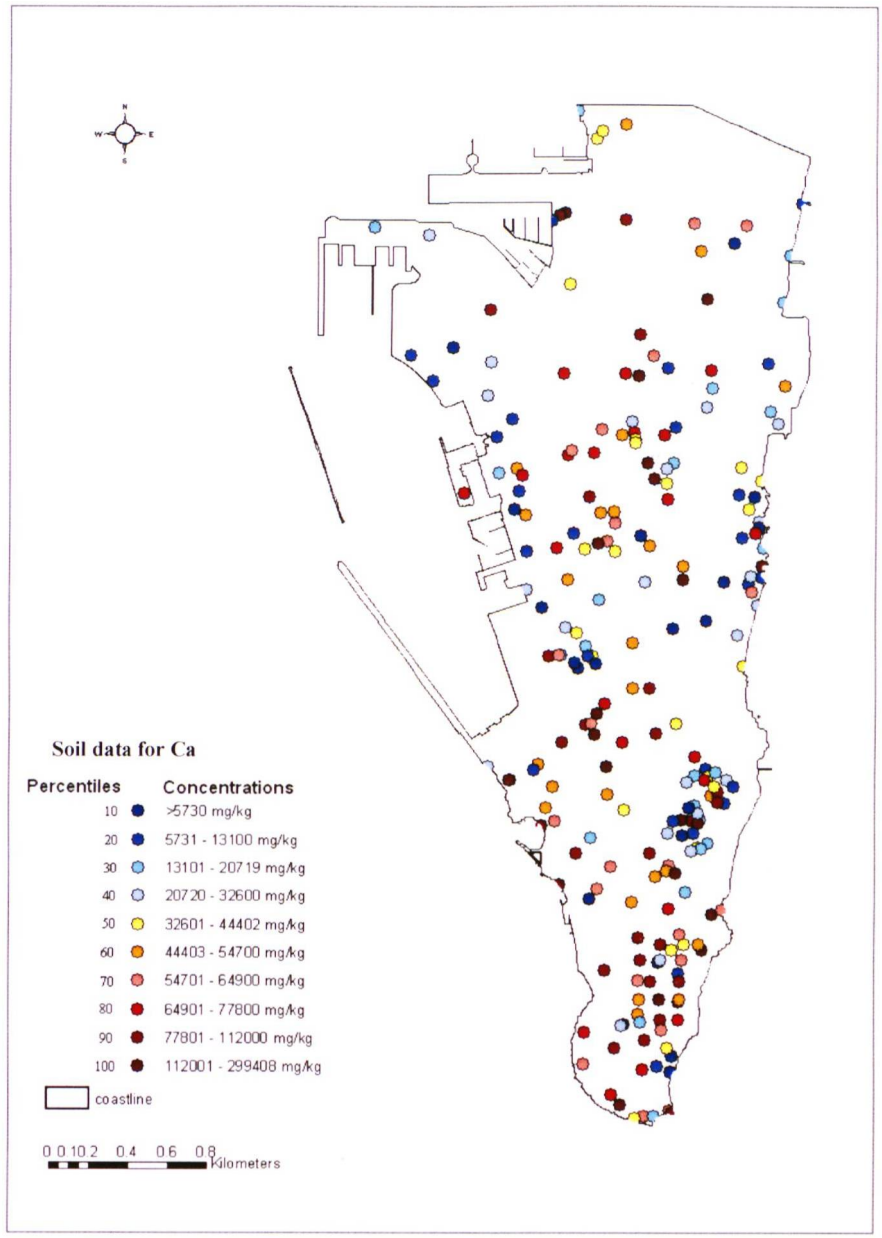
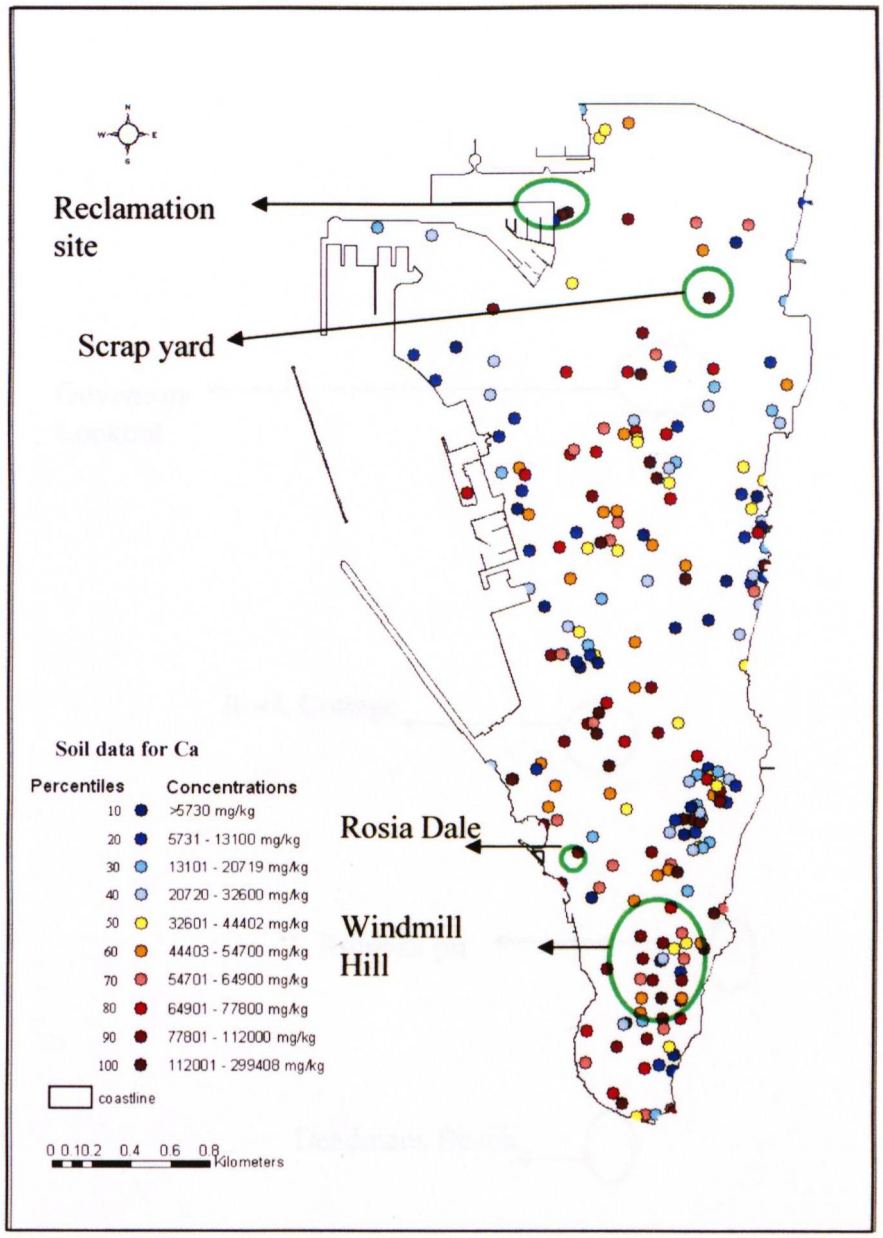


Figure 7.9 Ca concentrations in soils (0-15 cms) from Gibraltar. (n=238)

Samples taken form natural soil on limestone parent material soil have concentrations of Ca that are higher than other areas. Values are generally lower in garden soils imported from Spain and on the areas of fill and made ground. The only exception is the reclamation site near the airport which was unfinished when the samples were taken, that is, the ground had not been paved over and consisted of reclaimed sands on the surface. Once again the same sites (namely Windmill hill, Scrap yard, Cave shelter) have Ca concentrations above the 95th percentile value of 125000 mg/kg.



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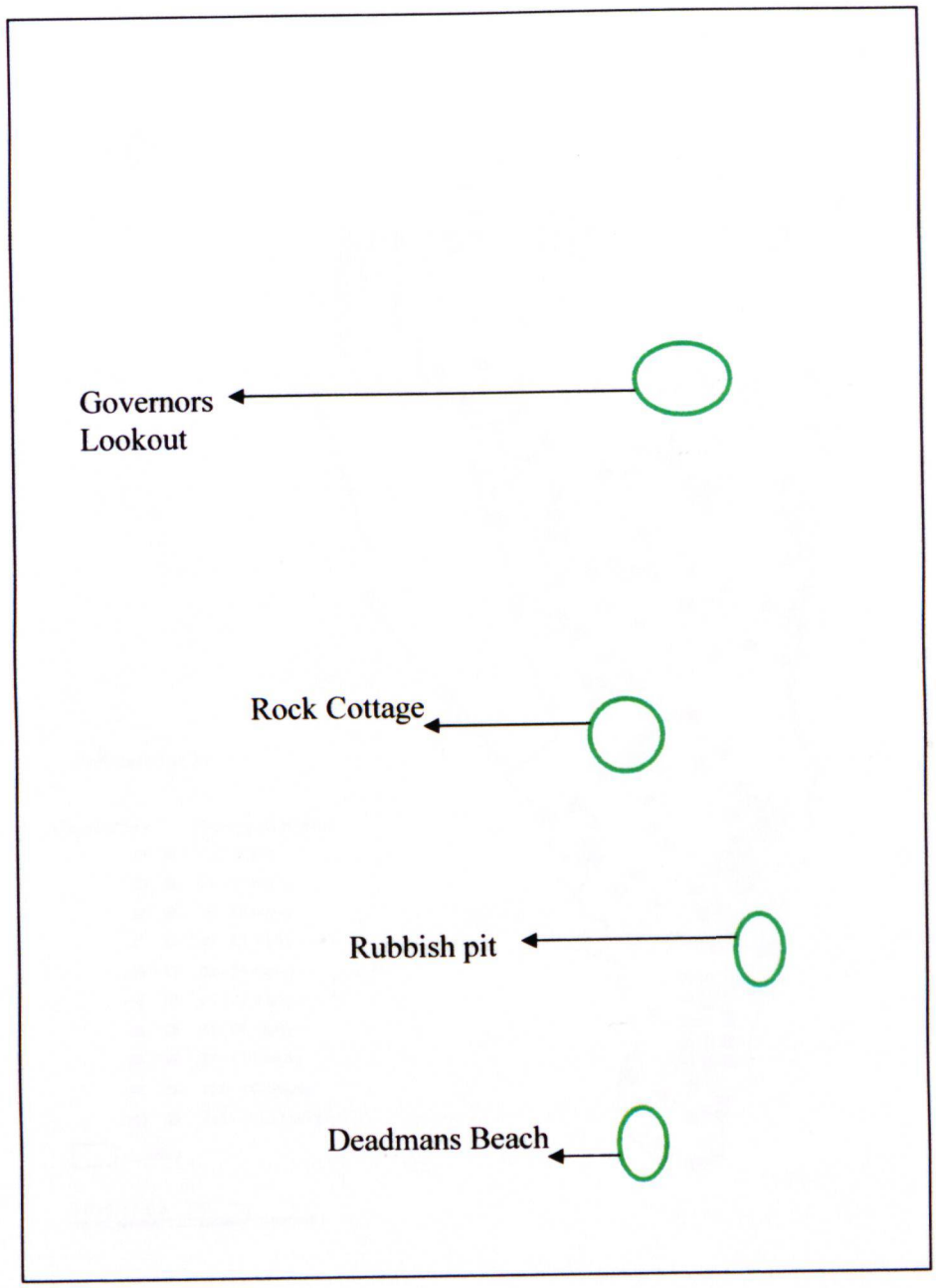

Governors
Lookout
Rock Cottage
Rubbish pit
Deadmans Beach

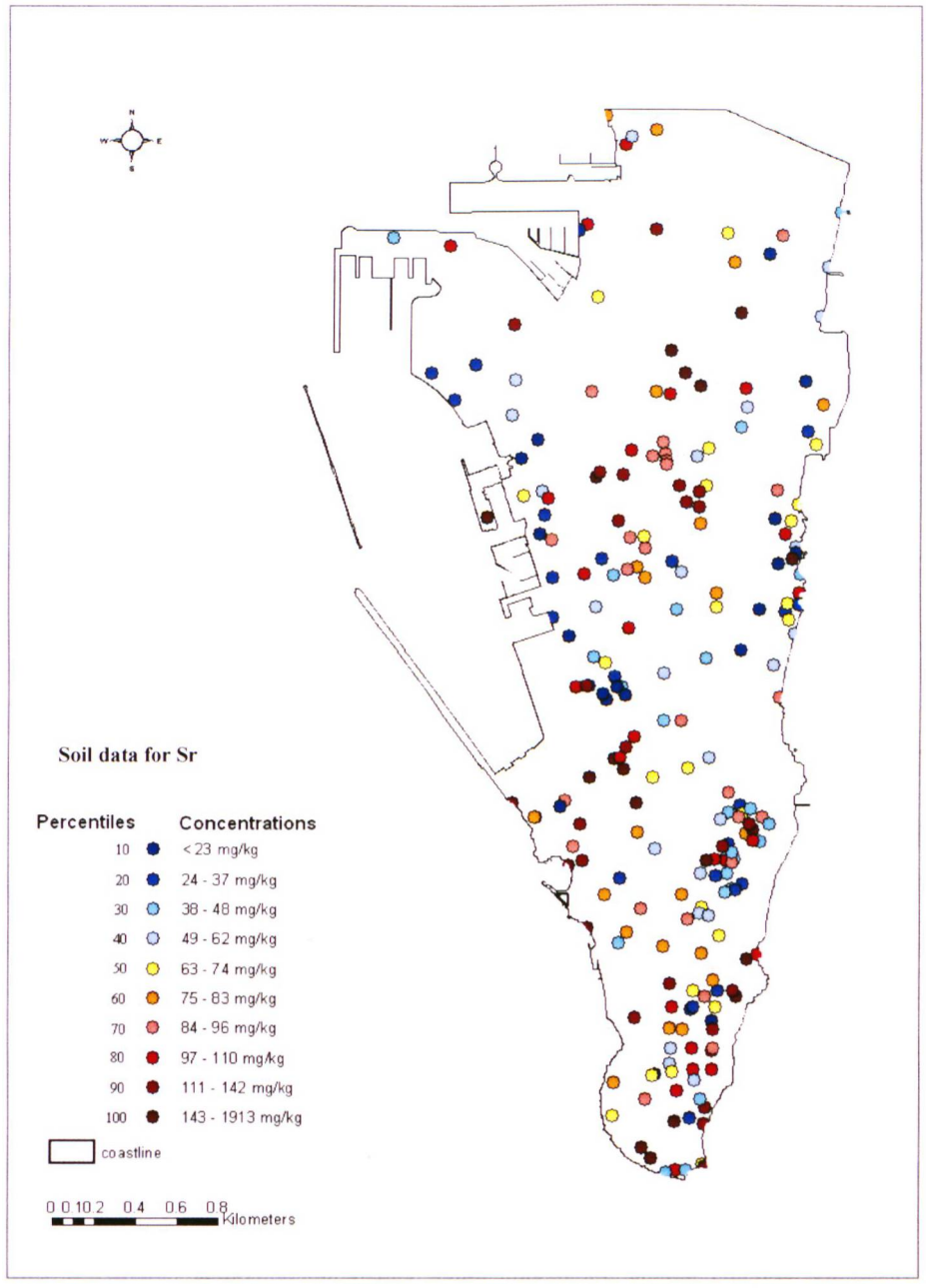
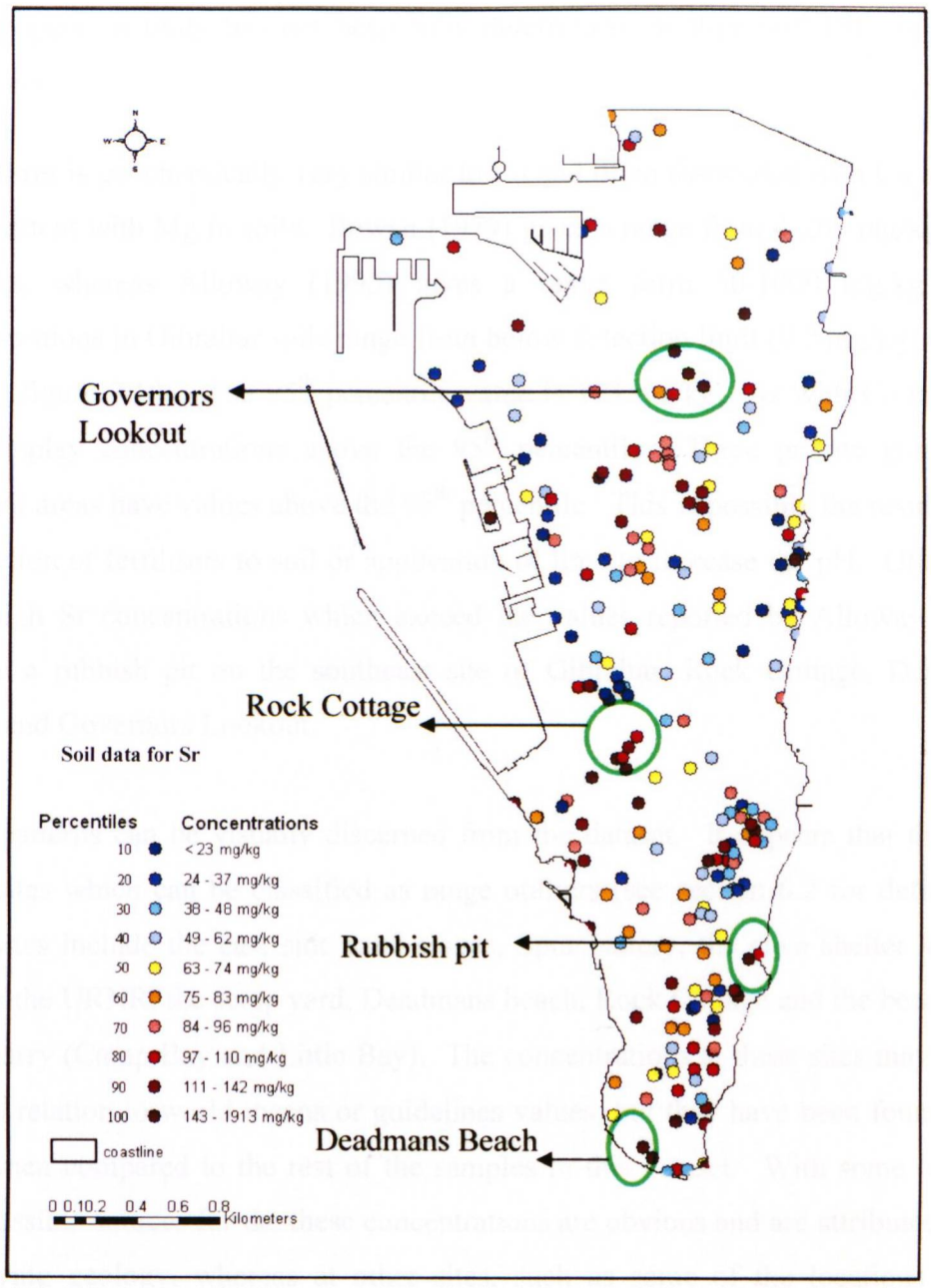


Figure 7.10 Sr concentrations in soils (0-15cms) from Gibraltar. (n=238)

Three sites, which show the possible influence of anthropogenic activity to the addition of Ca, include the incinerator, Spur Battery, the scrap yard and the reclamation site by the airport. Sites which show the influence of the underlying geology include those in the URNR that are found on dark grey dolomite and pale grey dolomite, a sample in Rosia Bay found on interbedded dolomite and limestone, and samples on Windmill Hill, again taken from limestone dolomite material. It should be noted however, that the exact influence of the underlying geology and



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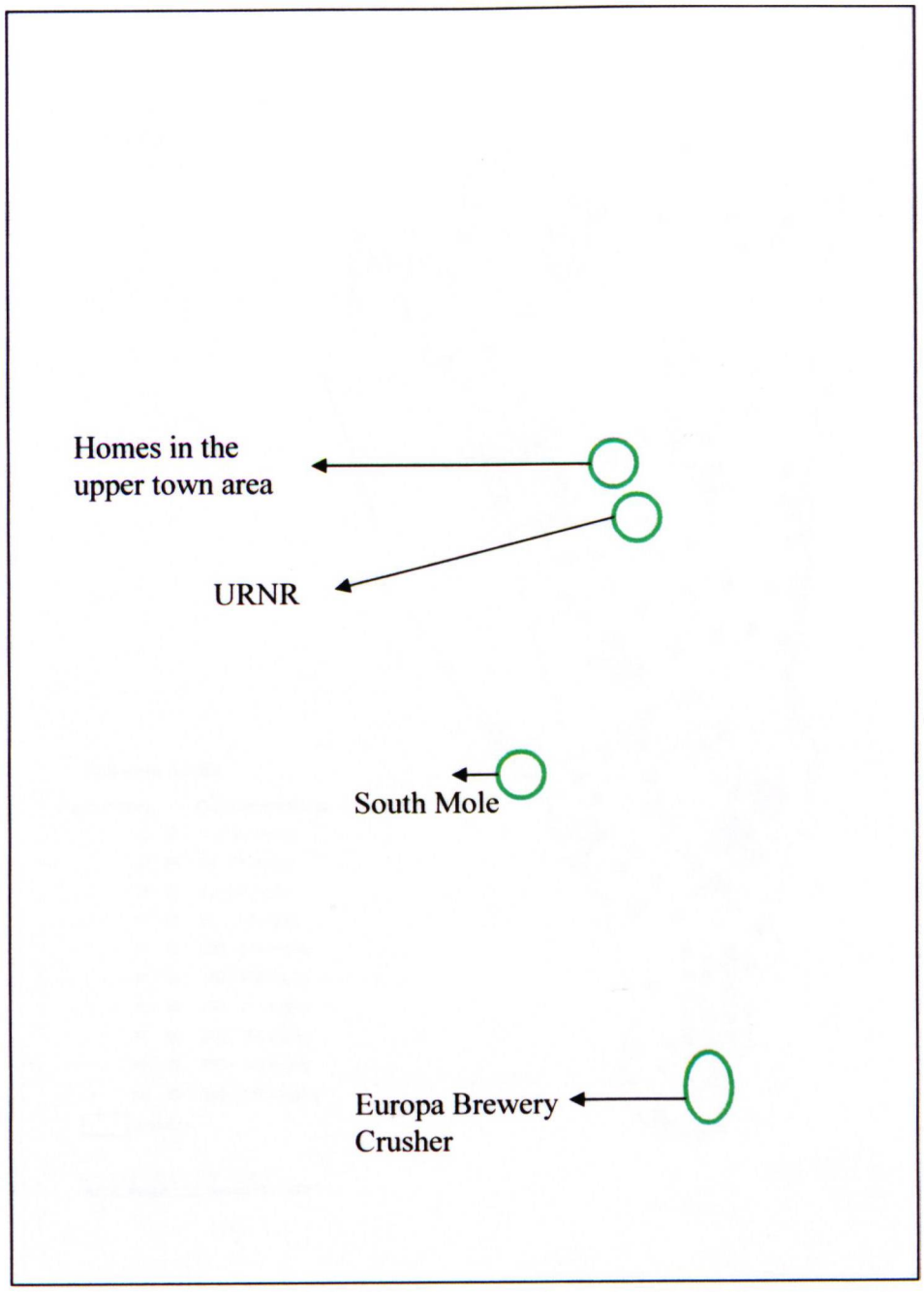
anthropogenic activity has not been fully determined on Windmill Hill as it is an MOD site.

Strontium is geochemically very similar to Ca and often associated with Ca and to a lesser extent with Mg in soils. Bowen (1979) gives a range from 4-200 mg/kg for Sr in soils, whereas Alloway (1995) gives a range form 50-1000 mg/kg. The concentrations in Gibraltar soils range from below detection limit (0.2 mg/kg) to 1913 mg/kg (figure 7.10). The 95th percentile value is 173 mg/kg. As with Ca the same sites display concentrations above the 95th percentile. Three private gardens in different areas have values above the 95th percentile. This is possibly the result of the application of fertilisers to soil or application of lime to increase the pH. Other sites with high Sr concentrations which exceed the values reported by Alloway (1995) include a rubbish pit on the southeast site of Gibraltar, Rock Cottage, Deadmans Beach and Governors Lookout.

Some patterns can be visually discerned from the dataset. It appears that there are some sites which can be classified as range outliers (see section 6.2 for definition). Such sites include the east side sand slopes, Spur battery, the cave shelter selected sites in the URNR, the scrap yard, Deadmans beach, Rock Cottage and the beaches by the Quarry (Camp Bay and Little Bay). The concentrations at these sites may not be high in relation to world means or guidelines values, but they have been found to be high when compared to the rest of the samples in this dataset. With some of these sites possible sources for the these concentrations are obvious and are attributed to the underlying geology, whereas at other sites, such as some of the locations in the URNR, the case of establishing possible sources responsible for the concentrations found is not so simple and the need for further investigations is apparent.

Barium is naturally related to K due to its similar ionic radius. It is not very mobile and is absorbed easily onto clay minerals. A different pattern emerges with Ba in regards to the range outliers. The sites which have been classified as range outliers for the major and trace elements discussed so far (Li, Na, K, Be, Mg, Ca, and Sr) do not apply for Ba. The concentrations reported in Gibraltar soils range from below detection limit (0.02 mg/kg) to 1070 mg/kg (figure 7.11).


Homes in the
upper town area
URNR
South Mole
Europa Brewery
Crusher

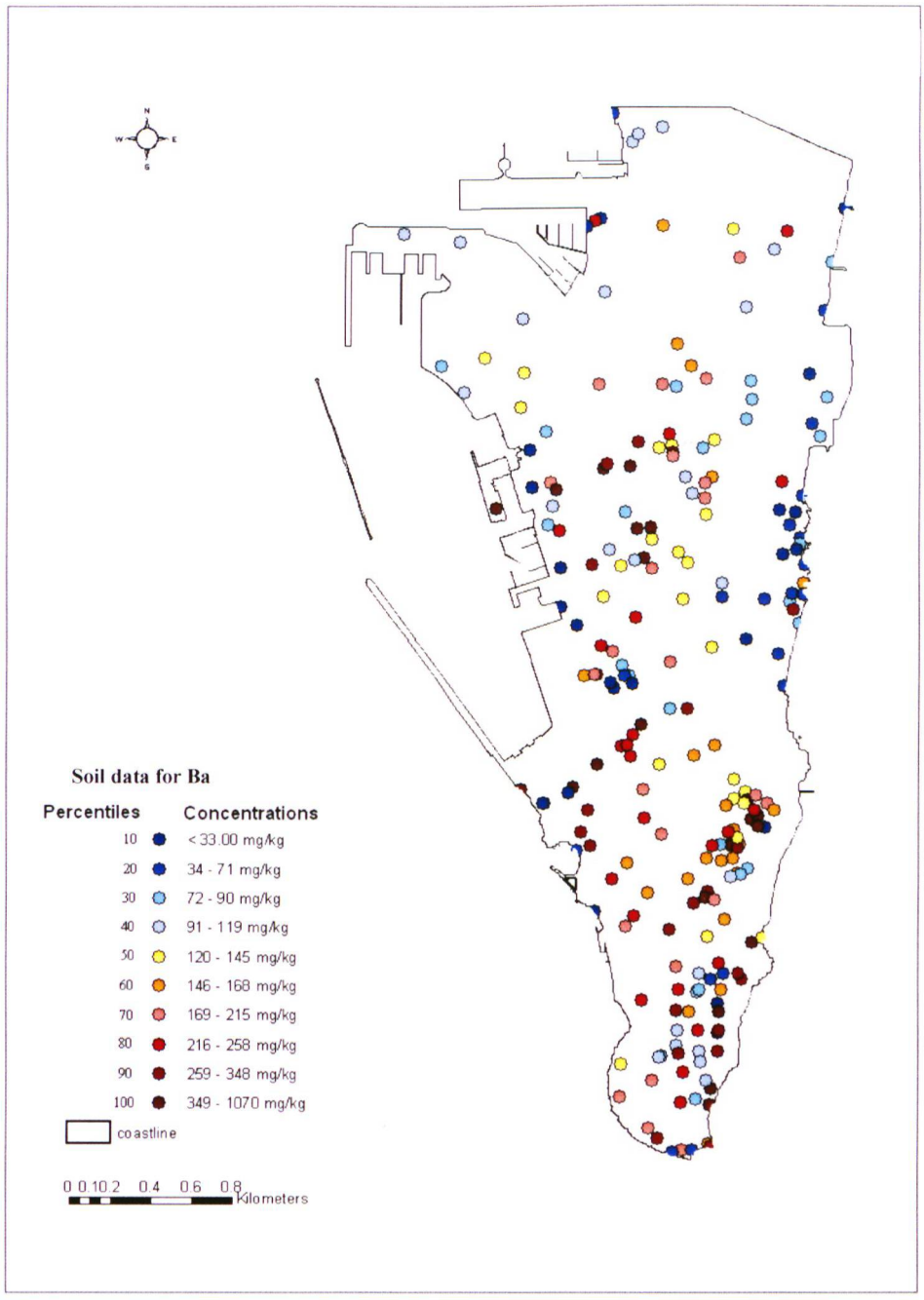
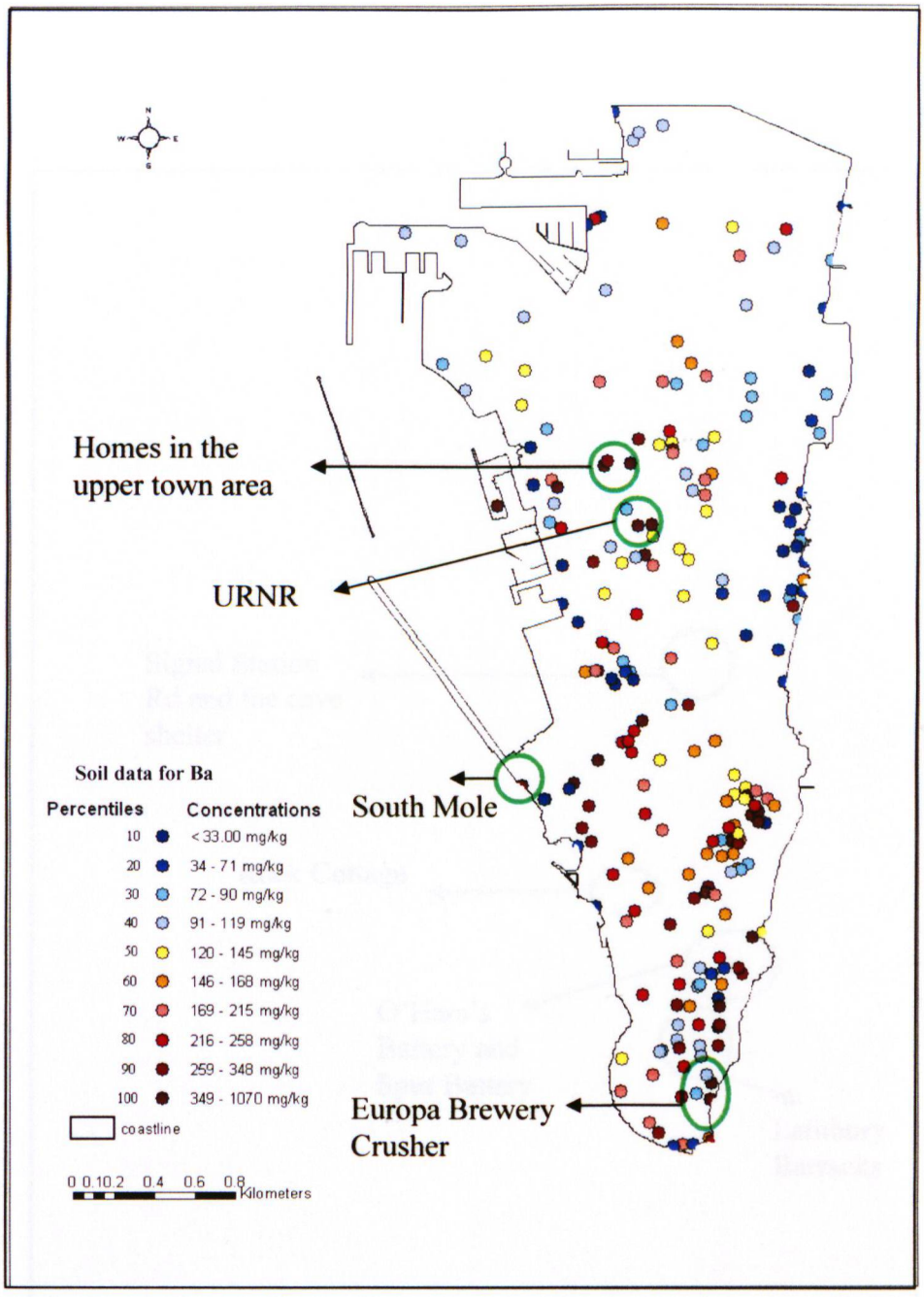


Figure 7.11 Ba concentrations in soils (0-15cms) from Gibraltar. (n=238)

The concentrations in Gibraltar soils are lower than those reported by Bowen (1979) 100–3000 mg/kg for world means but higher than the means reported by Alloway (1995) 100-300 mg/kg for contaminated soils and Ure and Berrow (1982) 72-387 mg/kg for world means. The 95th percentile value is 503 mg/kg and there are eleven sites with concentrations exceeding this value. These include soils near two pre-war buildings in the old upper town area, four sites in the URNR, the clay pigeon shooting



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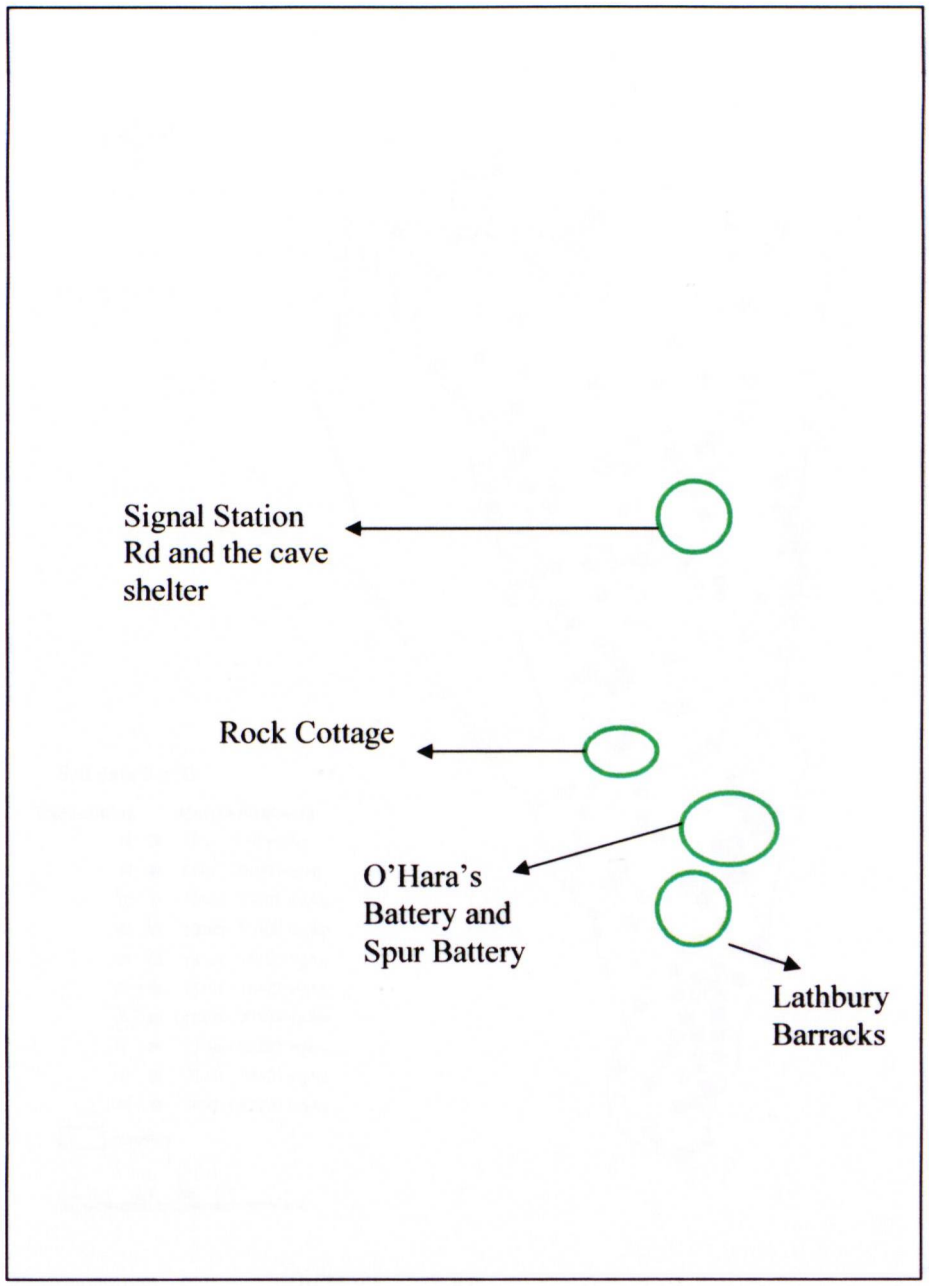

Signal Station
Rd and the cave
shelter
Rock Cottage
O'Hara's
Battery and
Spur Battery
Lathbury
Barracks

range, South Mole by the dockyard and an area called Europa Brewery Crusher, used to store shot blasting sand and other waste materials.

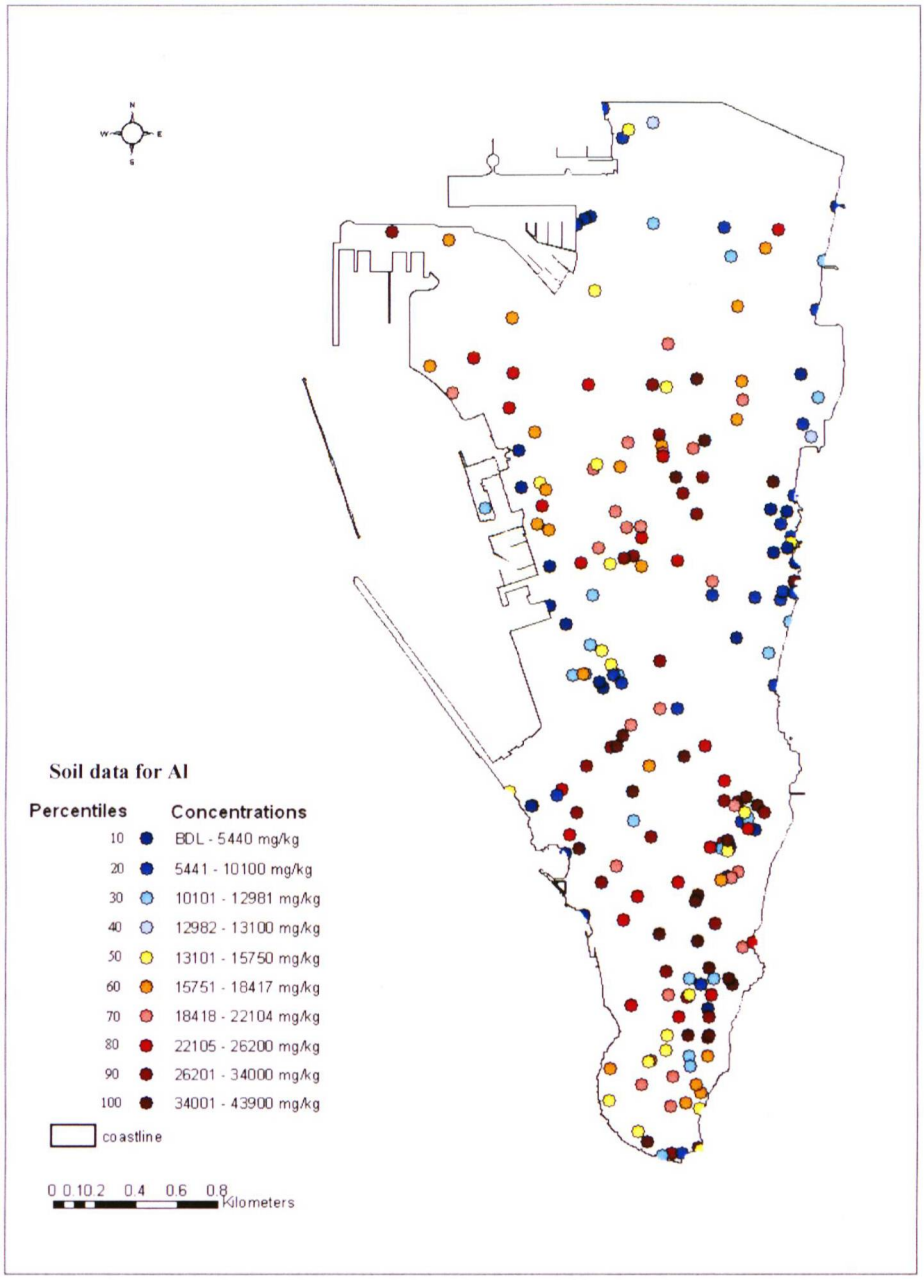


Figure 7.12 Al concentrations in soils (0-15 cms) from Gibraltar

A point to take note of is that all of these sites also have high (when compared to the entire dataset, as well as establishes SGV's and reported world means) Pb and Zn concentrations suggesting an anthropogenic influence possibly from traffic (see section on Pb, figure 7.24.

range, South Mole by the dockyard and an area called Europa Brewery Crusher, used to store shot blasting sand and other waste materials.

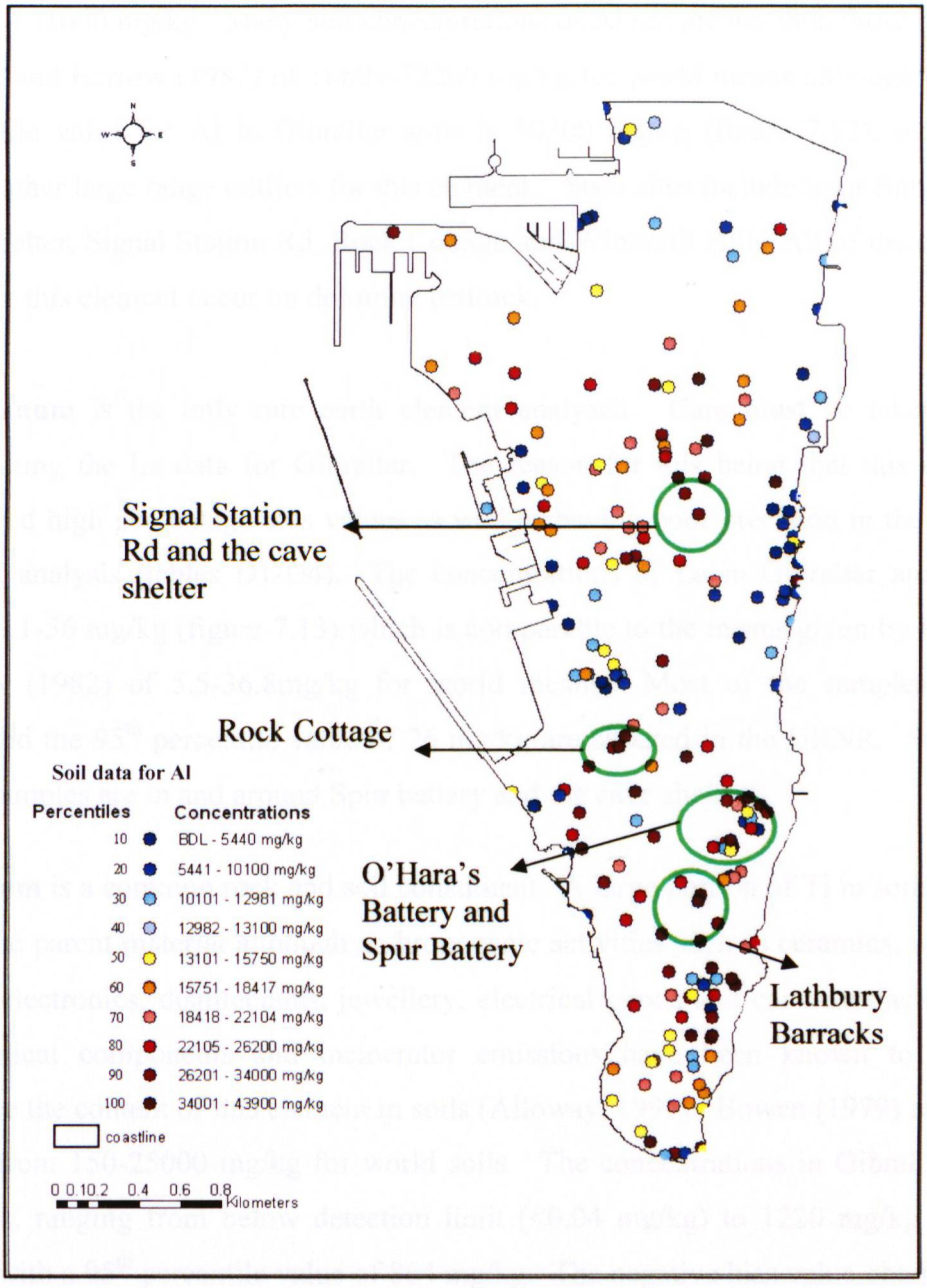


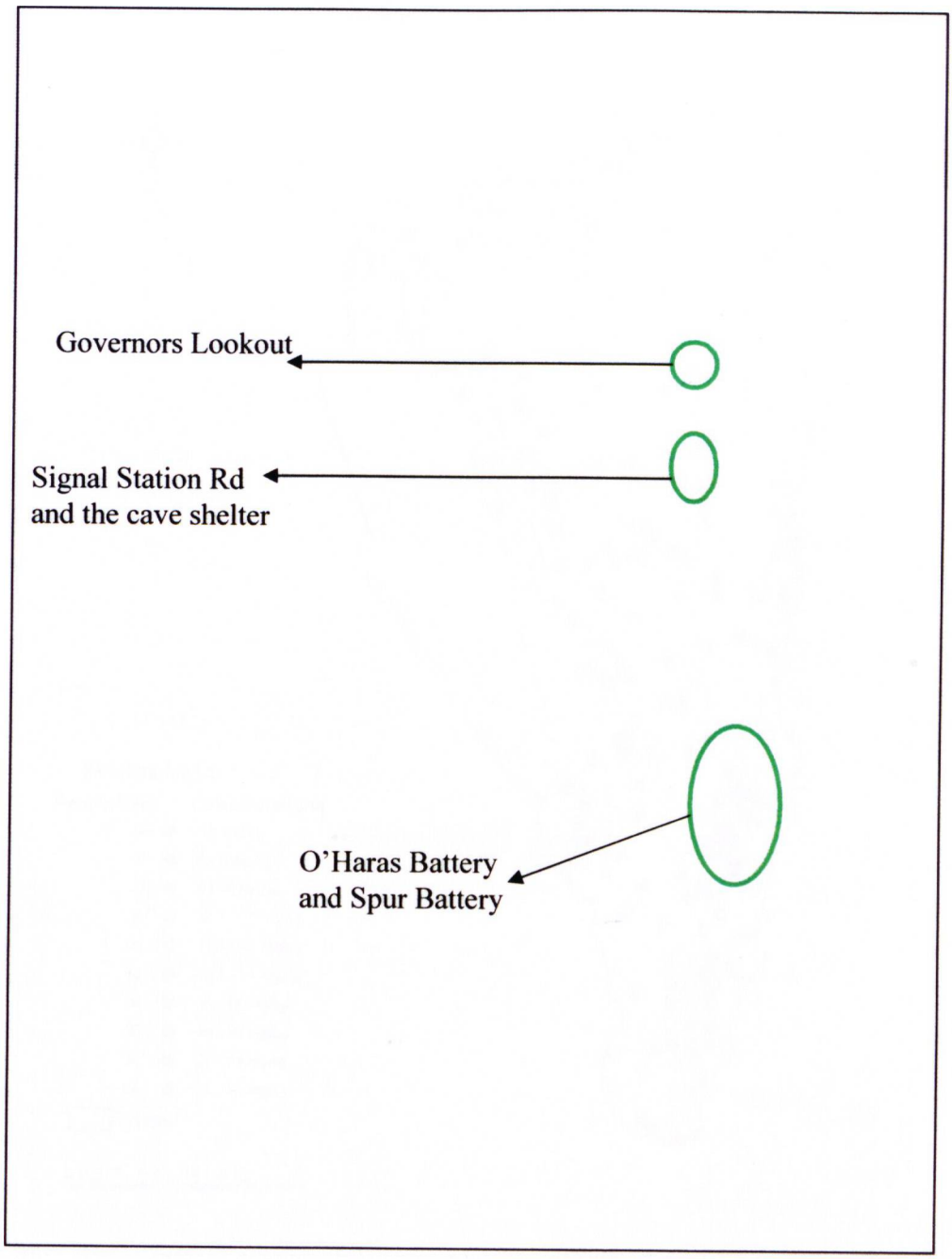
Figure 7.12 Al concentrations in soils (0-15 cms) from Gibraltar

A point to take note of is that all of these sites also have high (when compared to the entire dataset, as well as establishes SGV's and reported world means) Pb and Zn concentrations suggesting an anthropogenic influence possibly from traffic (see section on Pb, figure 7.24.

Aluminium is a main component of the earth's crust. It is one of the least mobile elements during weathering therefore its composition in soils largely reflects the composition of the parent rocks. The concentrations found in Gibraltar soils range from 2-131000 mg/kg. Many soil concentrations of Al are greater than those reported by Ure and Berrow (1982) of 16600-72200 mg/kg for world means although the 95th percentile value for Al in Gibraltar soils is 50300 mg/kg (figure 7.12), indicating some rather large range outliers for this element. Such sites include Spur Battery, the cave shelter, Signal Station Rd, Rock Cottage and Windmill Hill. All of the outlying sites for this element occur on dolomite bedrock.

Lanthanum is the only rare earth element analysed. Care must be taken when interpreting the La data for Gibraltar. The reason for this being that this element displayed high percentage bias values as well as having poor precision in the quality control analysis (tables D1-D4). The concentrations of La in Gibraltar are in the range 0.1-56 mg/kg (figure 7.13) which is comparable to the means given by Ure and Berrow (1982) of 5.5-36.8mg/kg for world means. Most of the samples which exceeded the 95th percentile value of 26 mg/kg are situated in the URNR. Seven of these samples are in and around Spur battery and the cave shelter.

Titanium is a common rock and soil constituent. A large portion of Ti in soils comes from the parent material although anthropogenic activities such as ceramics, wire and cable, electronics, disinfectants, jewellery, electrical goods and car manufacture and mechanical components and incinerator emissions have been known to greatly increase the content of this element in soils (Alloway, 1995). Bowen (1979) reports a range from 150-25000 mg/kg for world soils. The concentrations in Gibraltar soils are less, ranging from below detection limit (<0.04 mg/kg) to 1220 mg/kg (figure 7.14), with a 95th percentile value of 864 mg/kg. The negative bias value obtained for Ti on the NIST SRMs (tables D3 and D4) is possibly an indication of partial dissolution of this element. As with most of the elements discussed above, sites such as Rock Cottage, Spur Battery, O'Haras Battery and Signal Station Road display concentrations which are greater than the majority of the dataset. Sites, which have not been mentioned so far, include the residential and commercial area of Europort, Jews Cemetery in the URNR and Lathbury Barracks (old abandoned barracks that used to belong to the MOD).


Governors Lookout
Signal Station Rd
and the cave shelter
O'Haras Battery
and Spur Battery

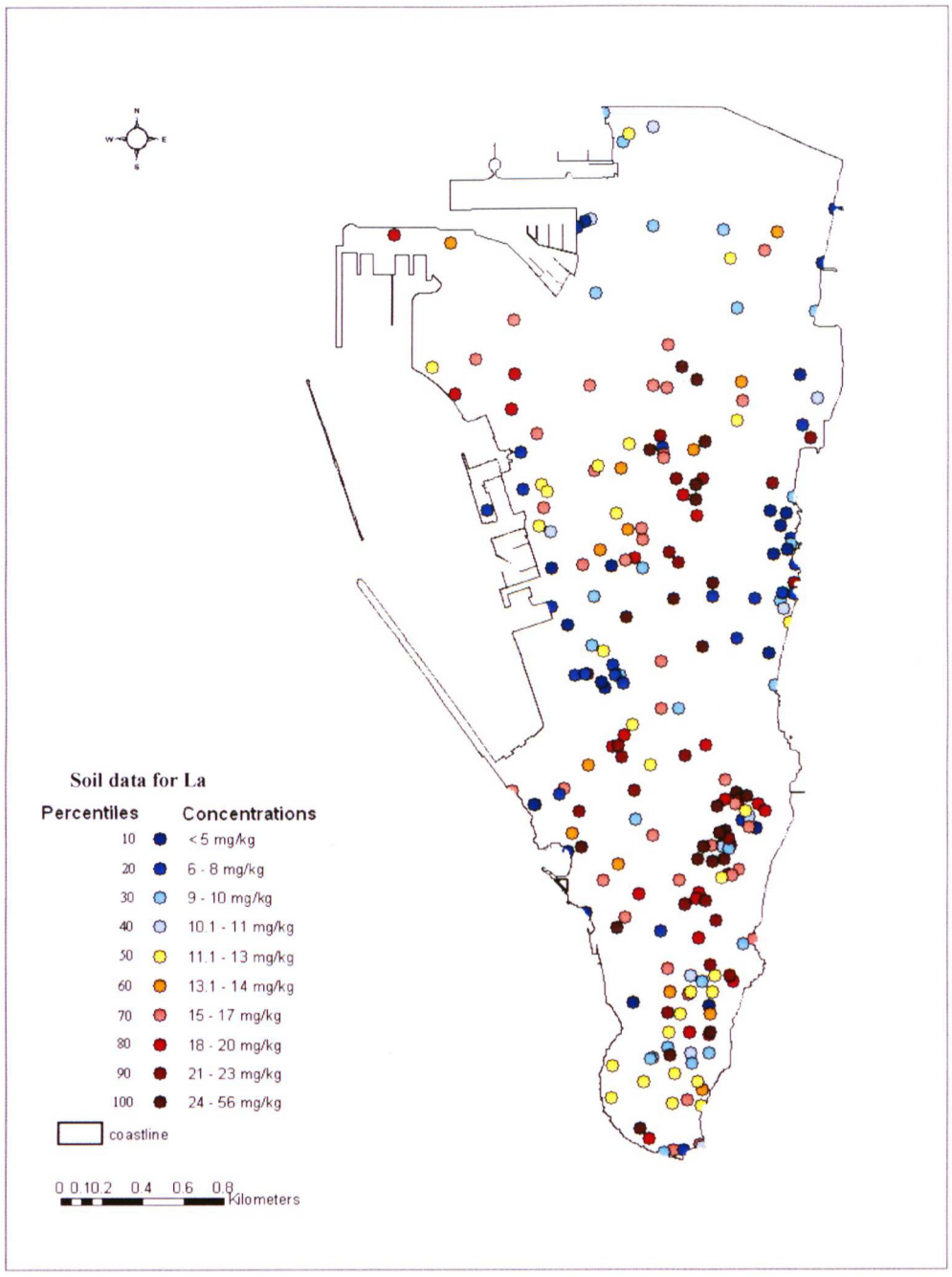


Figure 7.13 La concentrations in soils (0-15 cms) from Gibraltar. (n=238)

Please note, La data for Gibraltar displayed high bias values and poor precision in the QC. Care should be taken when interpreting the data.

In terms of the influence of the underlying geology, the samples with the highest concentrations once again occur on limestone dolomite, pale grey dolomite and interbedded limestone and dolomite.

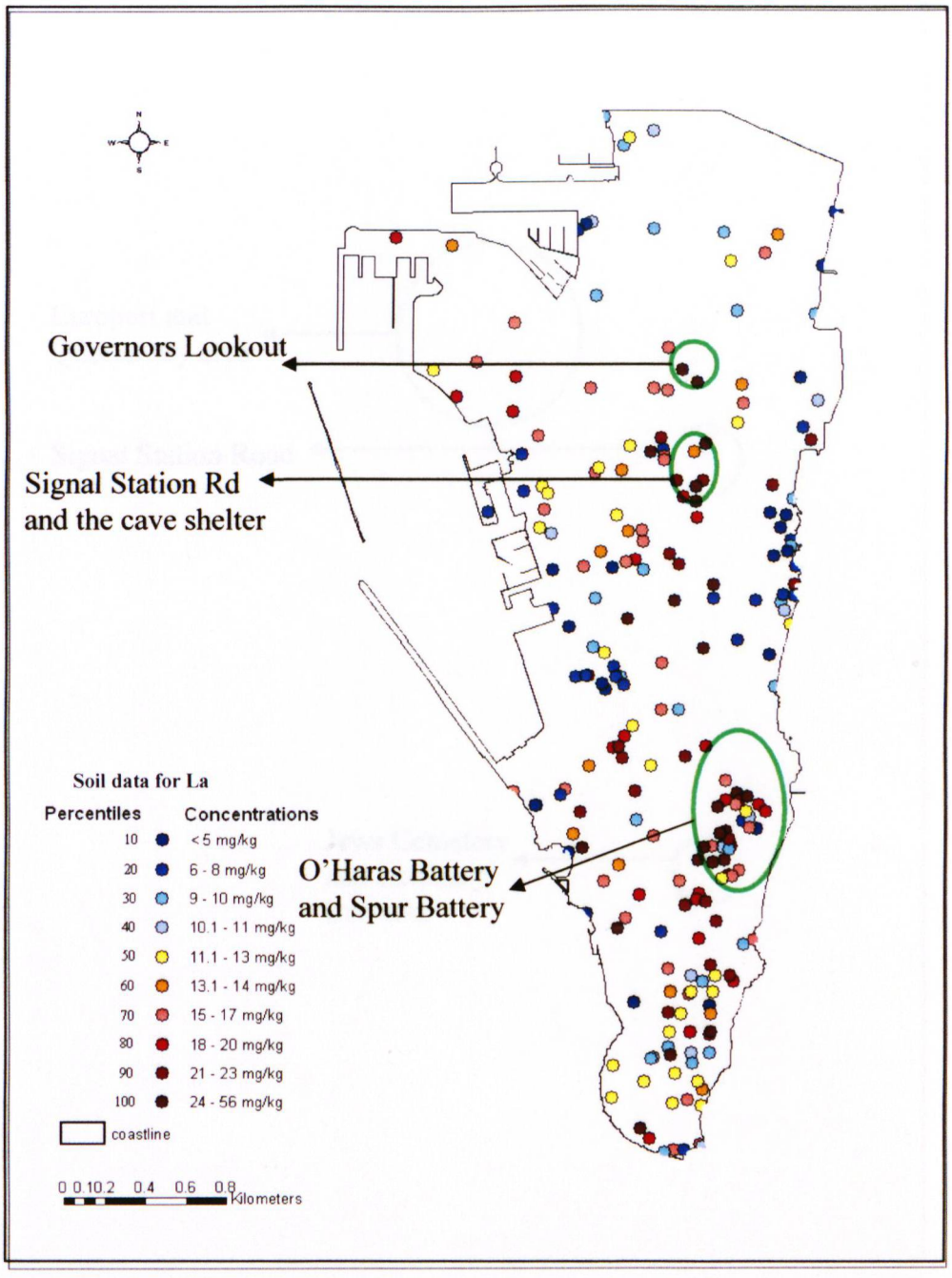


Figure 7.13 La concentrations in soils (0-15 cms) from Gibraltar. (n=238)

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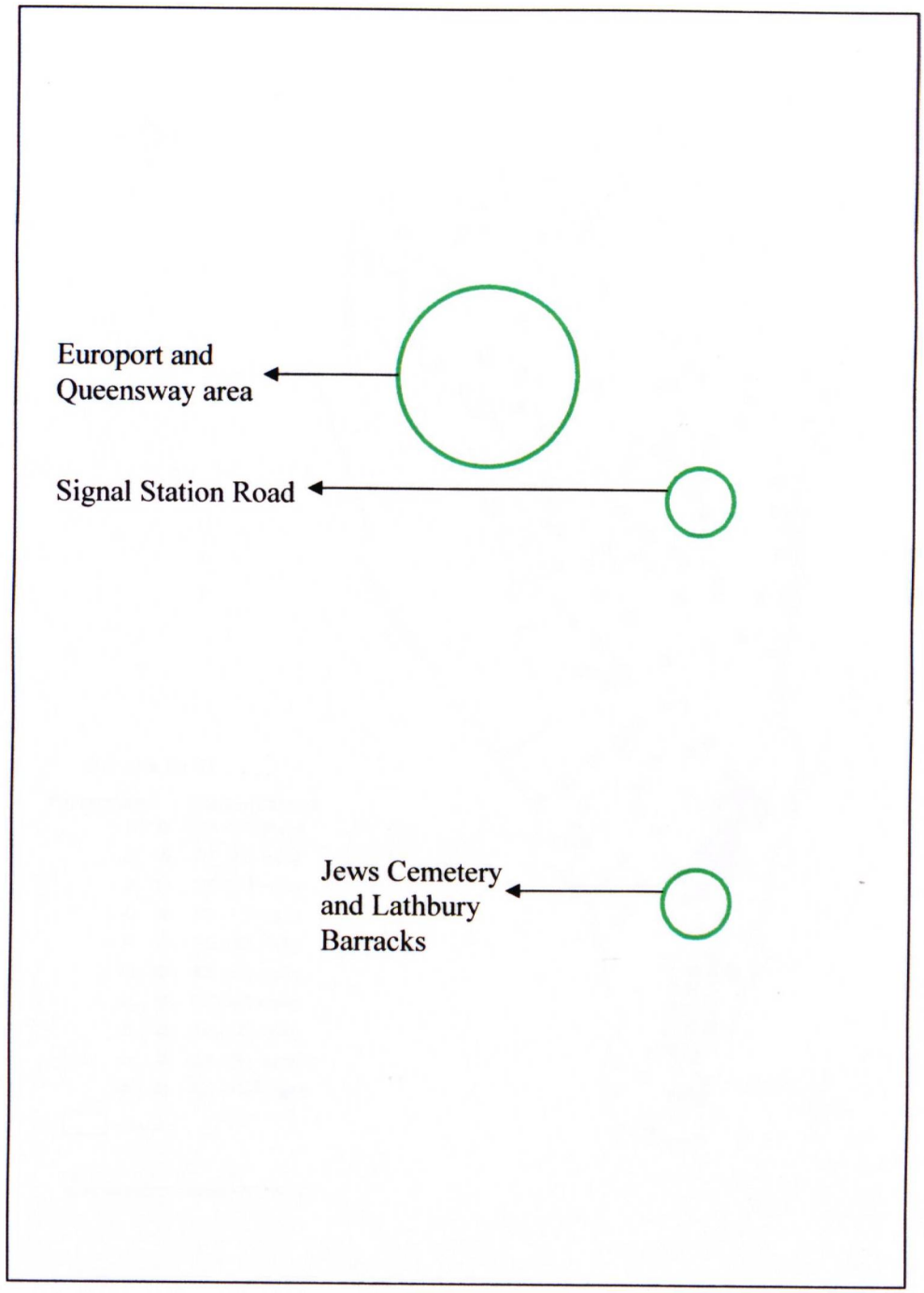

Europort and
Queensway area
Signal Station Road
Jews Cemetery
and Lathbury
Barracks

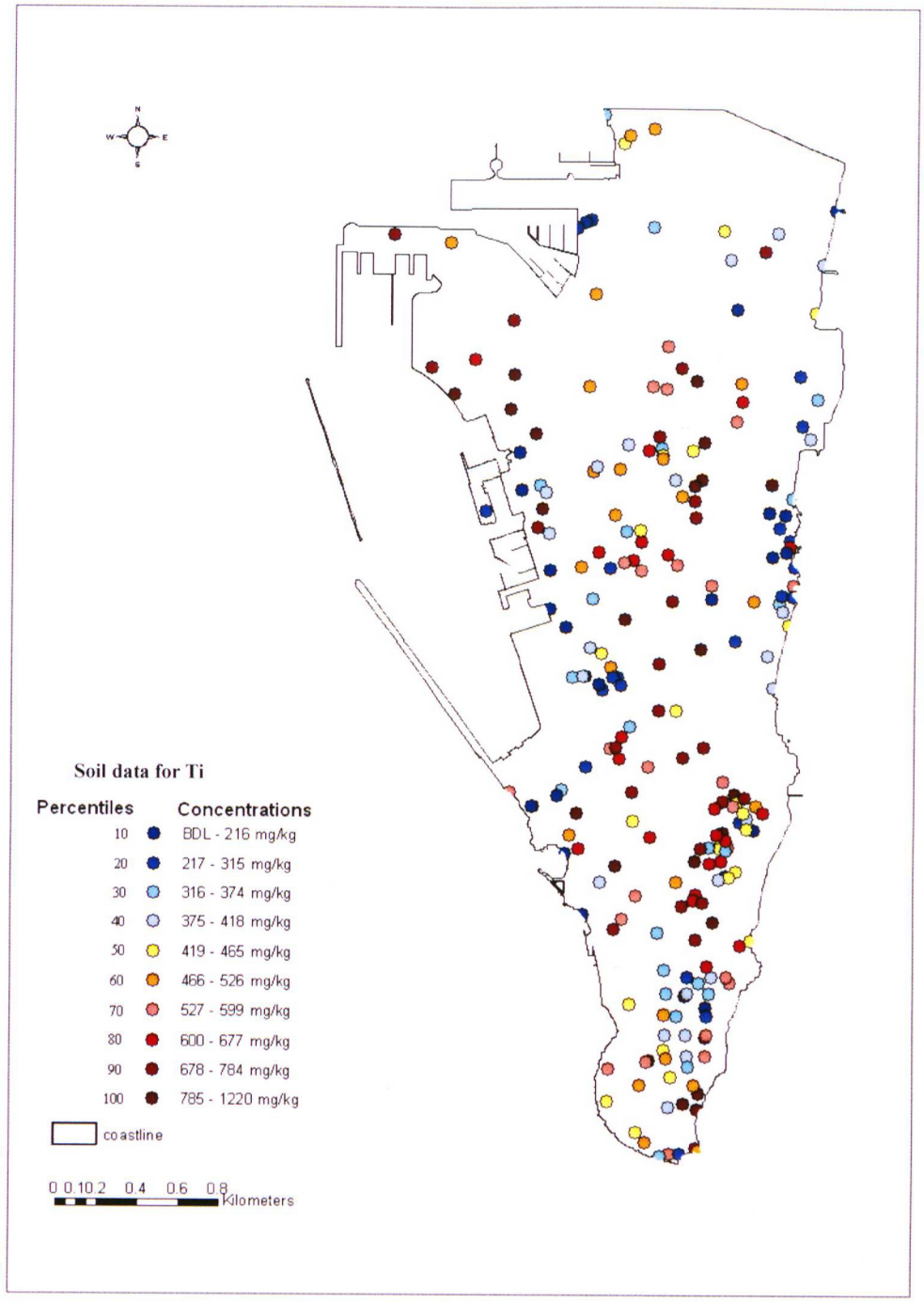


Figure 7.14 Ti concentrations in soils (0-15cms) from Gibraltar. (n=238)

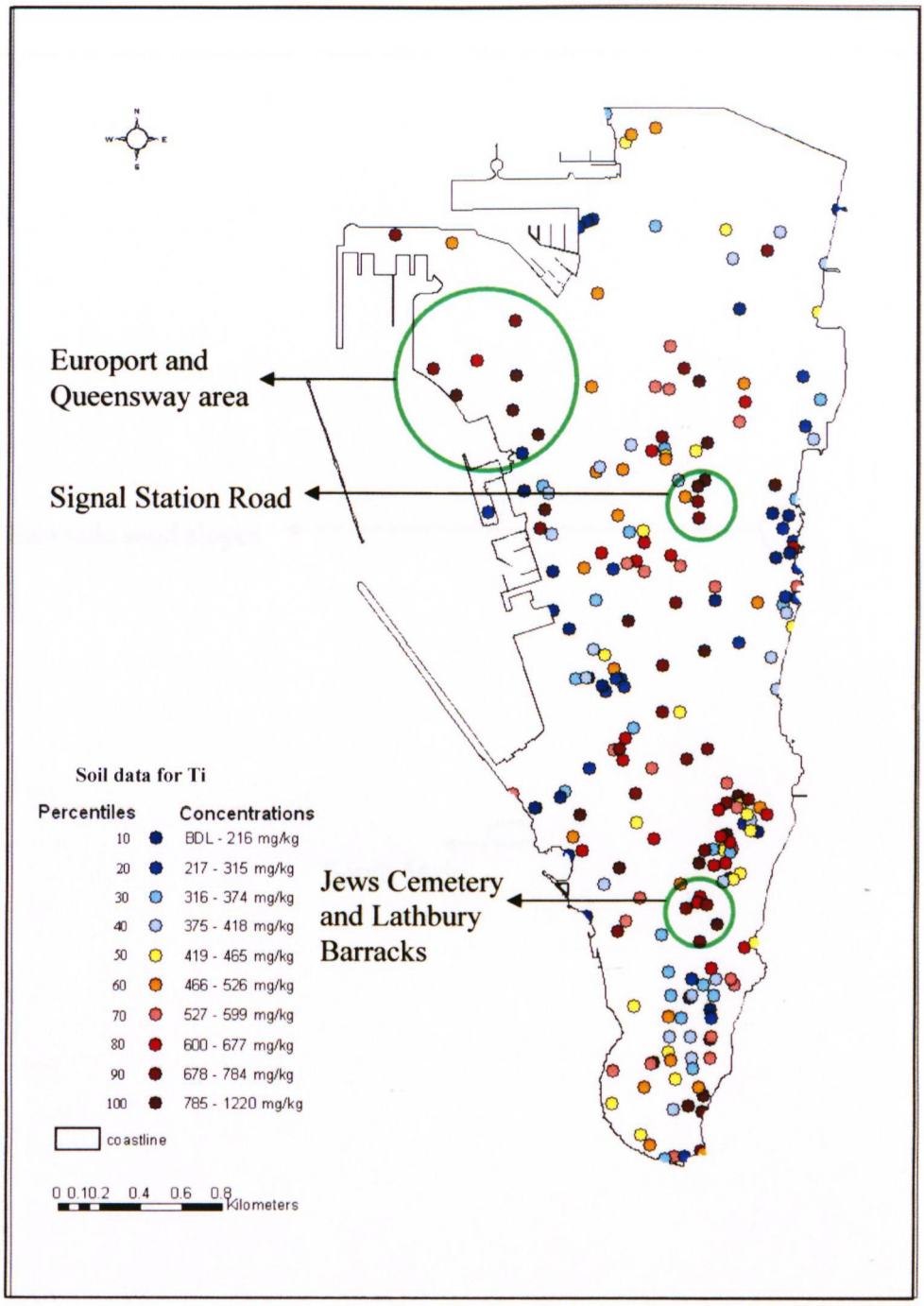
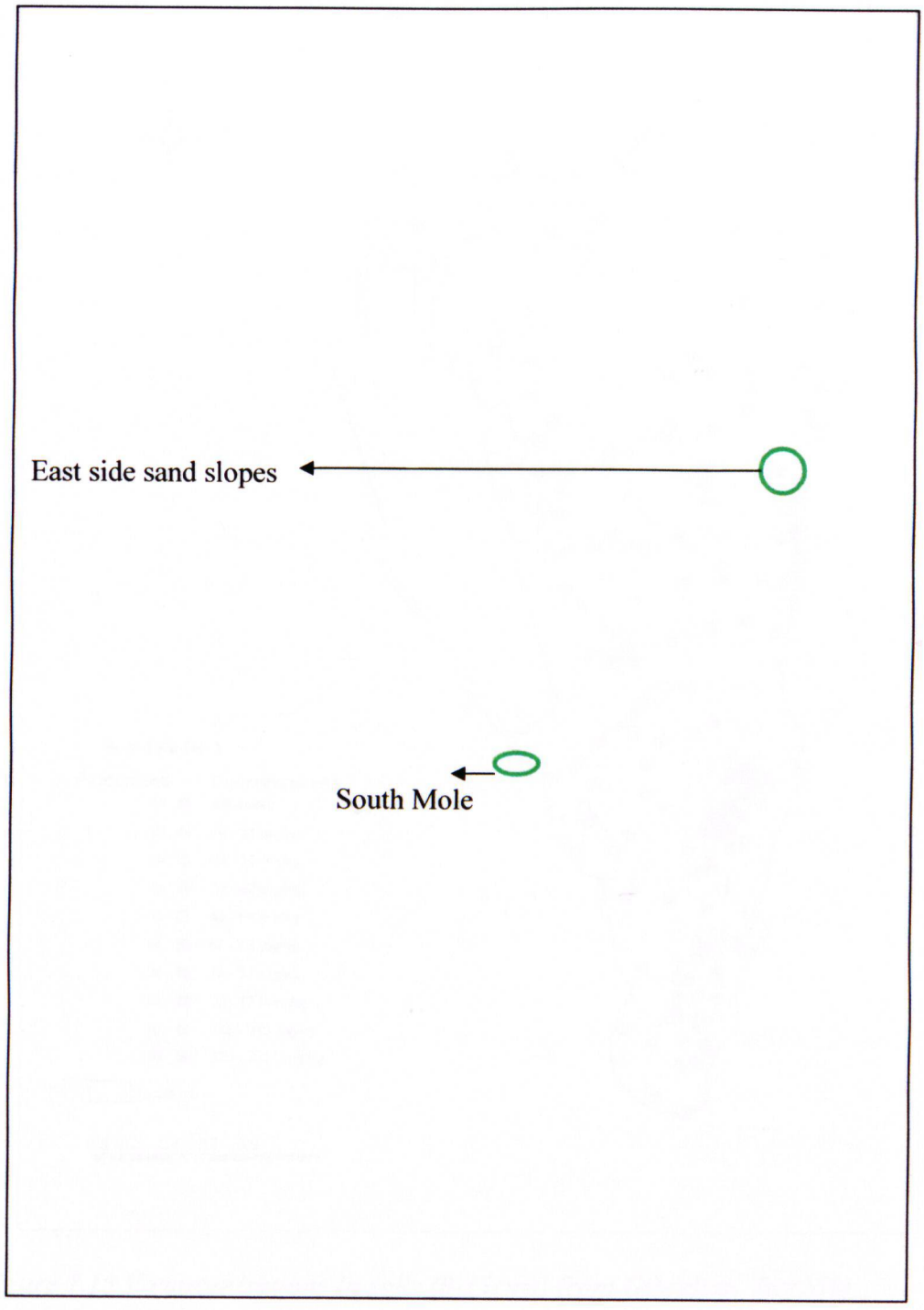


Figure 7.14 Ti concentrations in soils (0-15cms) from Gibraltar. (n=238)


East side sand slopes
South Mole

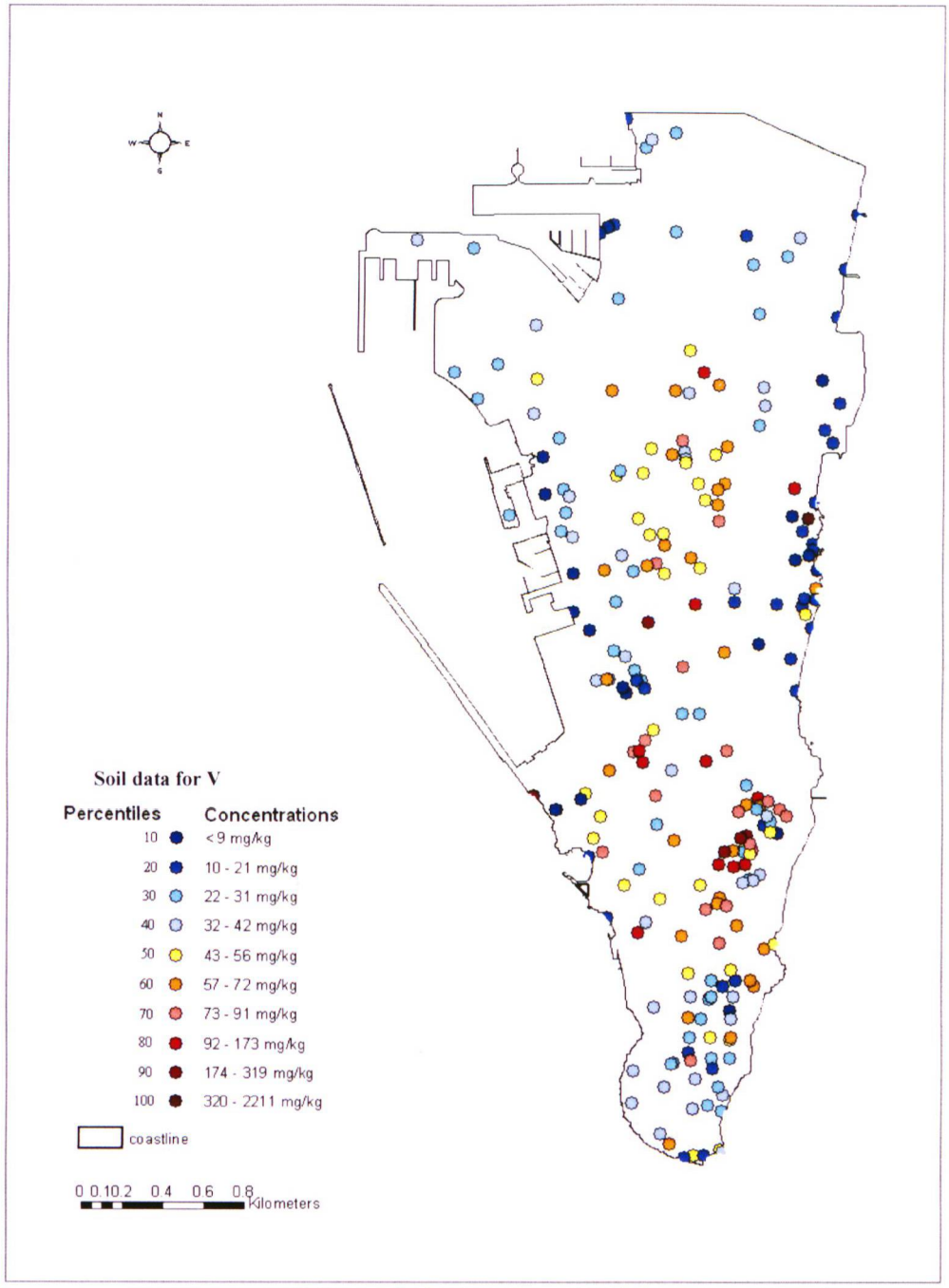


Figure 7.15 V concentrations in soils (0-15cms) from Gibraltar. (n=238)

The **Vanadium** content of soils depends on the soil parent material and the pedogenic processes associated with their development (Alloway, 1995). It has a wide industrial use but the major anthropogenic sources of V enrichment in soils are from the combustion of fossil fuels and wastes from such processes (Alloway, 1995). The crustal abundance of V is similar to that of Pb, Cu, Ni and Zn although it is more dispersed resulting in lower concentrations in soils. Bowen (1979) reports a range of

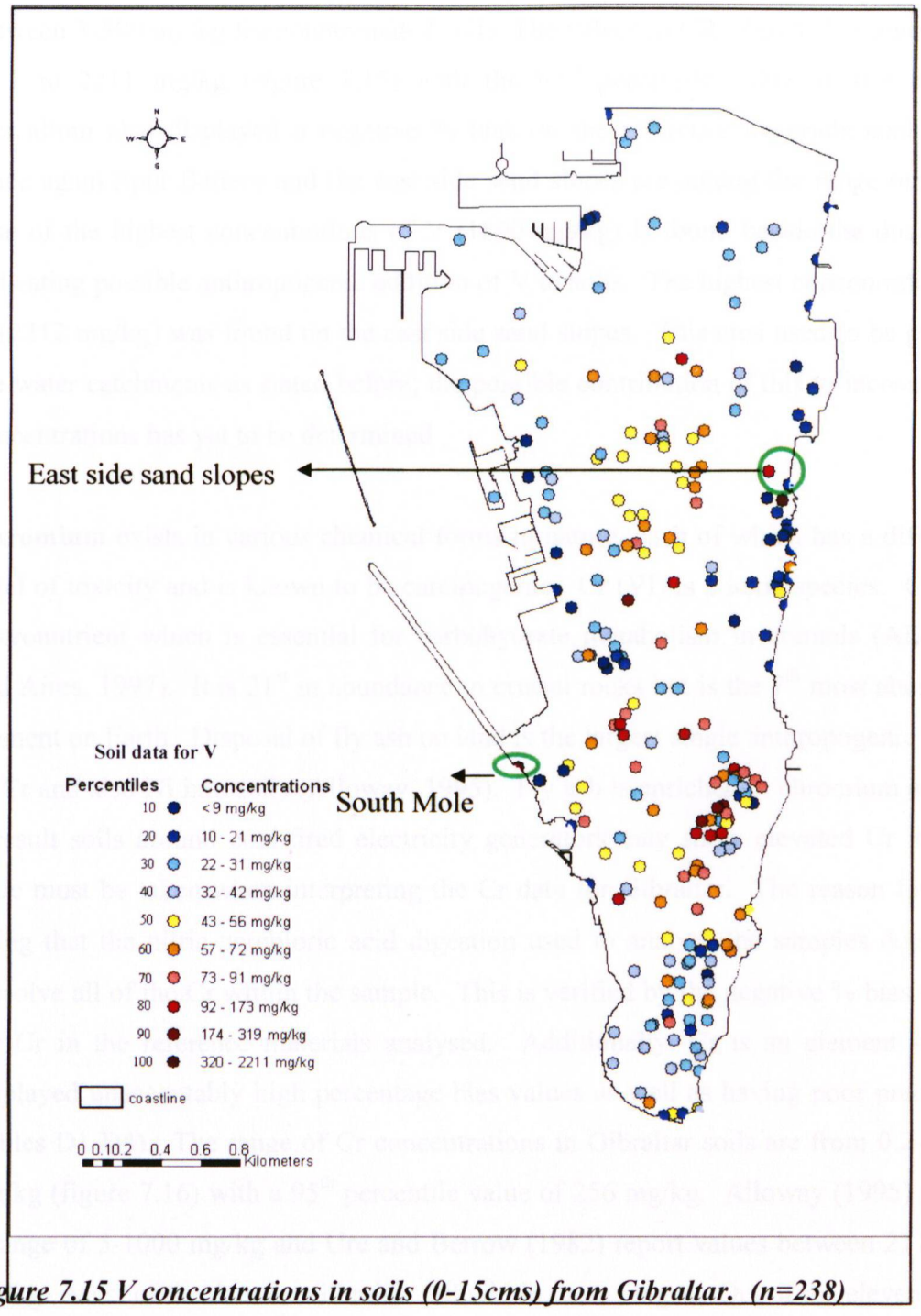


Figure 7.15 V concentrations in soils (0-15cms) from Gibraltar. (n=238)

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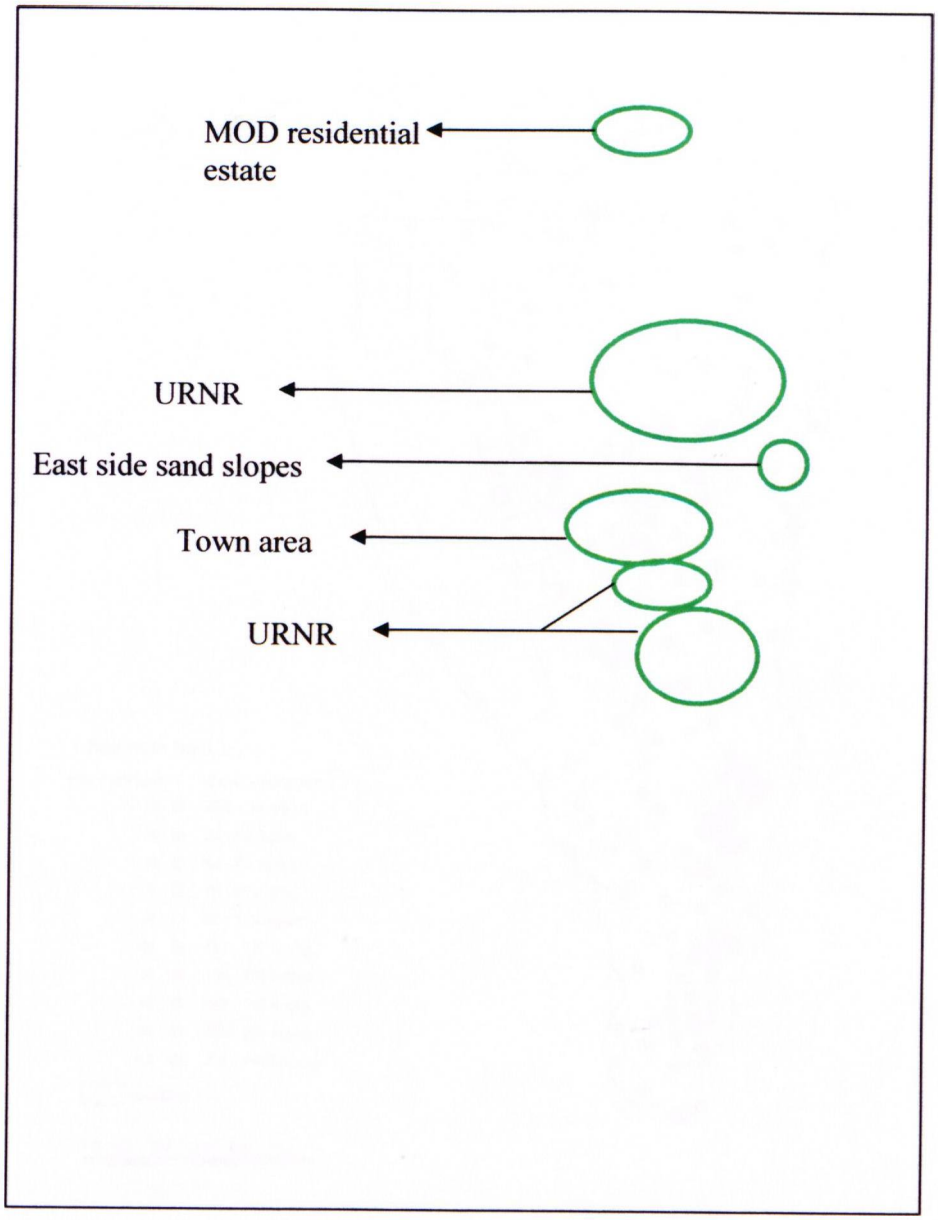
values between 3-300 mg/kg for world means, and Alloway (1995) reports a range between 3-500 mg/kg for contaminated soils. The values in Gibraltar soils range from <0.1 to 2211 mg/kg (figure 7.15) with the 95th percentile value of 109 mg/kg (vanadium also displayed a negative % bias on the reference materials analysed). Once again Spur Battery and the east side sand slopes are among the range outliers. One of the highest concentrations of V (1890 mg/kg) is found beside the dockyard indicating possible anthropogenic addition of V to soils. The highest concentration of V (2212 mg/kg) was found on the east side sand slopes. This area used to be part of the water catchments as stated before; the possible contribution of this to increased V concentrations has yet to be determined

Chromium exists in various chemical forms in nature, each of which has a different level of toxicity and is known to be carcinogenic. Cr (VI) is a toxic species. Cr is a micronutrient which is essential for carbohydrate metabolism in animals (Alloway and Aires, 1997). It is 21st in abundance in crustal rocks but is the 7th most abundant element on Earth. Disposal of fly ash on land is the largest single anthropogenic input of Cr and also Ni into soils (Alloway, 1995). Fly ash is enriched in chromium and as a result soils around coal-fired electricity generators may show elevated Cr levels. Care must be taken when interpreting the Cr data for Gibraltar. The reason for this being that the nitric-perchloric acid digestion used to analyse the samples does not dissolve all of the Cr within the sample. This is verified by the negative % bias value for Cr in the reference materials analysed. Additionally, Cr is an element which displayed unacceptably high percentage bias values as well as having poor precision (tables D1-D4). The range of Cr concentrations in Gibraltar soils are from 0.2-1445 mg/kg (figure 7.16) with a 95th percentile value of 256 mg/kg. Alloway (1995) gives a range of 5-1000 mg/kg and Ure and Berrow (1982) report values between 217-300 mg/kg. Most of the data for Gibraltar fall within these ranges. Out of the eleven sites with high Cr concentrations 8 of them are found in the URNR.


MOD residential estate
URNR
East side sand slopes
Town area
URNR

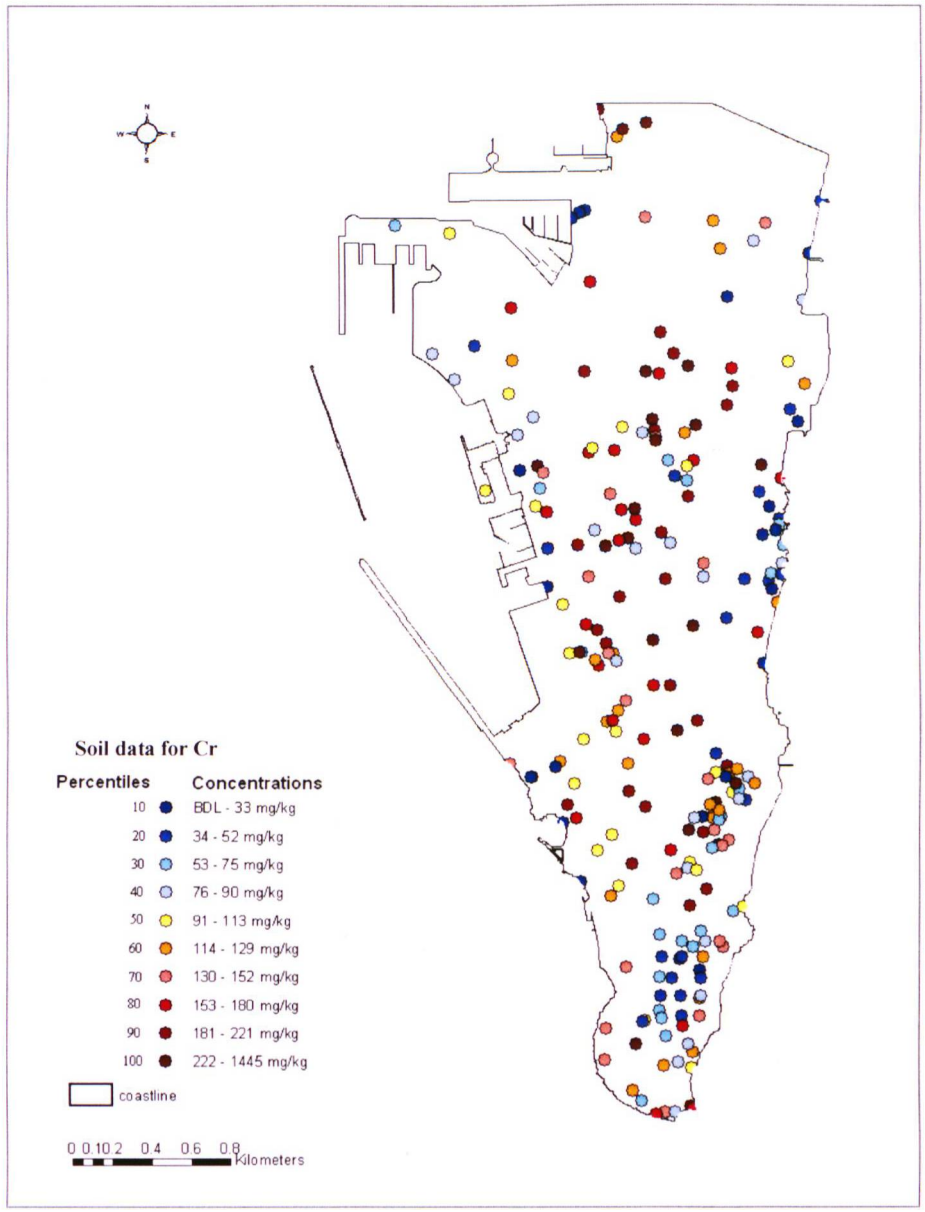


Figure 7.16 Cr concentrations in soils (0-15cms) from Gibraltar. (n=238)

Please note, Cr data for Gibraltar displayed high bias values and poor precision in the QC. Care should be taken when interpreting the data.

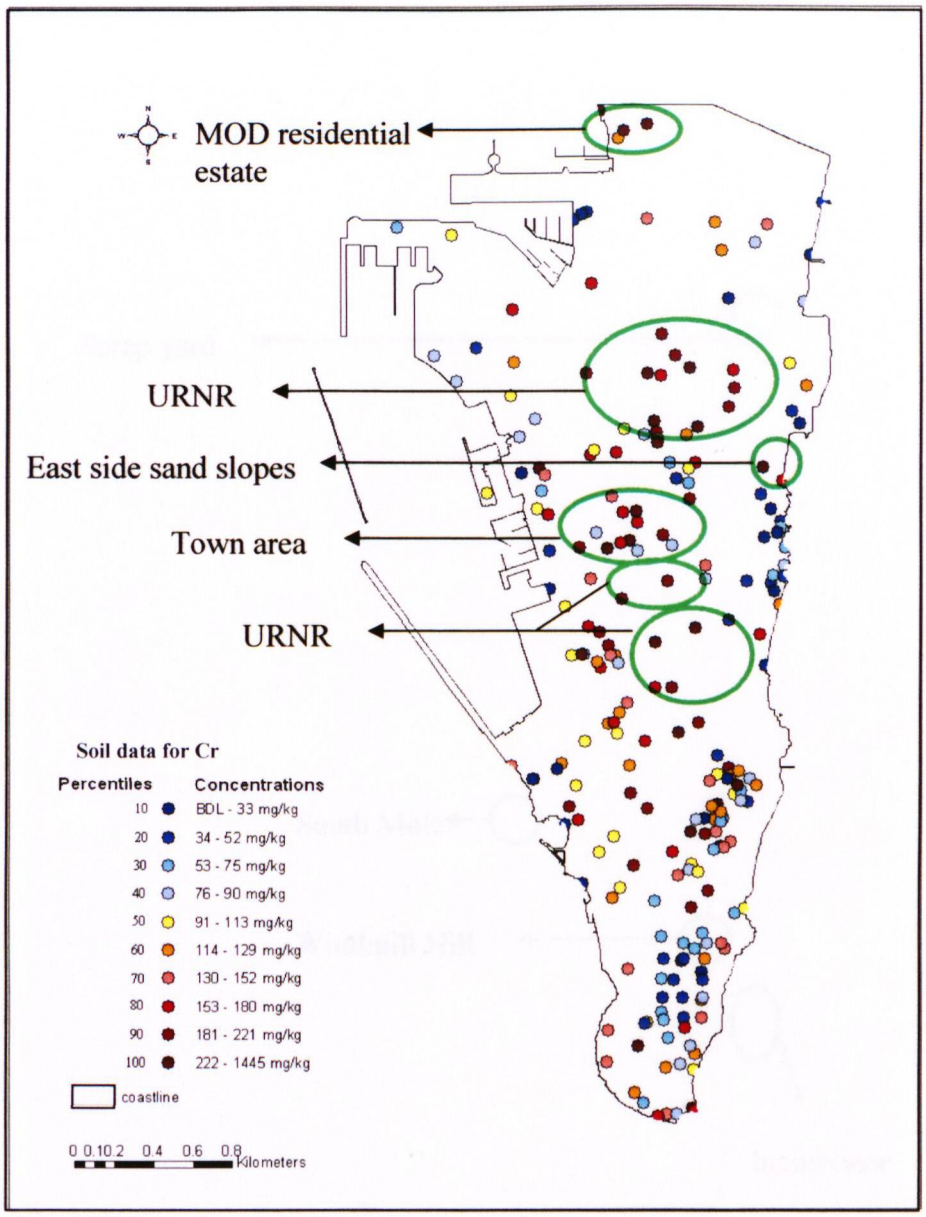


Figure 7.16 Cr concentrations in soils (0-15cms) from Gibraltar. (n=238)

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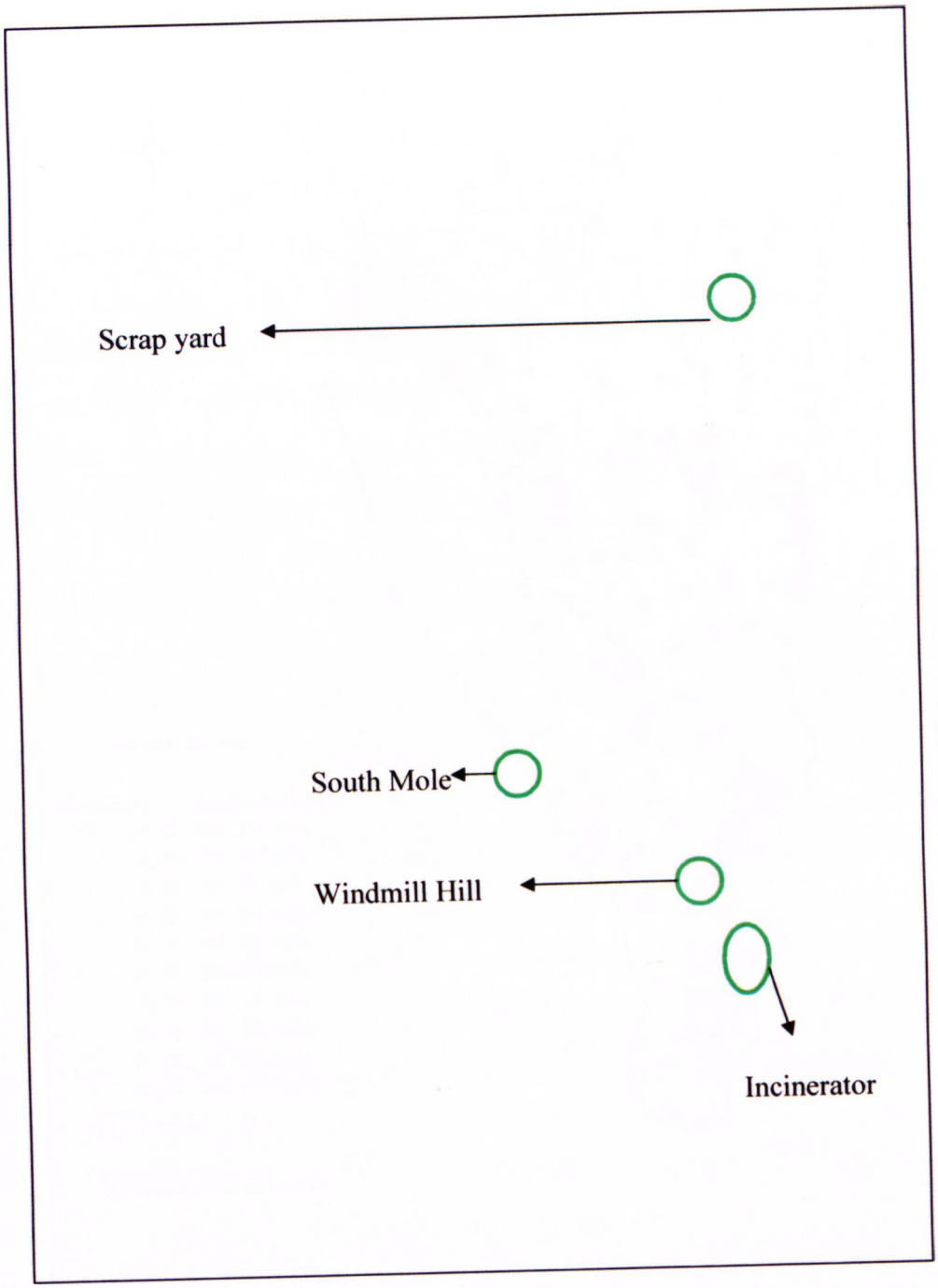
Scrap yard
South Mole
Windmill Hill
Incinerator

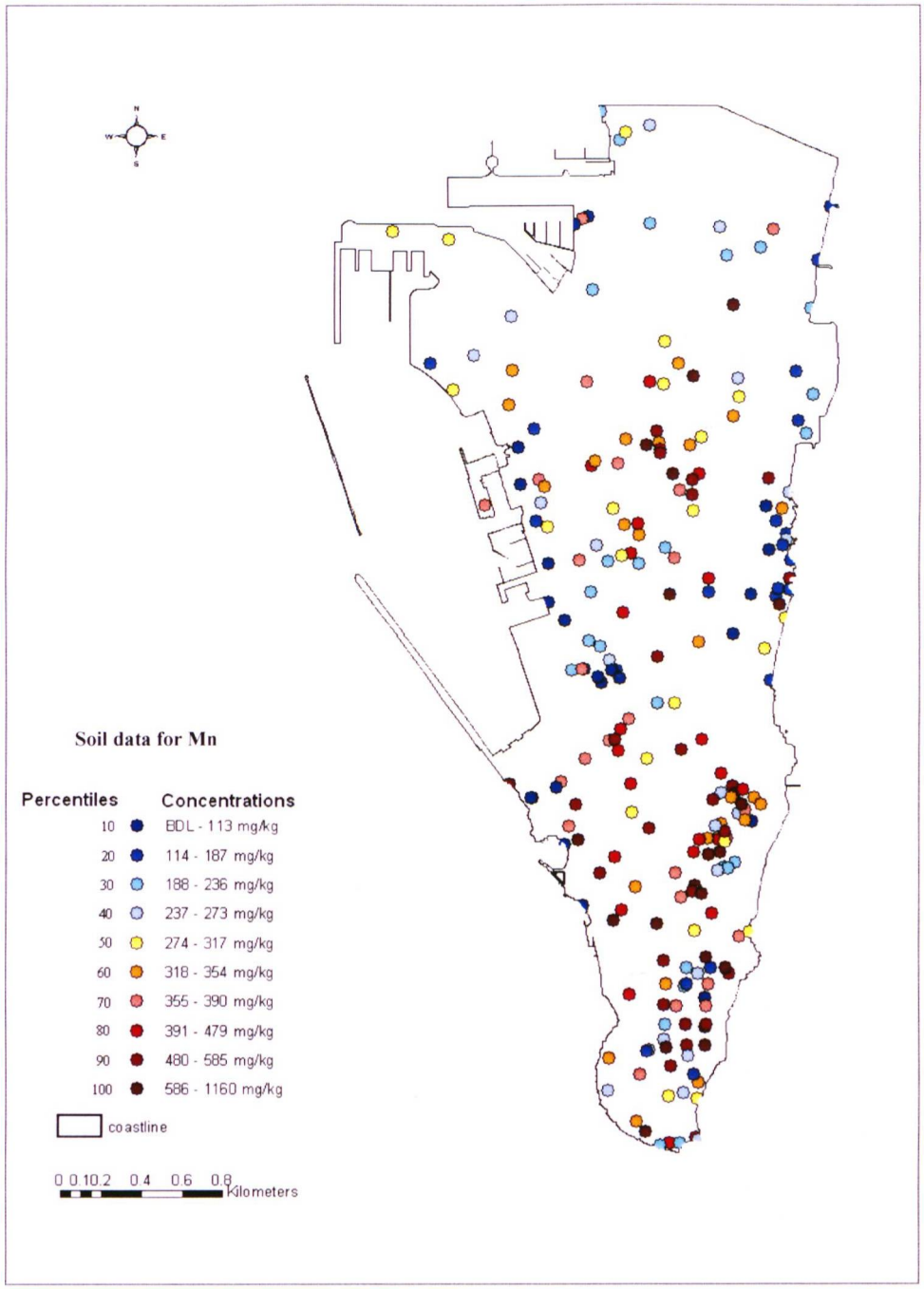

Figure 7.17 Mn concentrations in soils (0-15cms) from Gibraltar. (n=238)

Please note, Mn data for Gibraltar displayed high bias values and poor precision in the QC. Care should be taken when interpreting the data.

Manganese is widely distributed in the earth's crust. Scientific interest in Mn in soils is related to its role as an essential element for plants and animals. Manganese oxides can also act as a sequestering agent to other metals. Concentrations range from 20-10,000 mg/kg (Bowen, 1979; Alloway, 1995). In sedimentary rocks the concentration range in limestones is around 1100 mg/kg (Alloway, 1995), with lower concentrations

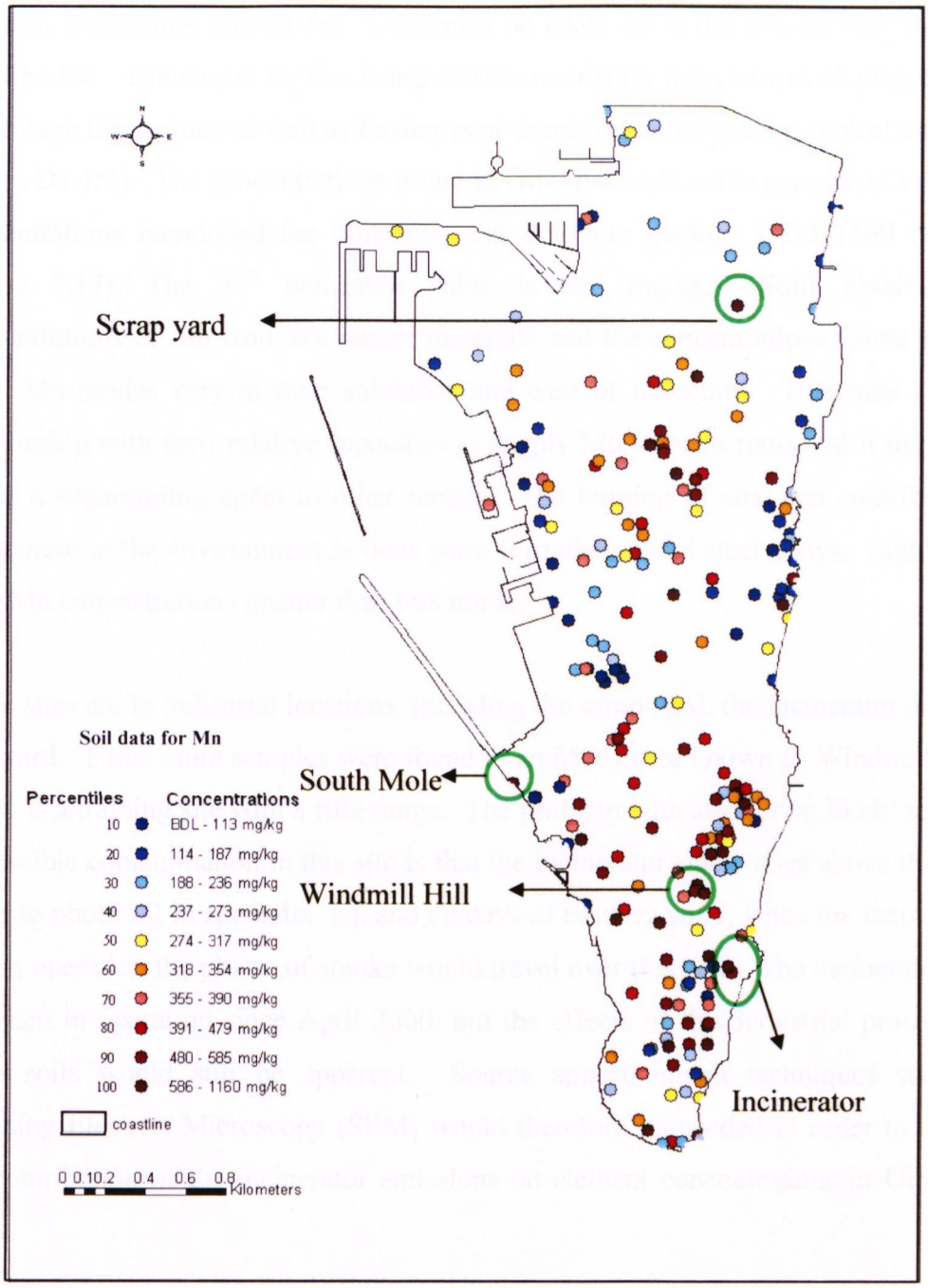

Figure 7.17 Mn concentrations in soils (0-15cms) from Gibraltar. (n=238)

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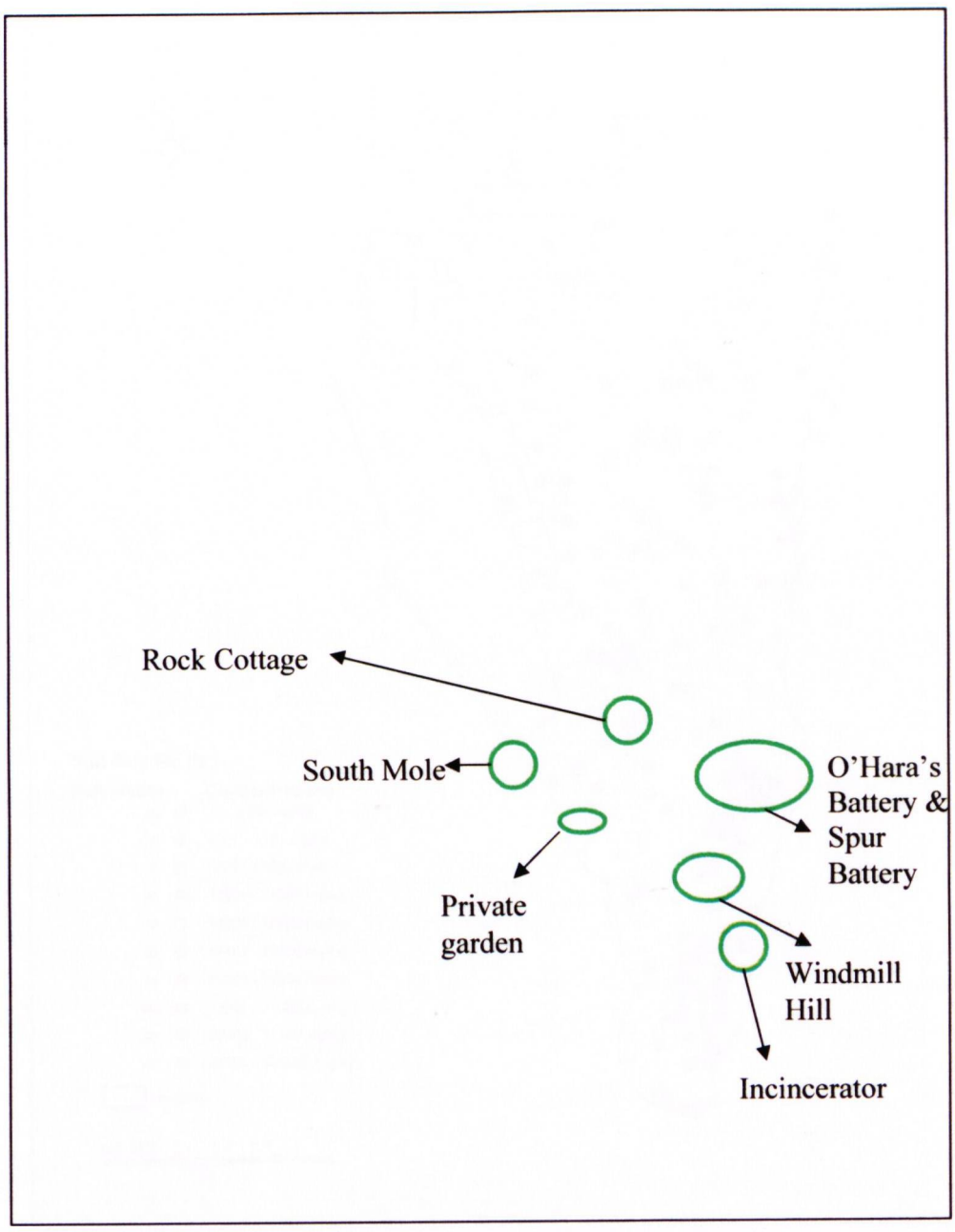
found in sandstones, and shales. Care must be taken when interpreting the Mn data for Gibraltar. The reason for this being that the results for this element displayed high percentage bias values as well as having poor precision in the quality control analysis (tables D1-D4). The concentrations found in Gibraltar soils are in agreement with the concentrations mentioned for limestone and dolomite geology (<0.1-1160 mg/kg) (figure 7.17). The 95th percentile value is 668 mg/kg. Soils obtain their concentrations of Mn from the parent materials and the concentrations found reflect this. Mn oxides vary in their solubility and ease of reduction. This may have a relationship with their relative capacities to supply Mn to plant roots and it may also act as a sequestering agent to other metals. The burning of coal can contribute to manganese in the environment as does paint formulation and steel alloys. Eight sites have Mn concentrations greater than 668 mg/kg.

Three sites are in industrial locations, including the scrap yard, the incinerator and the dockyard. Three more samples were found in an MOD area known as Windmill Hill, which is a training site with a rifle range. The problem with attributing likely sources of possible contamination in this site is that the incinerator stack, rises above this site (refer to photo E2 in appendix E), and on days of easterly wind, when the incinerator was in operation the plume of smoke would travel over this area. The incinerator has not been in operation since April 2000, but the effects of this industrial process on these soils would still be apparent. Source apportionment techniques such as Scanning Electron Microscopy (SEM) would therefore be needed in order to assess the contribution of the incinerator emissions on element concentrations in Gibraltar soils.

Iron makes up 5% of the earth's crust and is one of the most abundant metallic elements. The oxides of Fe play an important role in the chemical behaviour of metals in soils. Iron oxides can adsorb cations such as Cr, Cu, Mn, Ni and Zn. Iron is an essential element, but can be potentially toxic in all forms and by all routes of exposure. Generally ferrous compounds are more toxic than ferric compounds (Alloway, 1995). However more reported cases can be found in the literature of Fe deficiencies than Fe poisonings (Alloway, 1995; Kabata Pendias *et al.*, 1992). Iron oxides in the soil can act as a "mopping up agent" adsorbing metals onto the soil surface; Fe oxides act as sequestering agents.


Rock Cottage
South Mole
Private garden
O'Hara's Battery & Spur Battery
Windmill Hill
Incincerator

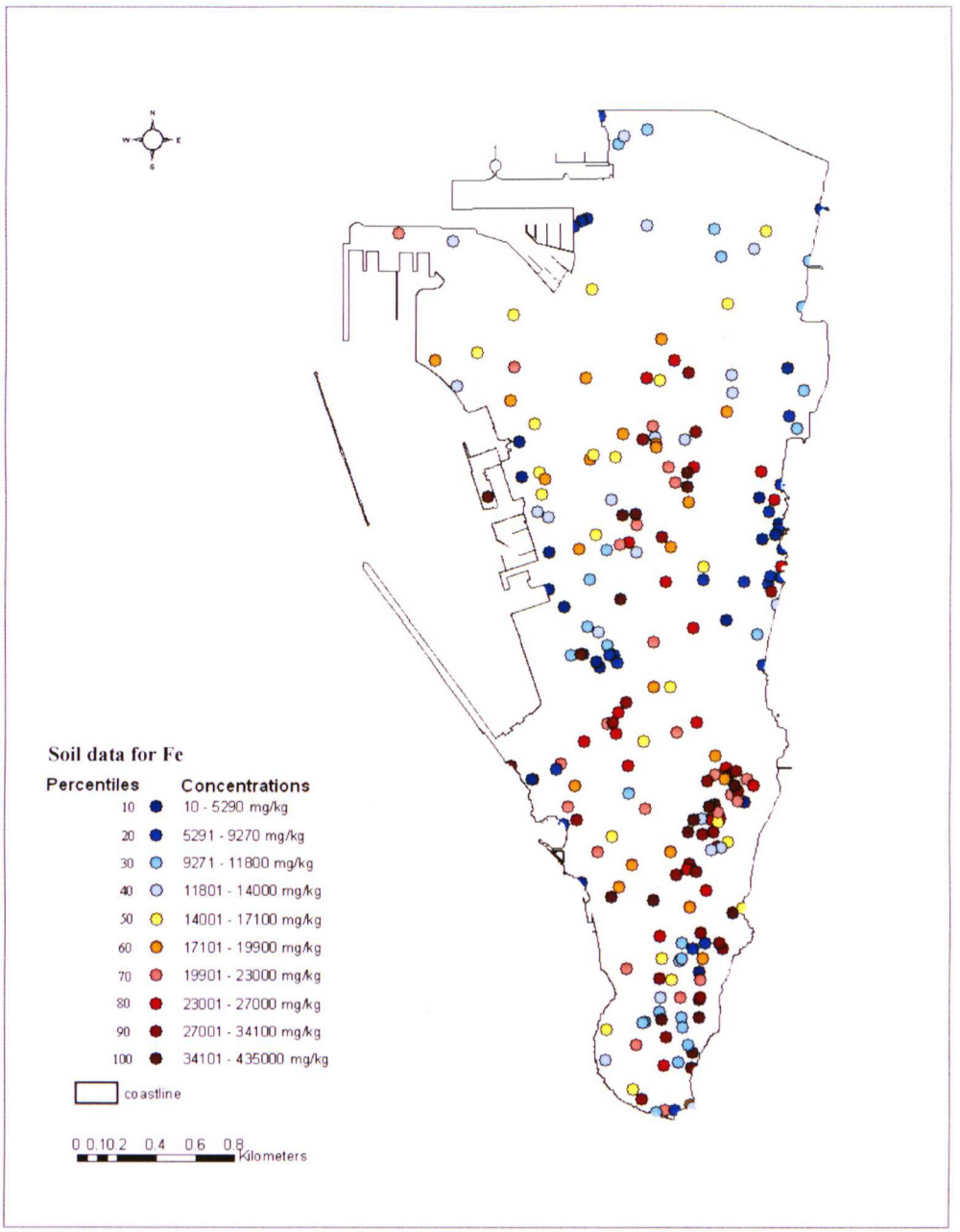
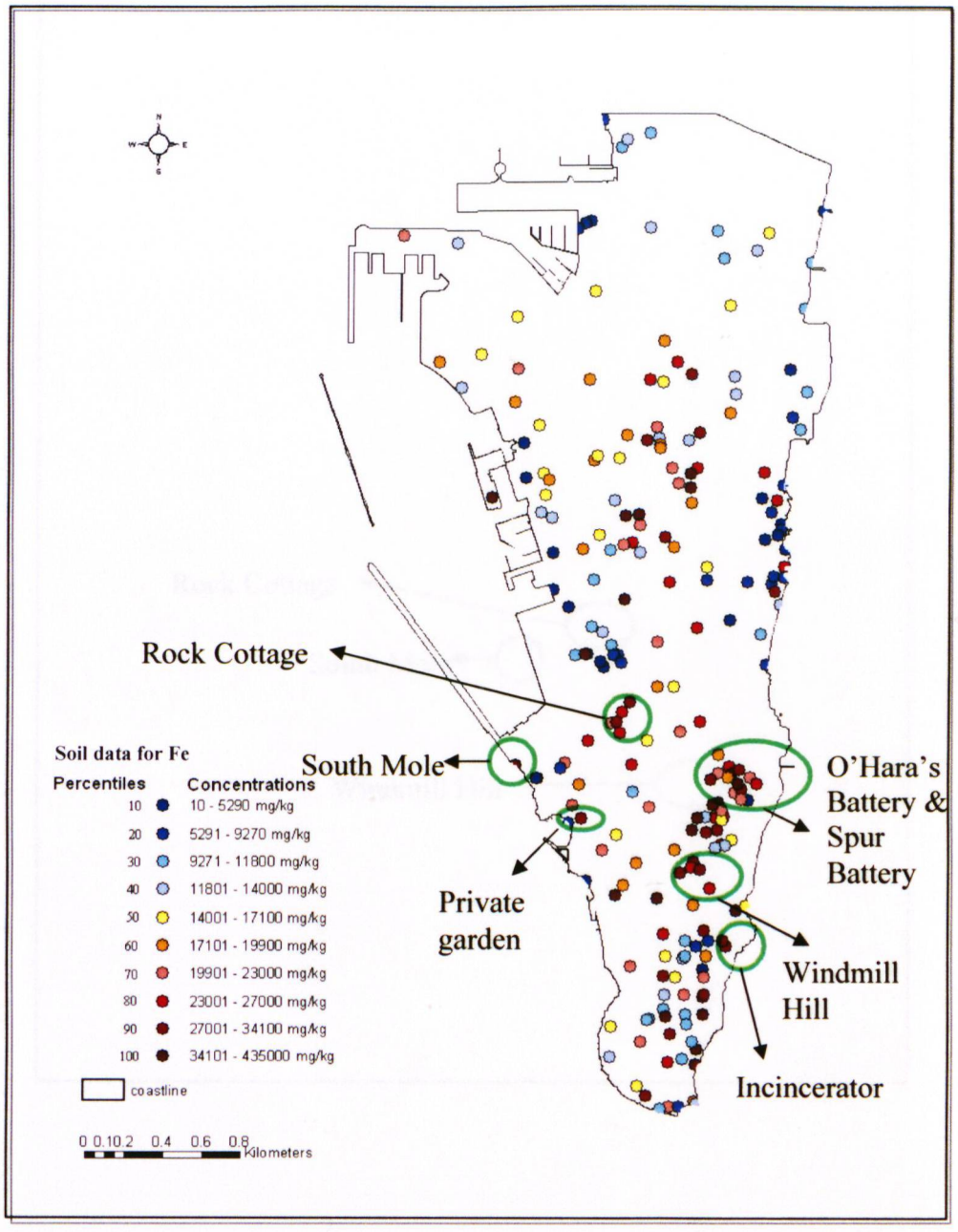


Figure 7.18 Fe concentrations in soils (0-15cms) from Gibraltar. (n=238)

Concentrations of Fe in Gibraltar are naturally high. Values range from 10-435000 mg/kg (figure 7.18). The 95th percentile value is 48300 mg/kg. Ure and Berrow (1982) give a range from 18000-42600 mg/kg. The seven sites which have concentrations exceeding the 95th percentile value are once again related to industry. These sites include the south mole, a private garden close to the dockyard, the incinerator, Windmill Hill and Spur Battery.



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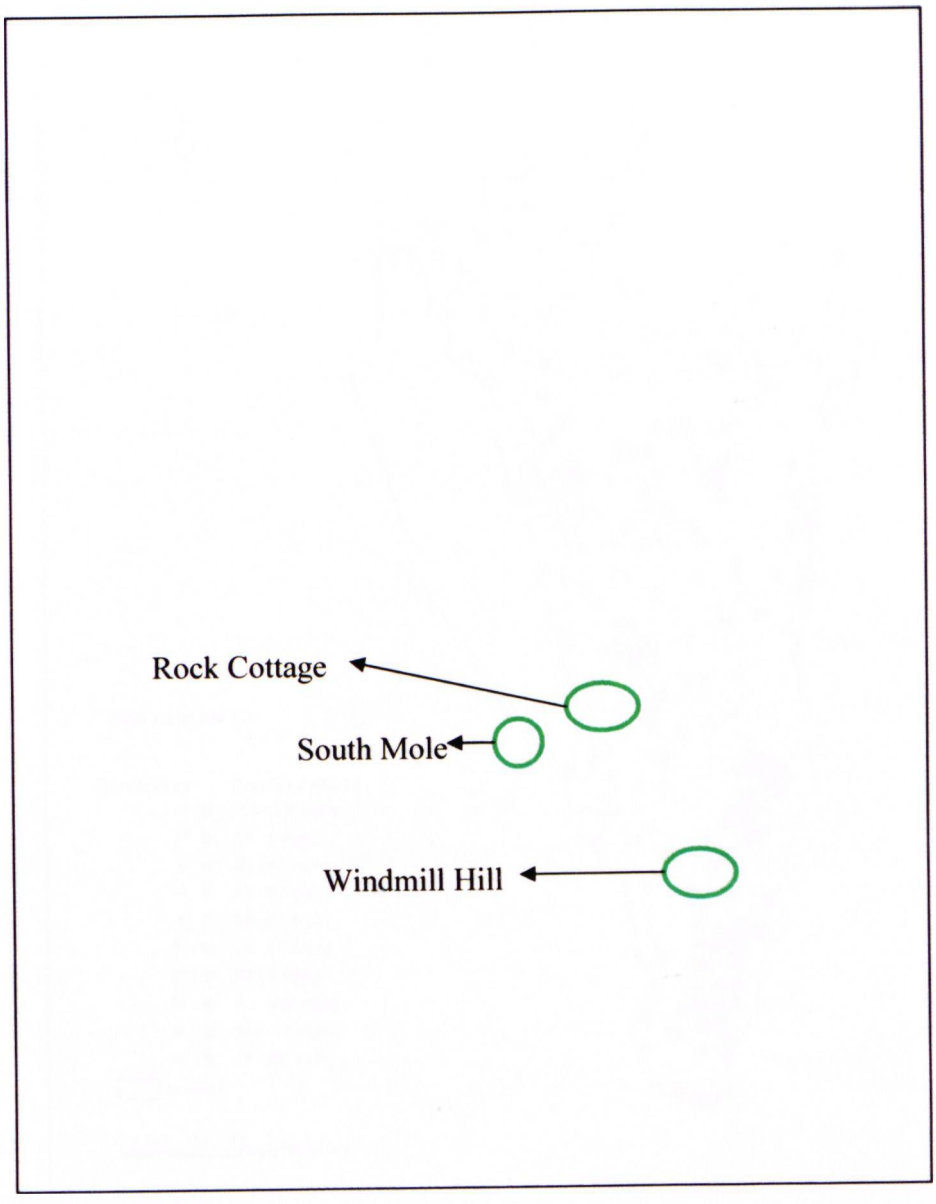

Rock Cottage
South Mole
Windmill Hill

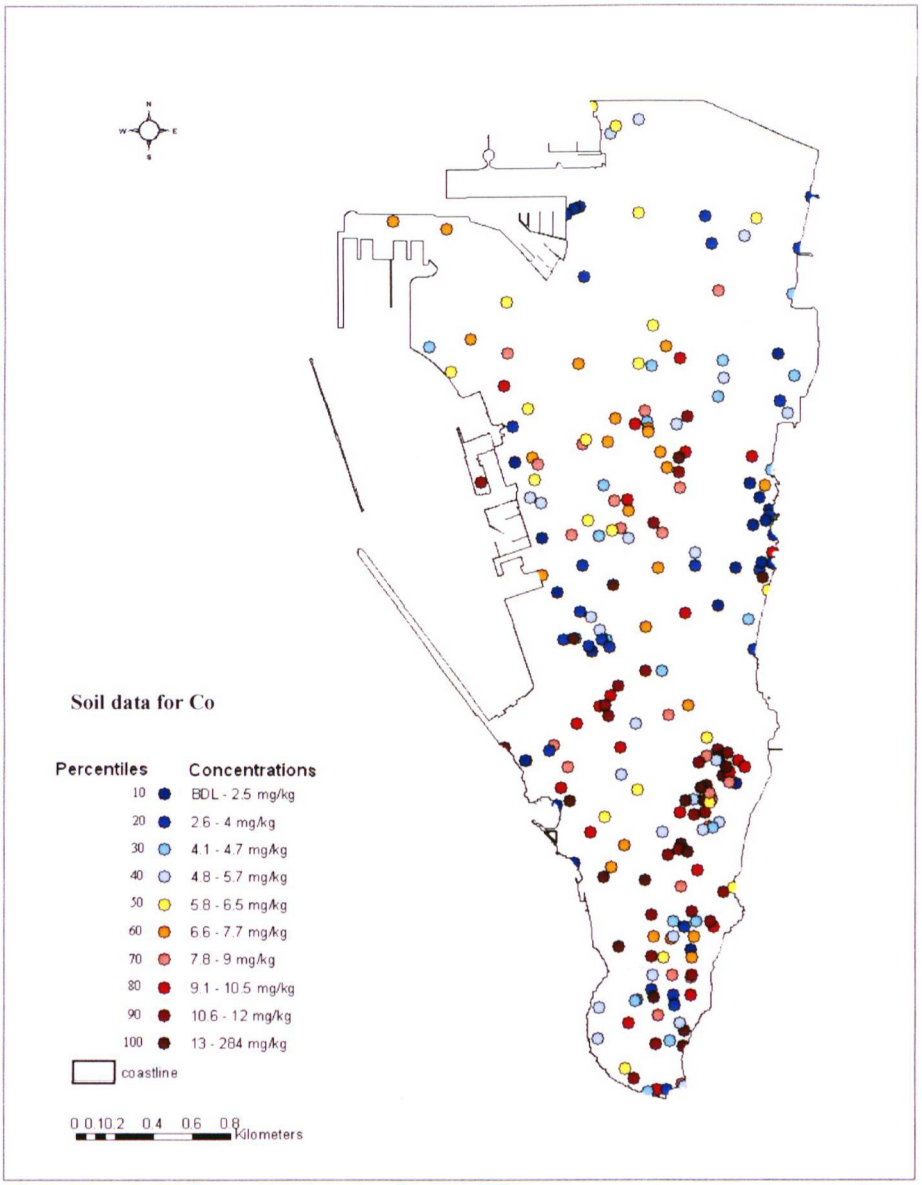
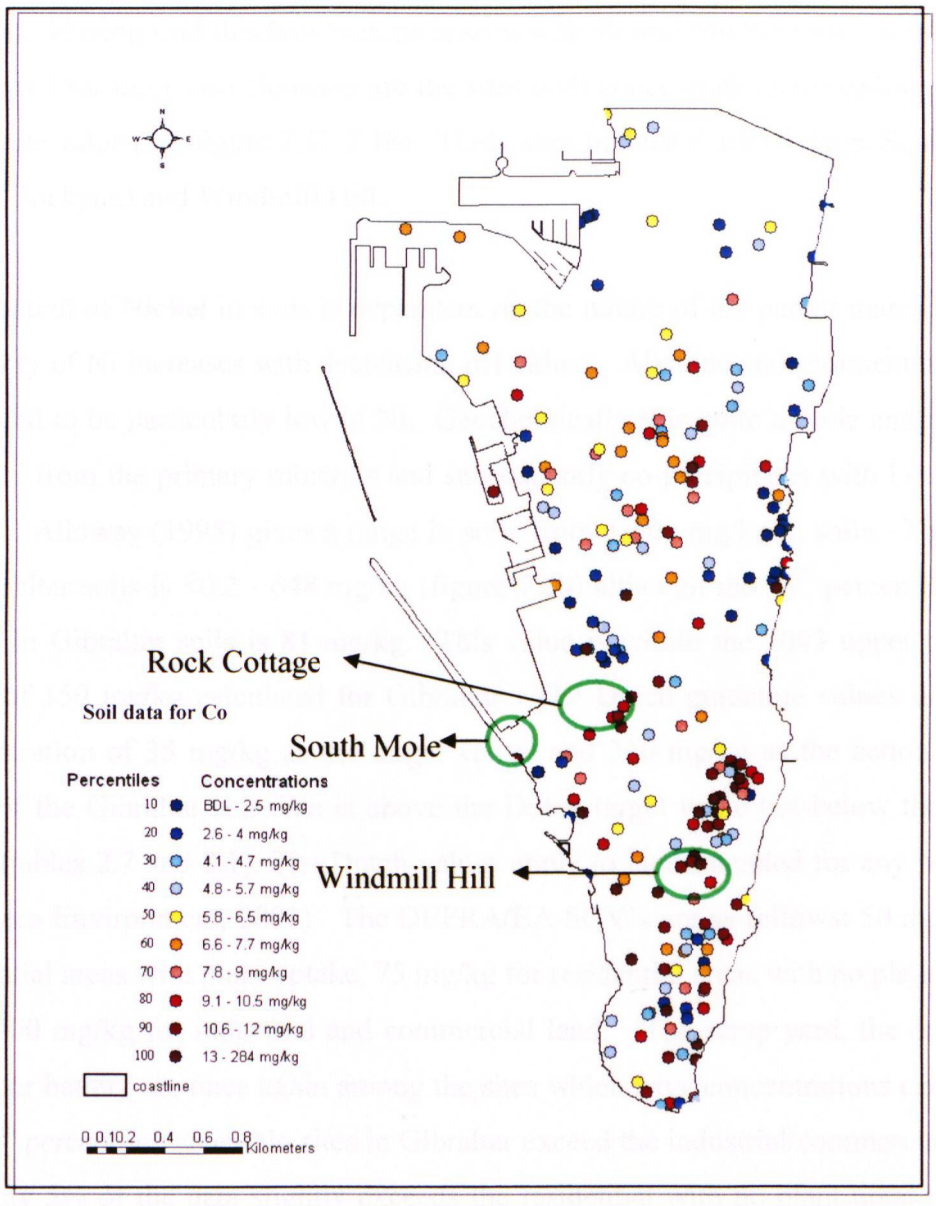


Figure 7.19 Co concentrations in soils (0-15cms) from Gibraltar. (n=238)

Cobalt is geochemically similar to Fe and Mn although it is much less abundant. Iron oxides are known to have a strong affinity for the selective absorption of Co and a similarity between the concentrations of Fe and Co in soil horizons has been shown (Kabata-Pendias *et al.*, 1992). Anthropogenic uses of Co include the manufacture of special steels, blue pigments and glass. Concentrations of Co in Gibraltar are generally in agreement with those reported as world means. Alloway (1995) gives a range from 1-40 mg/kg. The range in Gibraltar soils is <0.1 – 284 mg/kg (figure 7.19) with a 95th percentile value in Gibraltar is 16 mg/kg. Cobalt values in the QC



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analysis displayed a negative % bias, reflecting the possible partial dissolution of this element. Having said this however, as is seen with Fe and Mn the same sites as were mentioned for these two elements are the sites with concentrations exceeding the 95th percentile value (see figure 7.17-7.18). These sites include Rock Cottage, South Mole by the Dockyard and Windmill Hill.

The content of **Nickel** in soils is dependent on the nature of the parent material. The solubility of Ni increases with decreasing pH values. Alkaline and sedimentary rocks are found to be particularly low in Ni. Geochemically it is quite mobile and is easily released from the primary minerals and subsequently co-precipitates with Fe and Mn oxides. Alloway (1995) gives a range in soils from 5-500 mg/kg in soils. The range in Gibraltar soils is <0.2 - 648 mg/kg (figure 7.20) although the 95th percentile value for Ni in Gibraltar soils is 81 mg/kg. This value is within the 2003 upper baseline range of 159 mg/kg calculated for Gibraltar. The Dutch guideline values display a concentration of 35 mg/kg as the target value[1] and 210 mg/kg as the action value[2]. Most of the Gibraltar soil data is above the Dutch target value but below the action value (tables 2.7 and 8.1). The Dutch values apply to land intended for any potential use (Zero Environment, 2001). The DEFRA/EA SGV's are as follows: 50 mg/kg for residential areas with plant uptake, 75 mg/kg for residential areas with no plant uptake and 5000 mg/kg for industrial and commercial land. The scrap yard, the dockyard and Spur battery are once again among the sites which have concentrations exceeding the 95th percentile value. No sites in Gibraltar exceed the industrial/commercial target and only 5% of the data slightly exceeds the residential with no plant uptake target. The two sites with the highest concentrations (336 and 648 mg/kg) are situated by the dockyard. In these sites, plant uptake may be possible.

Copper is widely distributed in nature and is one of the most important essential elements for plants and animals. Copper is associated with soil organic matter, oxides of iron and manganese oxide, soil silicate clays and other minerals (Alloway, 1995). It is essential to flora ad fauna in small amounts but can be toxic in large quantities.

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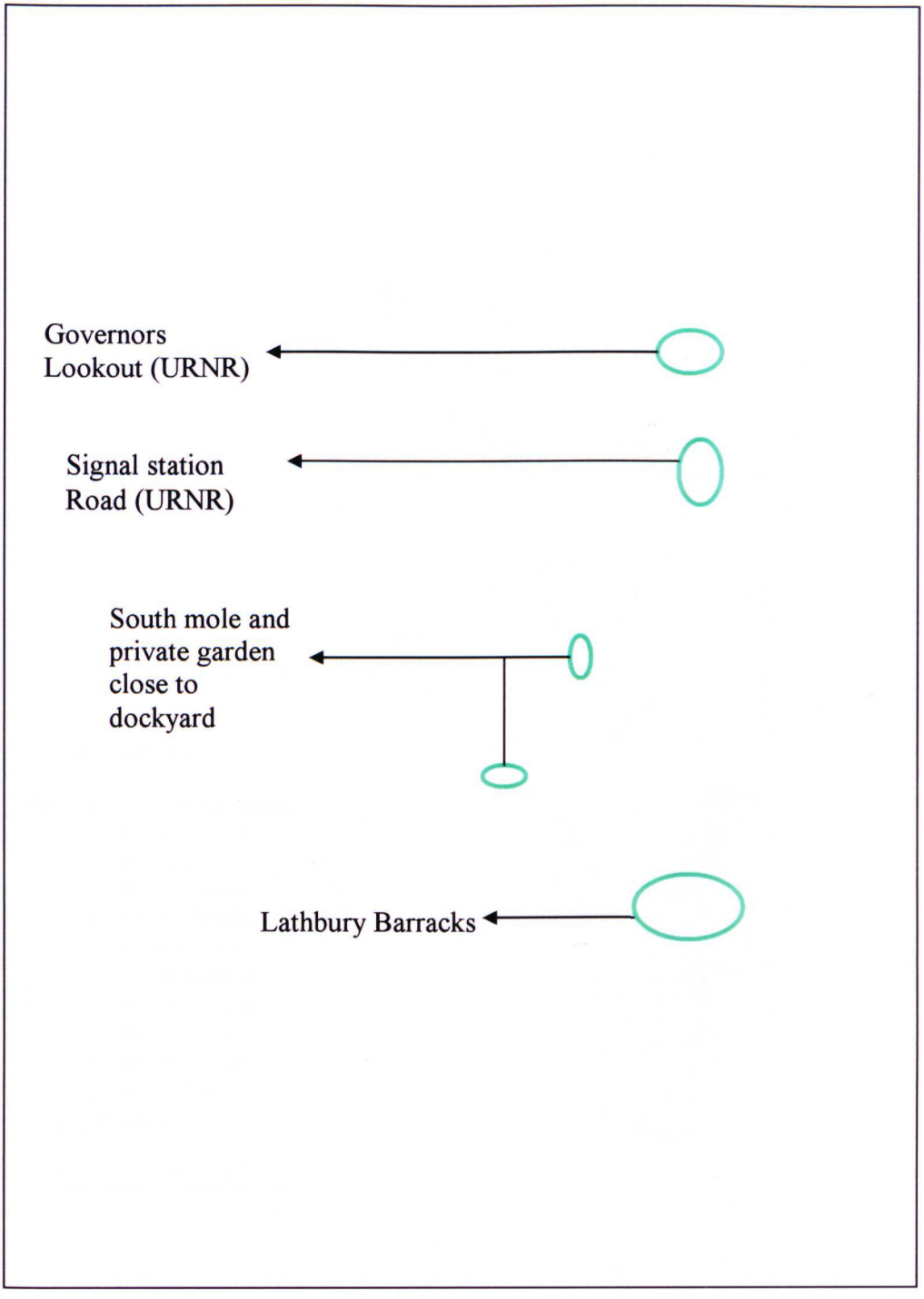
[1] The *target value* is the Dutch baseline concentration below which compounds and/or elements are known or assumed not to affect the natural properties of the soil.

[2] The *intervention value* is the maximum tolerable concentration above which remediation is required. This occurs if one or more compounds are present in concentrations equal to or higher than the intervention value of more than 25 m^3 of soil or 1000 m^3 of ground water.

The level and distribution of total and extractable Cu in the soil profile varies with soil type and parent material. It is one of the trace metals, which moves the least within the soil profile as it is specifically adsorbed onto soil organic matter and clays. Limestones and sandstones contain a range of 5-20 mg/kg and shales 30-150 mg/kg (Alloway, 1995). The large use of Cu in tools, weapons, utensils and ornaments means that when such items are discarded whether by disposal to landfill or incineration, the potential for contamination arises.

The range of Cu concentrations for Gibraltar soils is <0.02-12500 mg/kg (figure 7.21) with a 95th percentile value for of 411 mg/kg, higher than the ranges reported by Alloway (1995) 2-250 mg/kg and Bowen (1979) 2-250 mg/kg. This value is within the 2003 upper baseline range of 977 mg/kg calculated for Gibraltar. The Dutch guideline values display a concentration of 36 mg/kg as the target value and 190 mg/kg as the action value. Most of the Gibraltar soil data is above the Dutch target value but below the action value, as the 75th percentile for Cu in Gibraltar soils is 65 mg/kg. Once again the same industrial sites that have been mentioned so far (Europa Brewery Crusher, the rubbish pit opposite the clay pigeon shooting range, the scrap yard, the upper town area, Coaling island and the south mole) are those with concentrations exceeding the 95th percentile value.

The sites by Europort and the East side reclamation which have very low values of Cu, <9 mg/kg could indicate potential Cu deficiency in some Gibraltar soils.


Governors
Lookout (URNR)
Signal station
Road (URNR)
South mole and
private garden
close to
dockyard
Lathbury Barracks

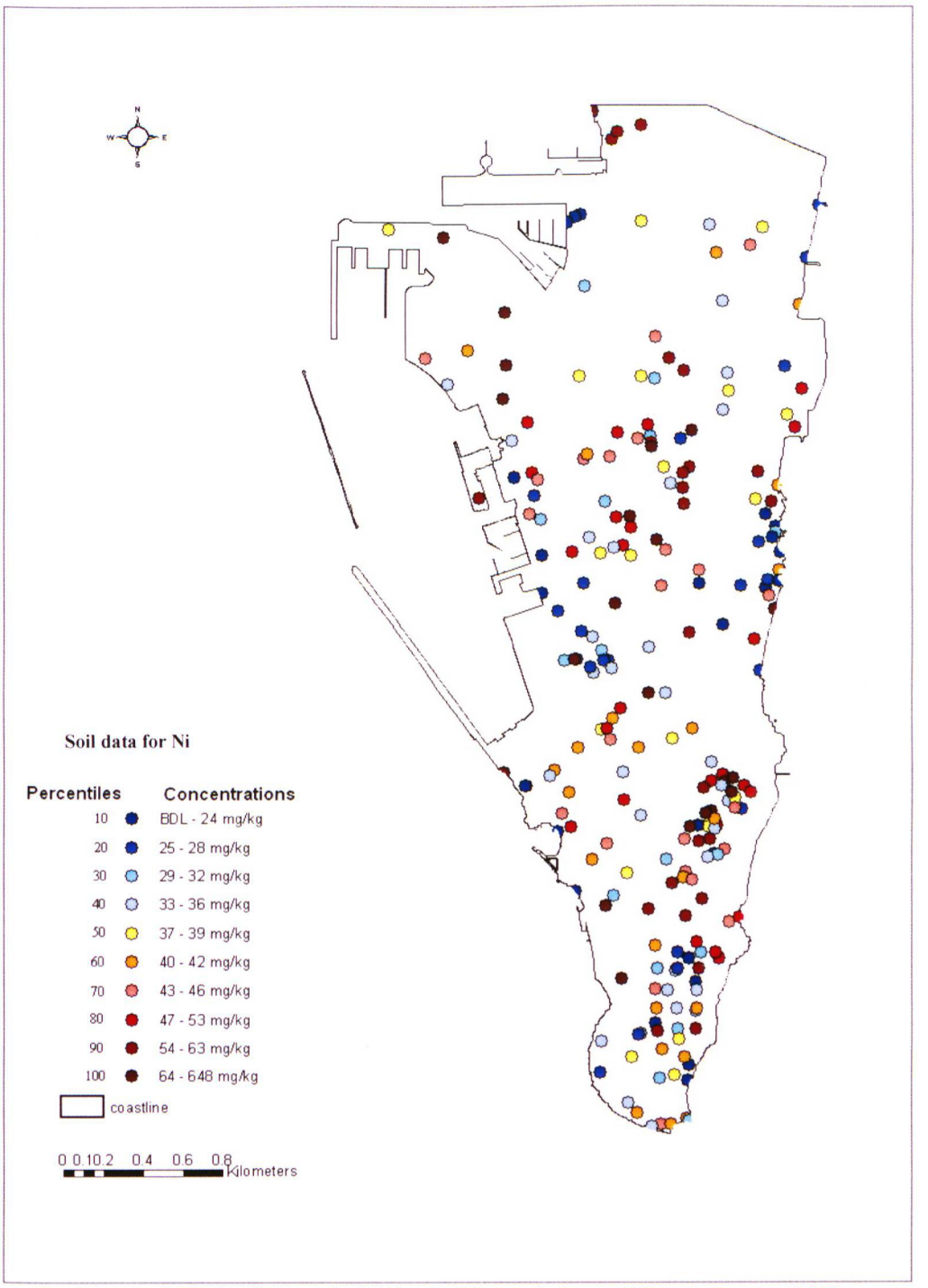
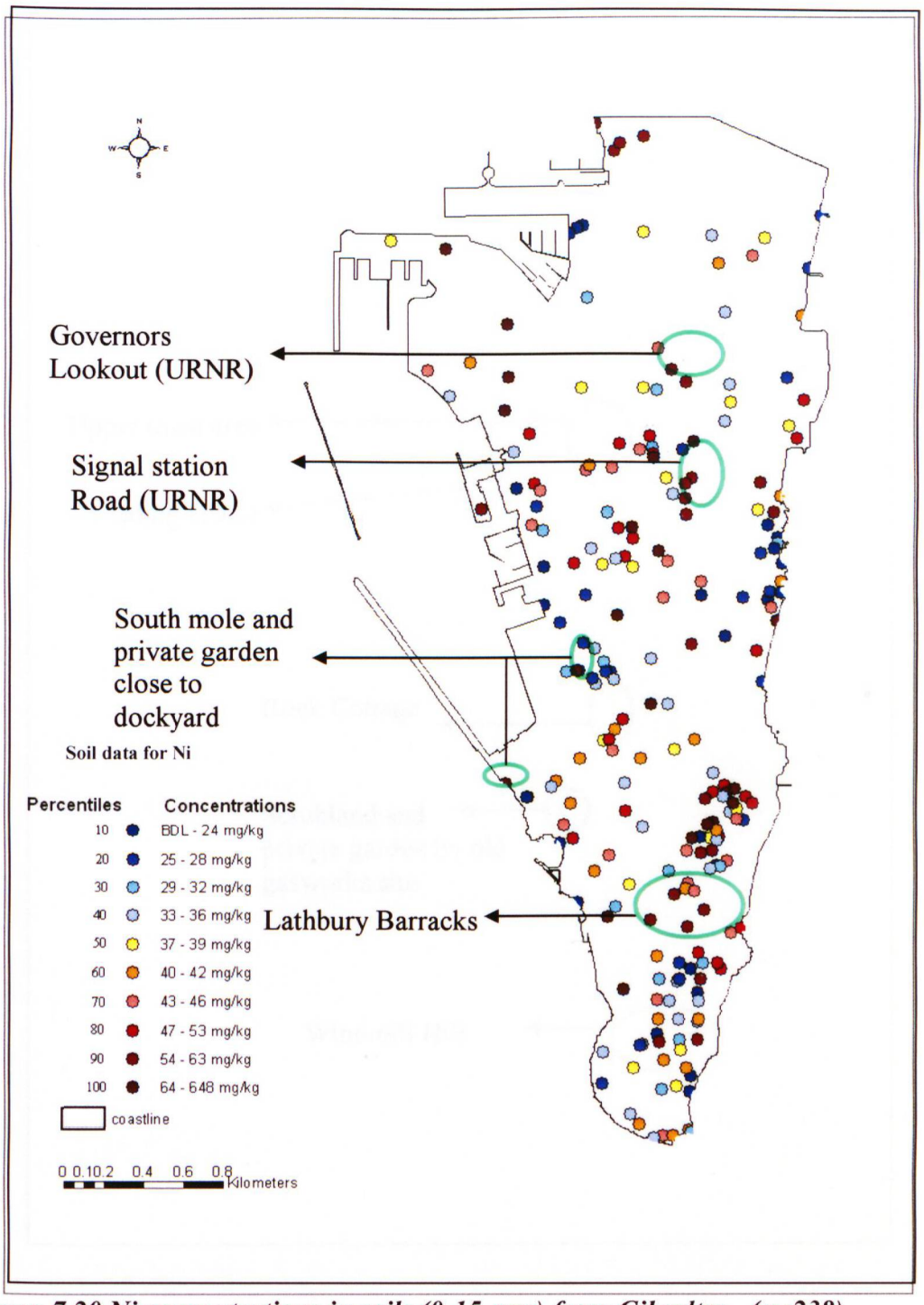


Figure 7.20 Ni concentrations in soils (0-15 cms) from Gibraltar. (n=238)



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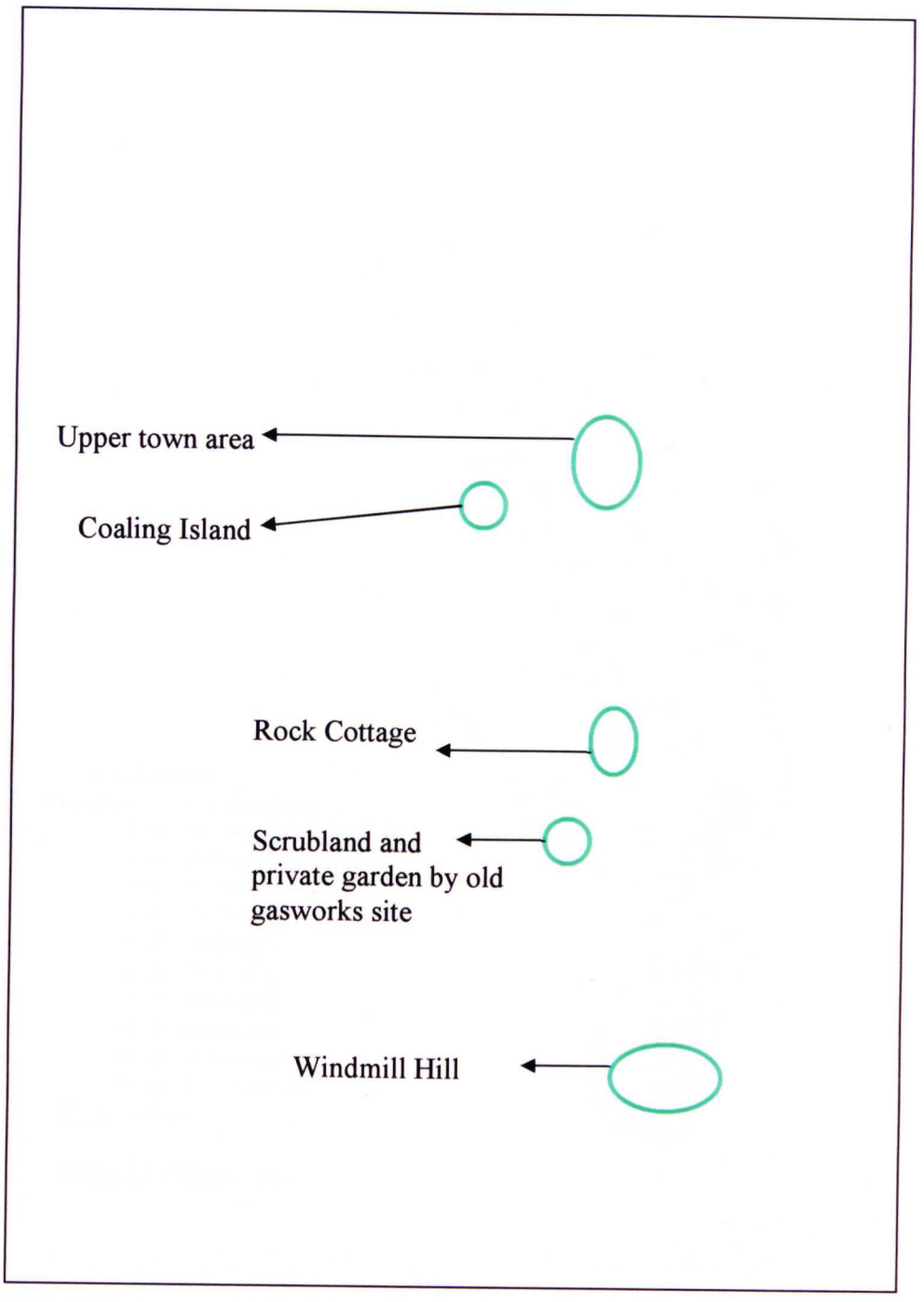

Upper town area
Coaling Island
Rock Cottage
Scrubland and
private garden by old
gasworks site
Windmill Hill

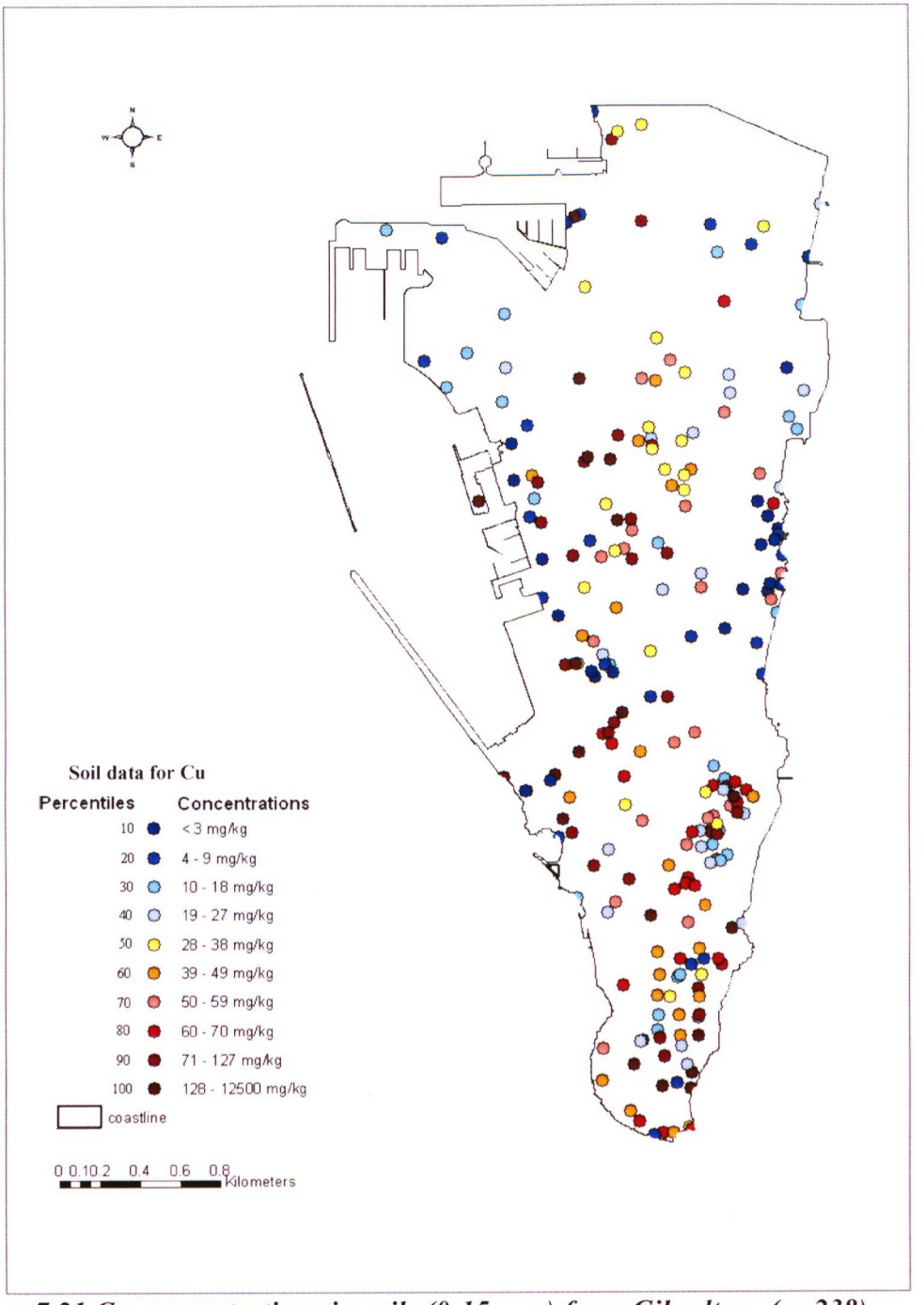


Figure 7.21 Cu concentrations in soils (0-15 cms) from Gibraltar. (n=238)

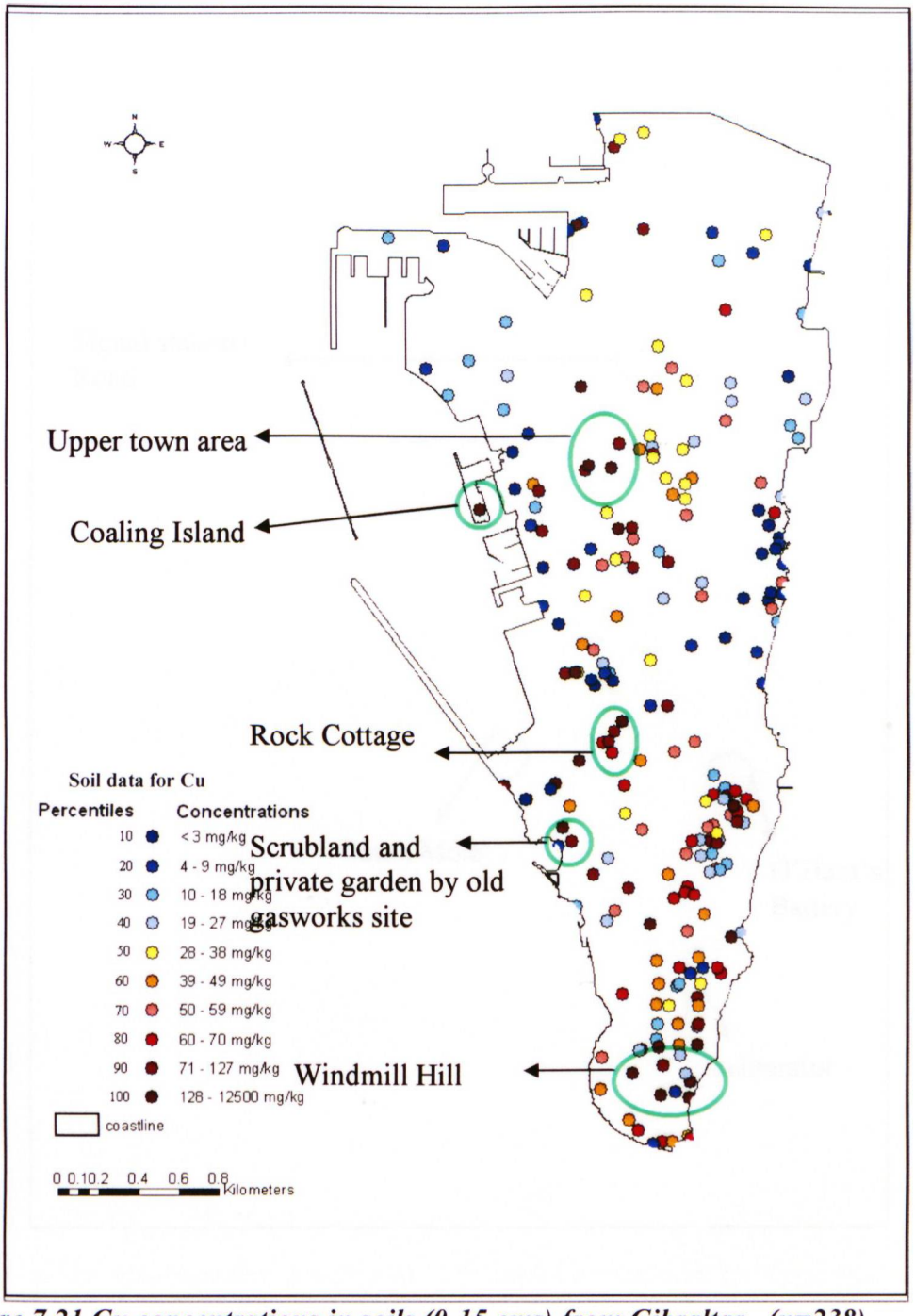
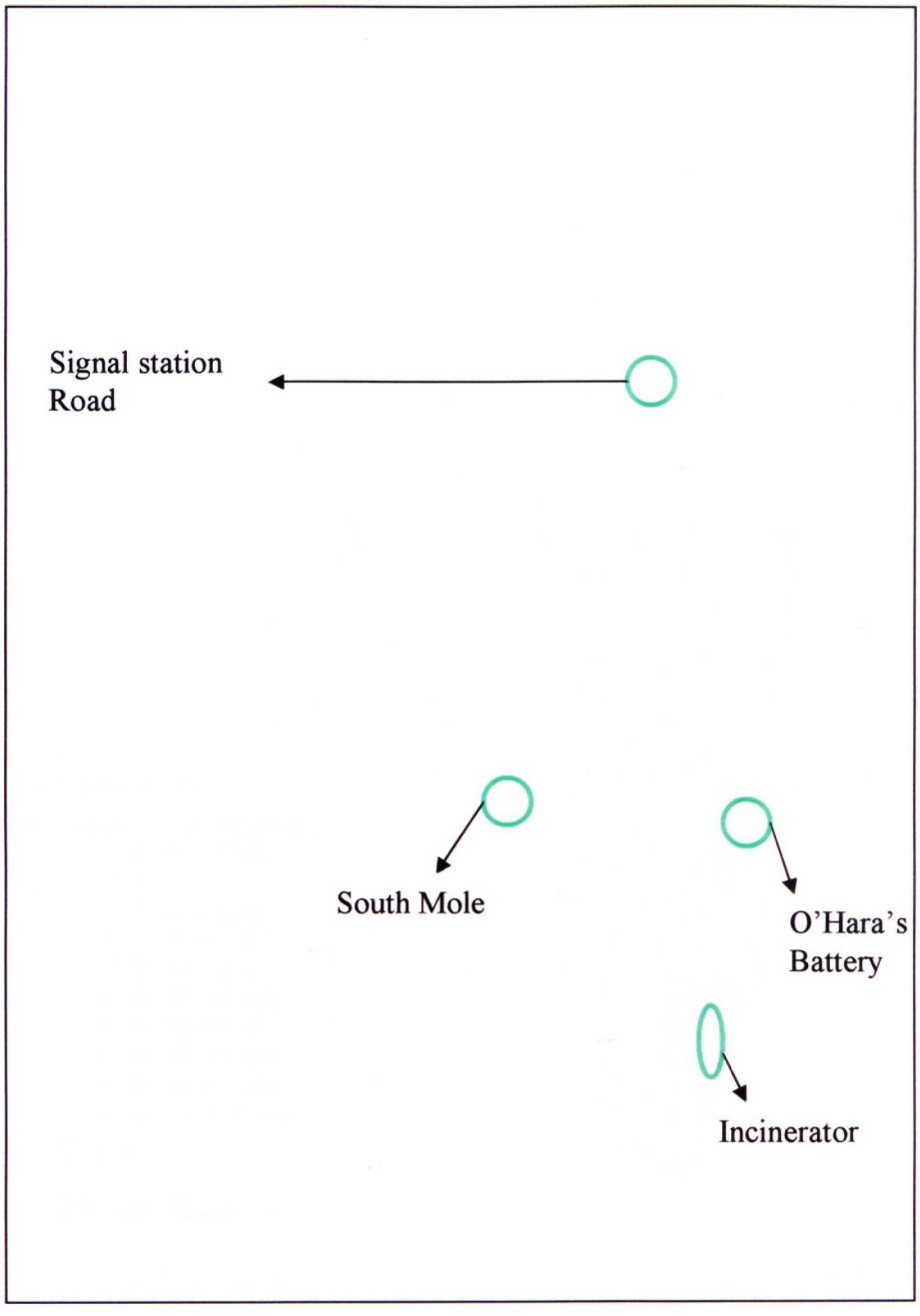


Figure 7.21 Cu concentrations in soils (0-15 cms) from Gibraltar. (n=238)


Signal station
Road
South Mole
O'Hara's
Battery
Incinerator

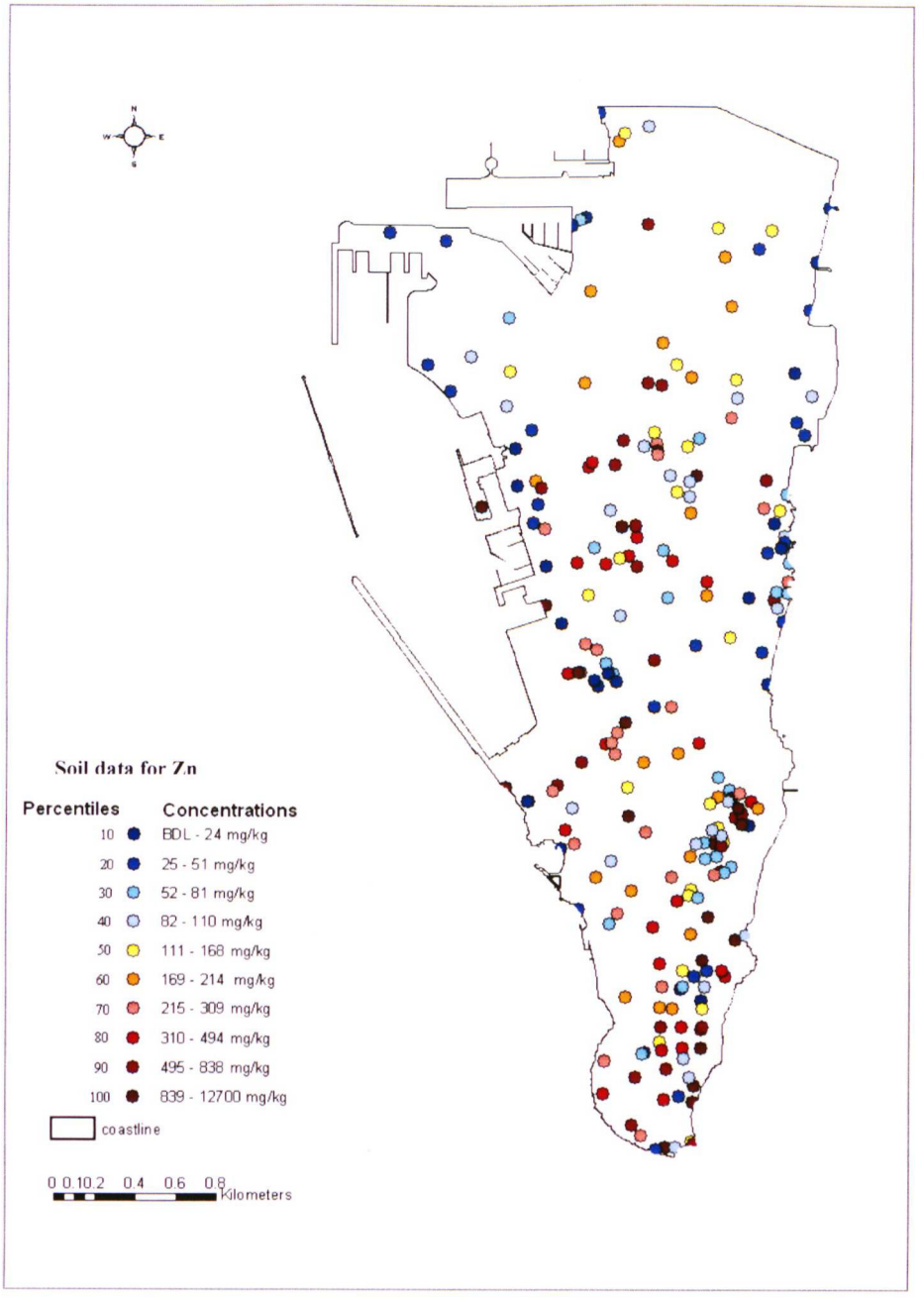
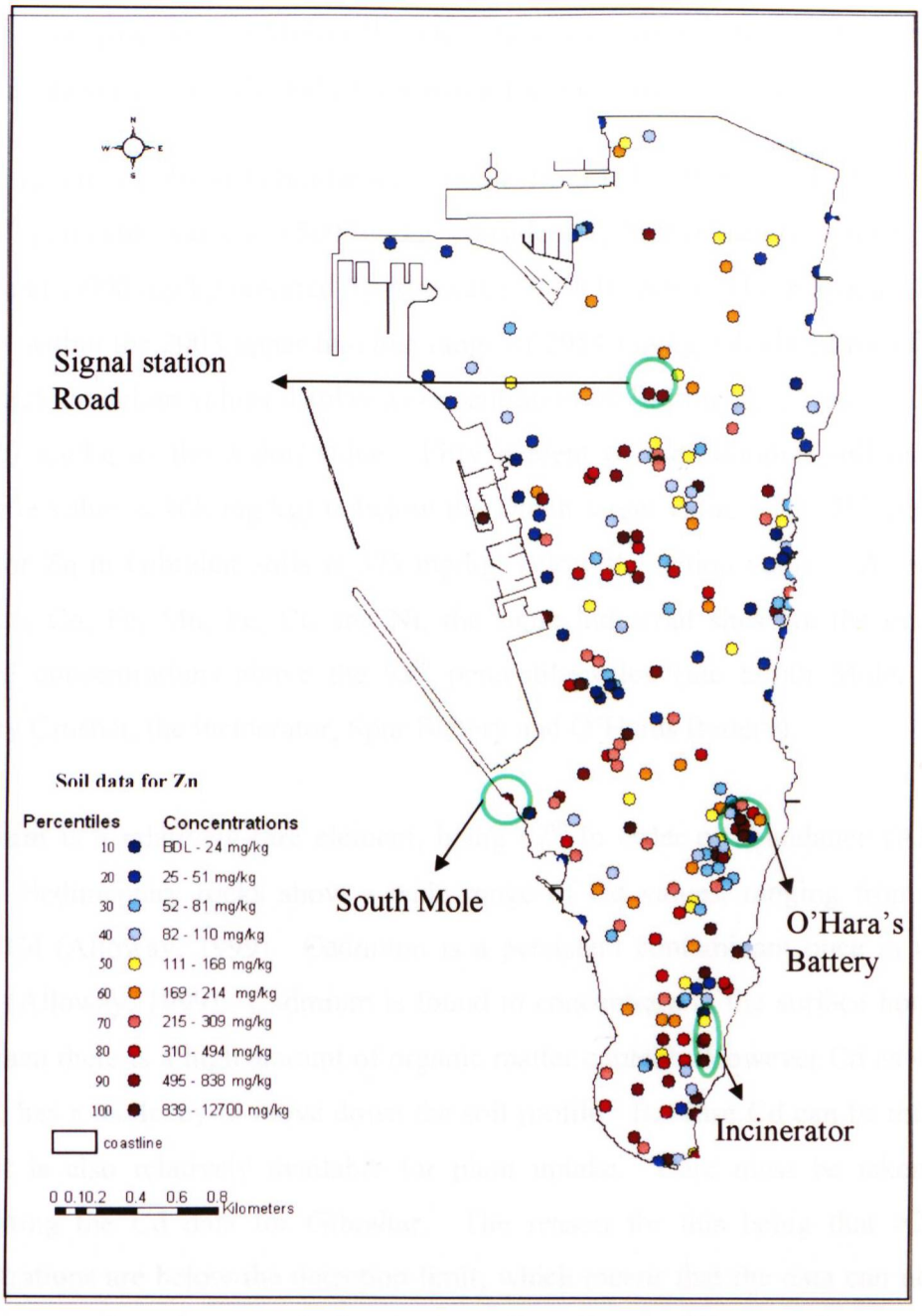


Figure 7.22 Zn concentrations in soils (0-15 cms) from Gibraltar. (n=238)

Zinc is an essential trace metal for humans, animals and higher plants. However, as is the case all essential elements, it can be toxic at high concentrations. Total Zn content of soil is very much dependent on the composition of the parent material. In sedimentary rocks the highest Zn content can be found in shales and clayey sediments while sandstone, limestones and dolomites have lower concentrations. Availability of Zn to plants decreases with increasing pH values of the soil, due to the lower solubility of Zn minerals and increasing adsorption of Zn by negatively charged



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colloidal soil particles. Additionally interaction with other nutrients (mainly Zn-Fe antagonism) but also Zn-Cu and Zn-Ca will affect the availability of Zn.

Concentrations of Zn in Gibraltar soils range from 0.4-12700 mg/kg (figure 7.22). The 95th percentile value is 1500 mg/kg, considerably higher than the ranges 10-300 mg/kg and 1-900 mg/kg reported by Alloway (1995) Bowen (1979) respectively. This value is within the 2003 upper baseline range of 2954 mg/kg calculated for Gibraltar. The Dutch guideline values display a concentration of 140 mg/kg as the target value and 720 mg/kg as the action value. Fifty percent of the Gibraltar soil data (50th percentile value is 168 mg/kg) is below the Dutch target value. The 75th percentile value for Zn in Gibraltar soils is 375 mg/kg, below the action value. As with the elements, Co, Fe, Mn, Fe, Cu and Ni, the same industrial sites are the ones with elevated concentrations above the 95th percentile value (the South Mole, Europa Brewery Crusher, the incinerator, Spur Battery and O'Haras Battery).

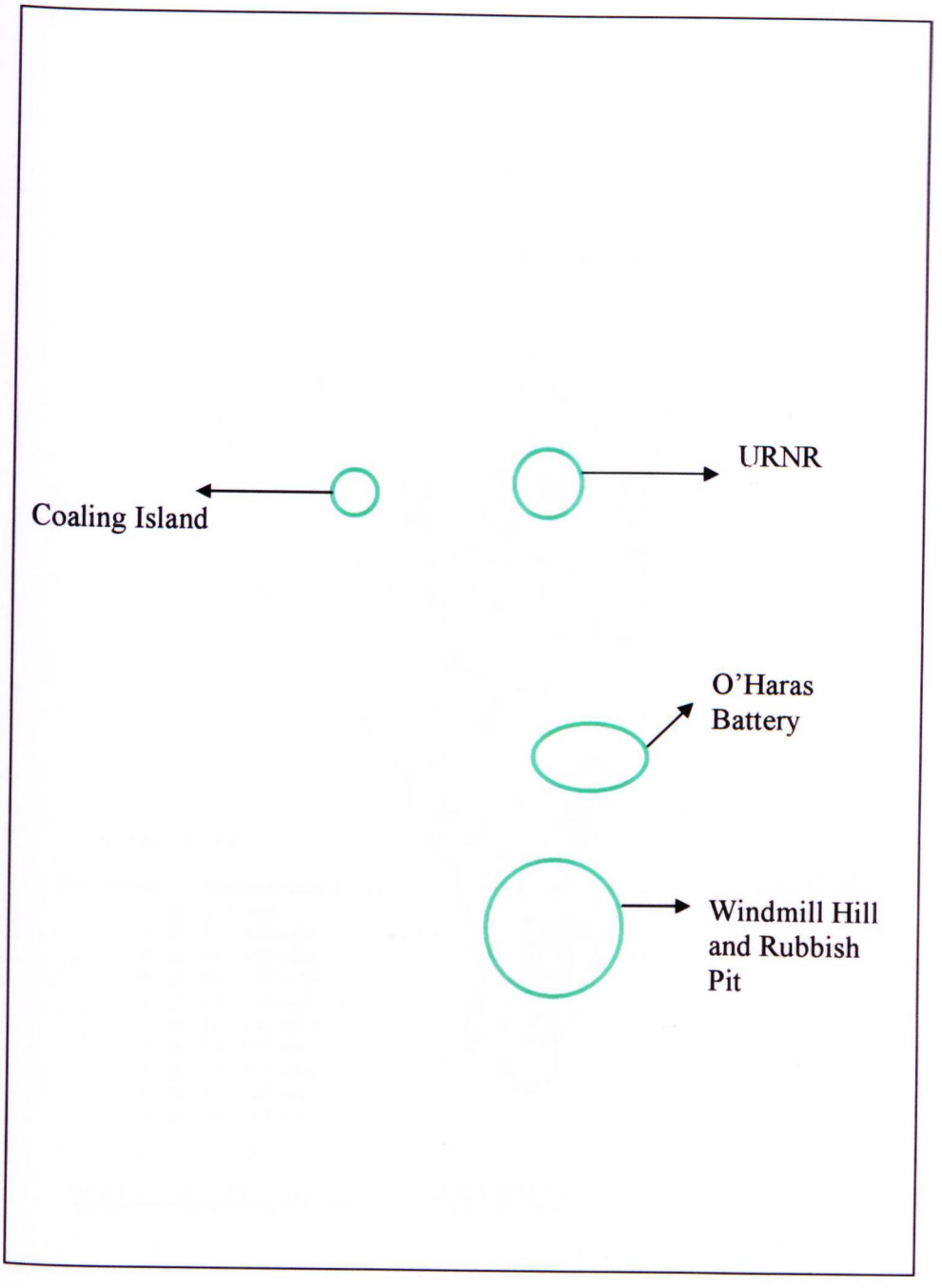
Cadmium is a relatively rare element, being 67th in order of abundance (Alloway, 1995). Sedimentary rocks show a wide range of Cd values, ranging from 0.3-11 mg/kg Cd (Alloway, 1999). Cadmium is a persistent contaminant once in the soil profile (Alloway, 1999). Cadmium is found to concentrate in the surface horizon of soils when there is a high amount of organic matter content. However Cd as with Zn and Ni, has a tendency to move down the soil profile. Because Cd can be mobile in soils, it is also relatively available for plant uptake. Care must be taken when interpreting the Cd data for Gibraltar. The reason for this being that >25% of concentrations are below the detection limit, which means that the data can not have either a normal or lognormal distribution, this then further contributes to high percentage bias values as well as poor precision (tables D1-D4).

Alloway (1995) has shown that soils containing free $CaCO_3$ (such as those in Gibraltar) can sorb Cd and reduce its bioavailability. Most of the Cd concentrations found in Gibraltar are below 3 mg/kg. The range is between <0.01-17 mg/kg (figure 7.23). The site with the highest concentration is Europa Brewery Crusher (16 mg/kg). Five sites with concentrations exceeding the 95th percentile value of 6 mg/kg are related to anthropogenic activity, namely the dockyard, the incinerator, the rubbish pit opposite the clay pigeon shooting range, Windmill Hill and Spur Battery. This value

is within the 2003 upper baseline range of 9 mg/kg calculated for Gibraltar. The Dutch guideline values display a concentration of 0.8 mg/kg as the target value and 12 mg/kg as the action value. Most of the Gibraltar soil data is above the Dutch target value but below the action value (tables 2.7 and 8.1). The DEFRA/EA SGV's are as follows: 8 mg/kg for residential areas with plant uptake (pH >7 as is found in Gibraltar), 30 mg/kg for residential areas with no plant uptake and 1400 mg/kg for industrial and commercial land. No sites in Gibraltar exceed the residential with no plant uptake target or the industrial/commercial target.

Lead is a non-essential element that can cause toxicity and mental impairment in young children (Thornton, 1995). Alloway (1995) states that shales and mudstones contain an average Pb content of 20 mg/kg. Sandstones have an average of 7 mg/kg while limestones and dolomites contain around 8 mg/kg. Lead tends to concentrate in the surface soil horizons and is very immobile; it binds tightly to the organic matter and surface colloids (Alloway, 1995). Lead has a half-life of 740-5900 years and a residence time from 400-3000 years in soils (Alloway, 1999). Alloway (1995) gives a range from 2-200 mg/kg in contaminated soils.

Concentrations in Gibraltar soils range from <0.6-8507 mg/kg and are generally slightly elevated with 40 sites containing concentrations greater than 500 mg/kg. This could represent anthropogenic factors such as traffic. The 95th percentile value is 1680 mg/kg and as with the other anthropogenically related elements the same sites as have already been mentioned are those with concentrations exceeding this value (see figure 7.24). The Dutch guideline values display a concentration of 85 mg/kg as the target value and 530 mg/kg as the action value. Around 40% of the Gibraltar soil data is below the Dutch target value and 25% above the action value. The DEFRA/EA SGV's are as follows: 450 mg/kg for residential areas with plant uptake, 450 mg/kg for residential areas with no plant uptake and 750 mg/kg for industrial and commercial land.


Coaling Island
URNR
O'Haras
Battery
Windmill Hill
and Rubbish
Pit

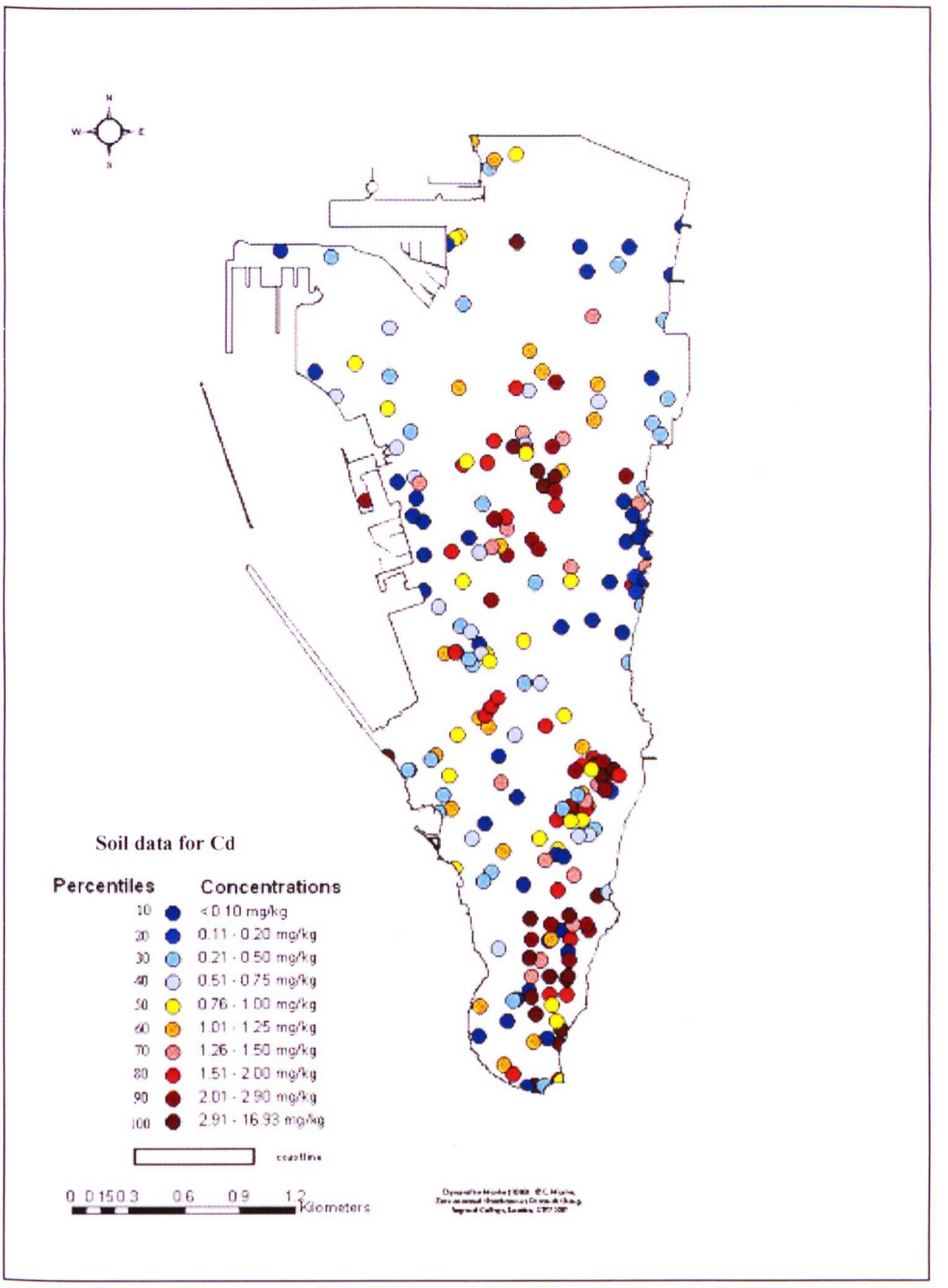
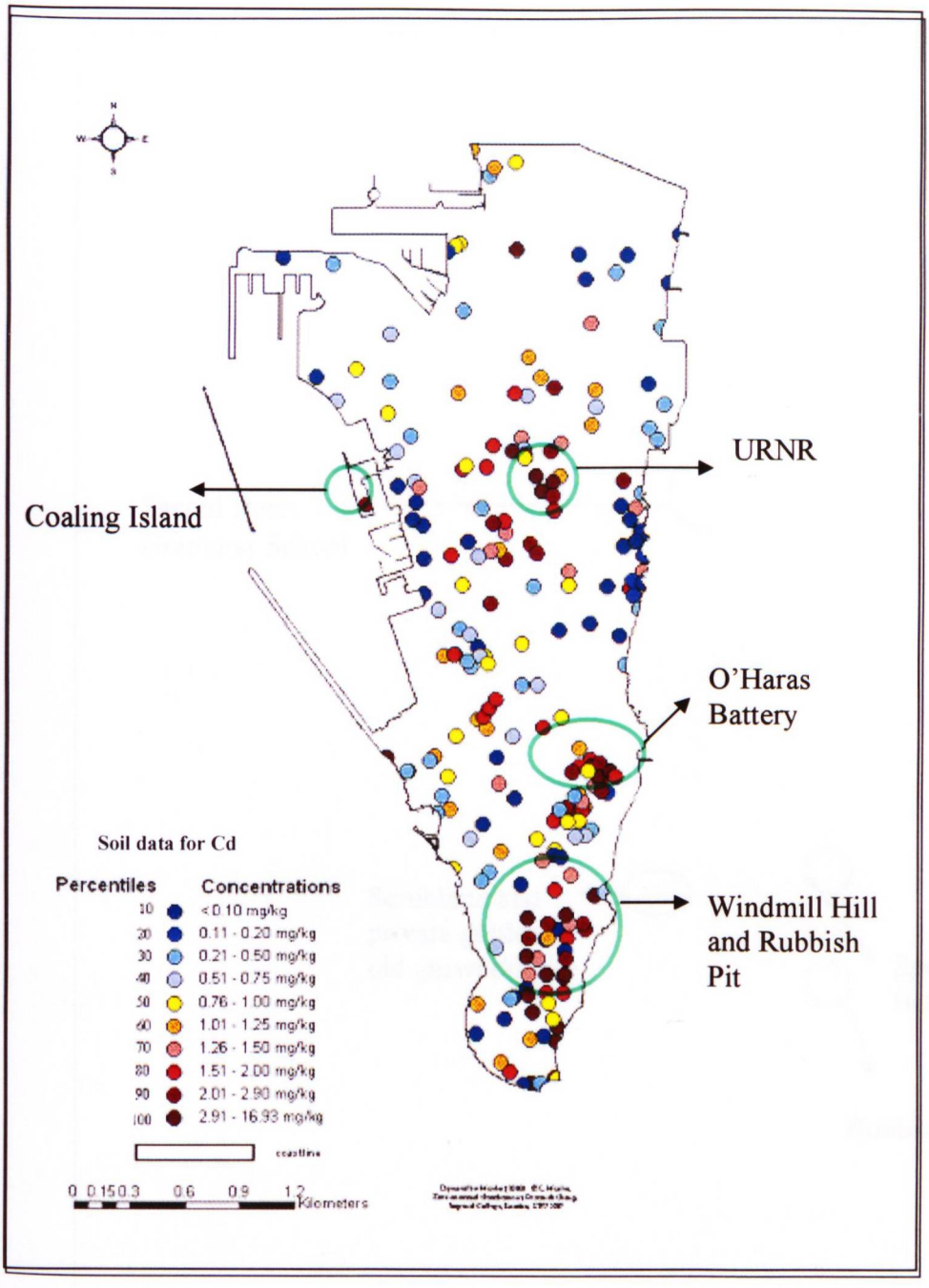


Figure 7.23 Cd concentrations in soils (0-15 cms) from Gibraltar. (n=238)

Please note, Cd data for Gibraltar displayed high bias values and poor precision in the QC. Care should be taken when interpreting the data.

Sites like Spur Battery in the URNR, the rubbish pit, Coaling Island and the samples taken adjacent to the former gas works site all contain elevated levels of Pb. Samples by Deadman's beach at the extreme south of Gibraltar also contained high levels of Pb as compared to the rest of the dataset. Some of these sites exceed the DEFRA/EA SGV's.



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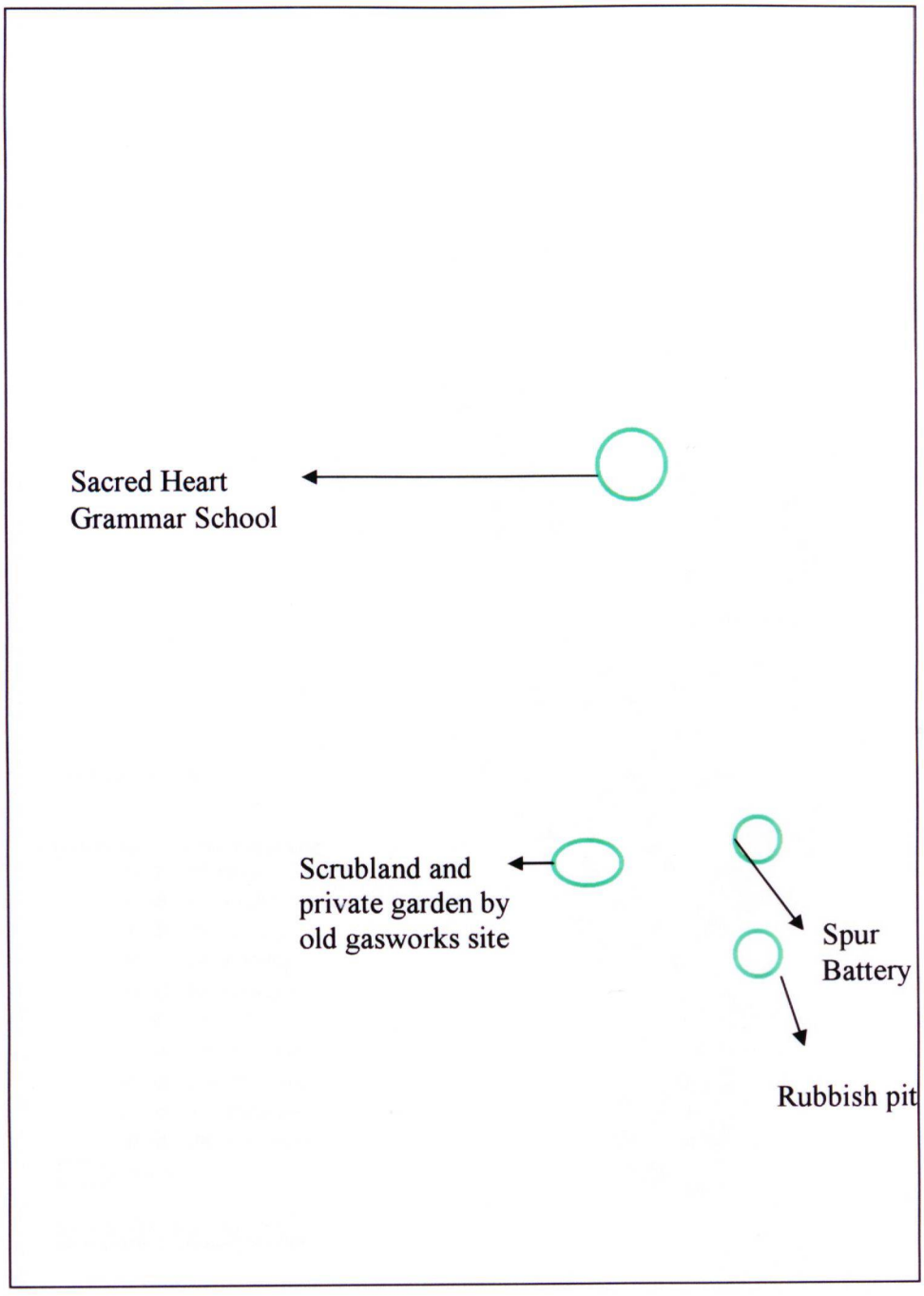

Sacred Heart
Grammar School
Scrubland and
private garden by
old gasworks site
Spur
Battery
Rubbish pit

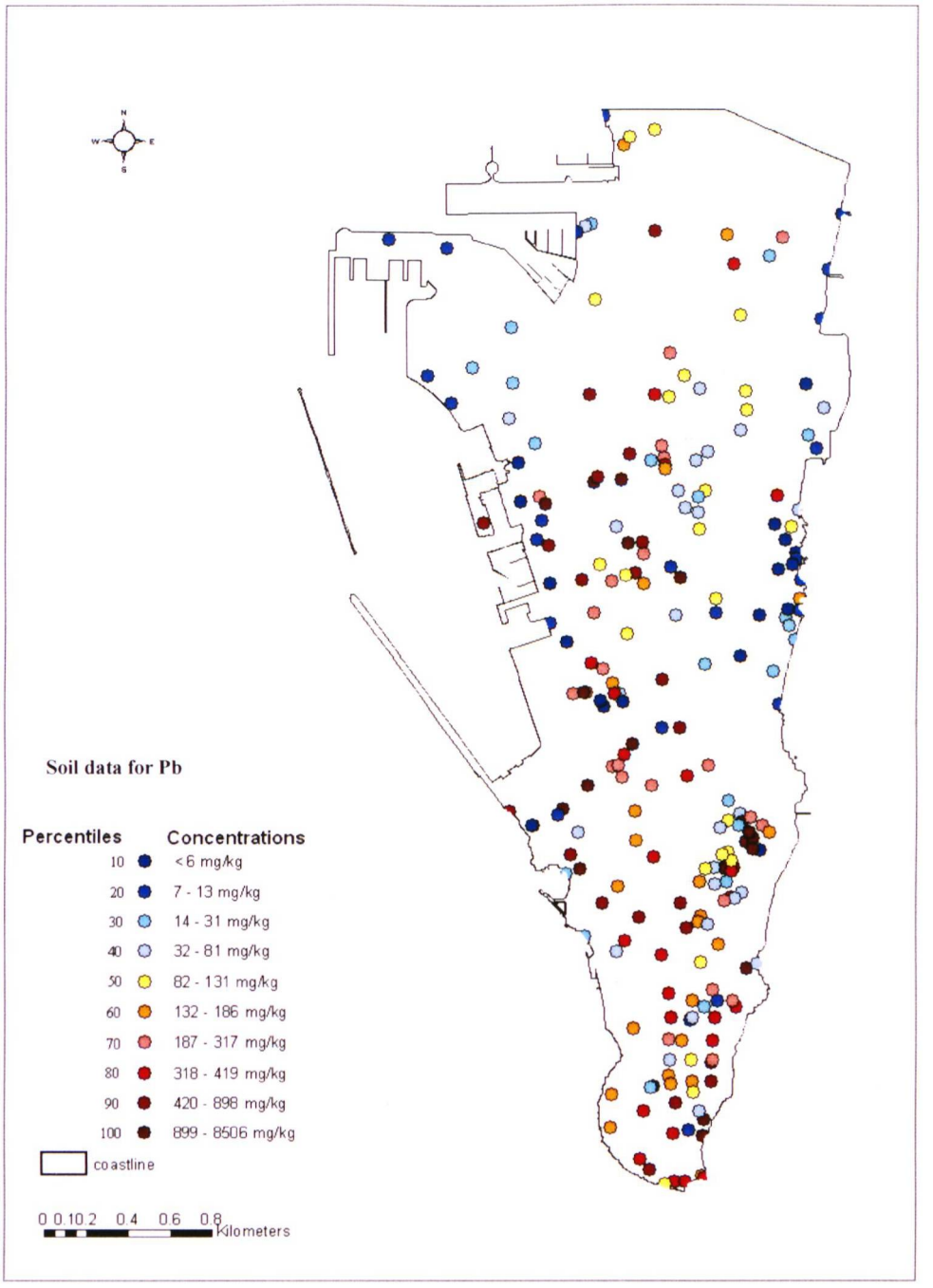
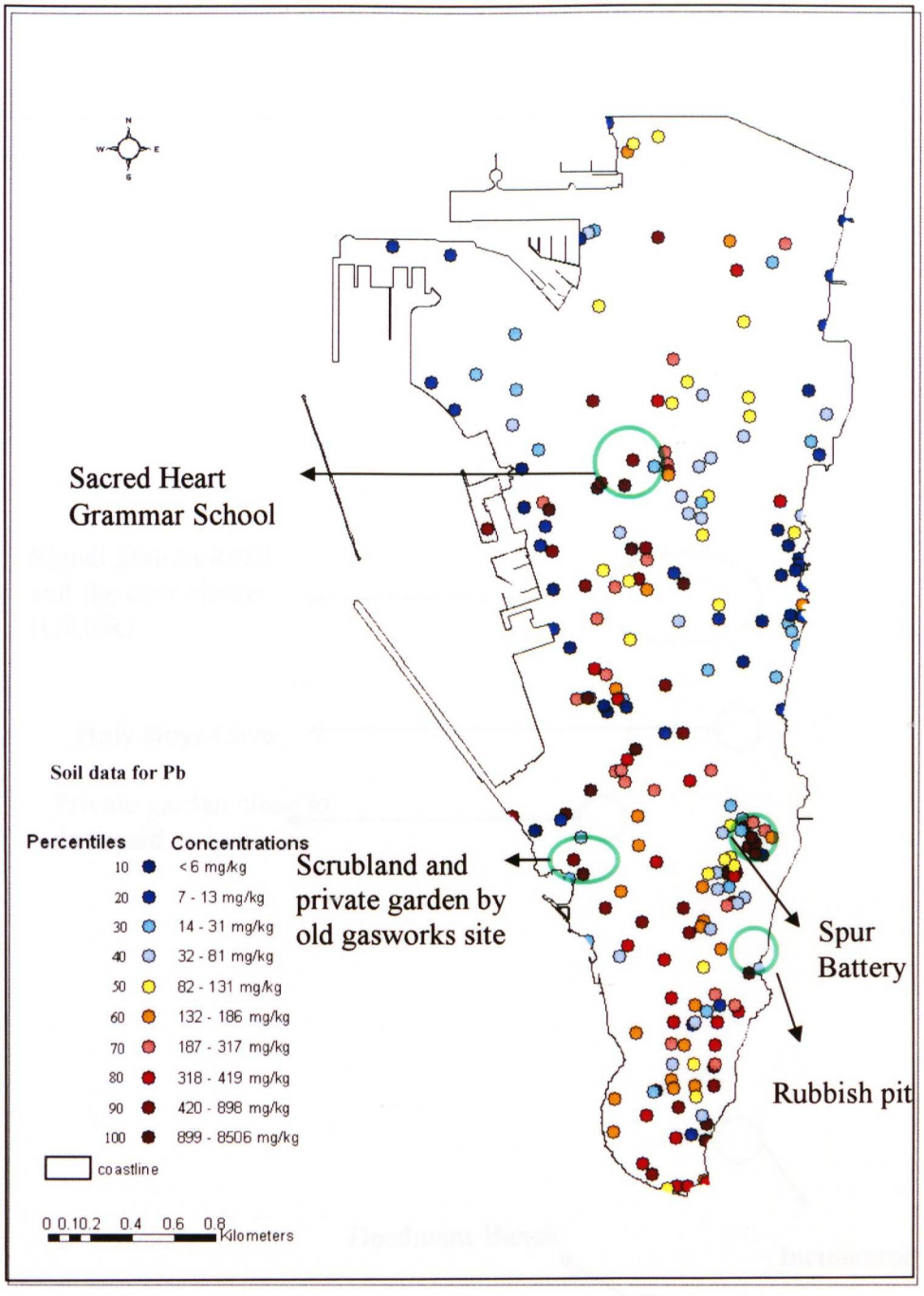


Figure 7.24 Pb concentrations in soils (0-15 cms) from Gibraltar. (n=238)

Samples taken at Sacred Heart Middle School displayed high levels of Pb in soils and also exceeds the DEFRA/EA SGV's. This site is in the upper town area, where a high urban density and narrow roads can be found. This district suffers from a very high traffic flow due to the high number of residential dwellings, the presence of two schools and the sole civilian hospital. Additionally, this district is an intervening area between the exit of the URNR and the rest of Gibraltar. It therefore follows that there



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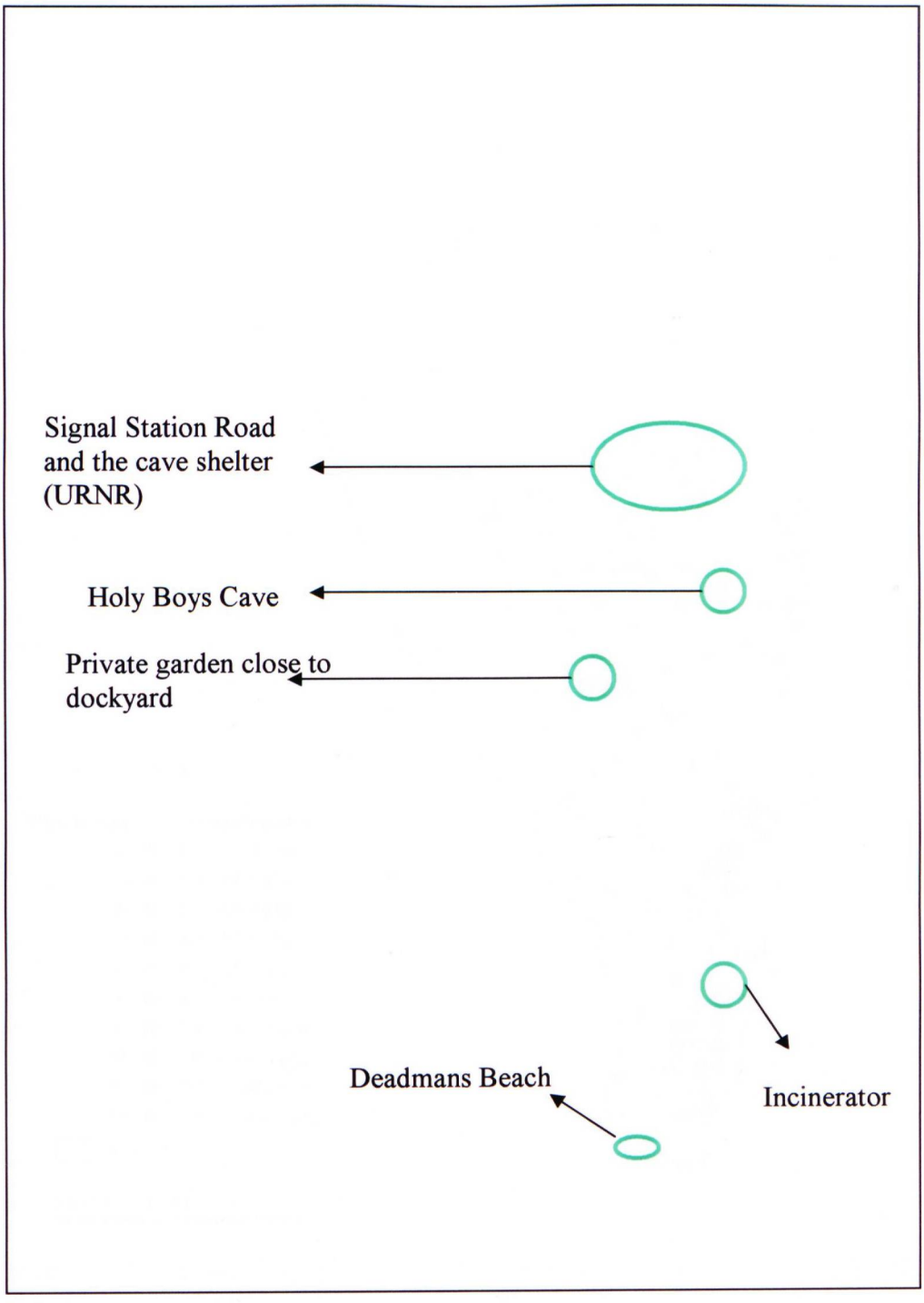
Signal Station Road
and the cave shelter
(URNR)
Holy Boys Cave
Private garden close to
dockyard
Deadmans Beach
Incinerator

is a further addition in traffic volume in the form of coaches, taxis and private vehicles visiting the nature reserve.

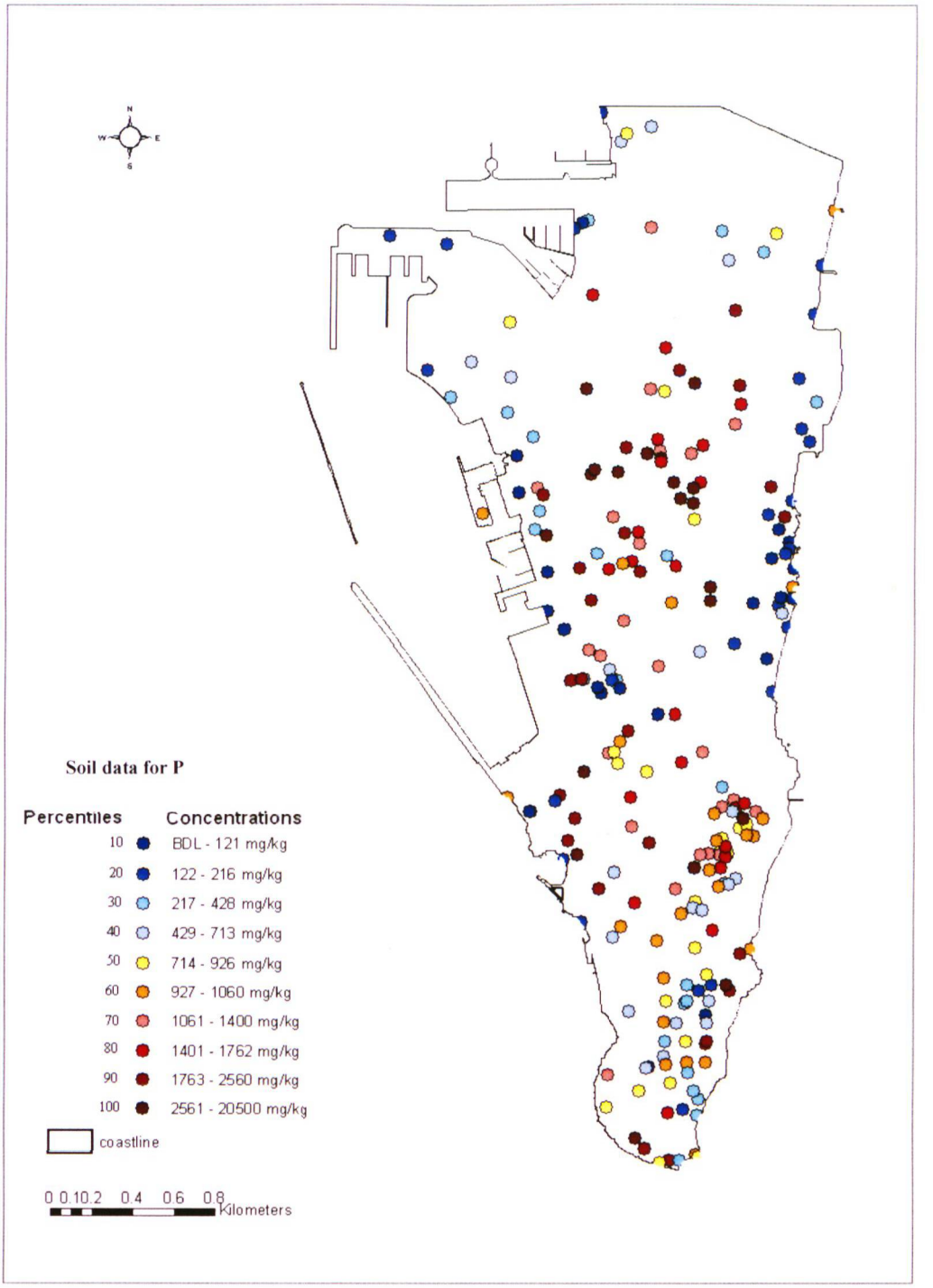

Figure 7.25 P concentrations in soils (0-15 cms) from Gibraltar. (n=238)

Phosphorous occurs in soil in inorganic and organic forms with the latter being mostly predominant. Concentrations in Gibraltar soils are generally high (<0.4-20500 mg/kg) (figure 7.25) when compared to the range provided by Ure and Berrow (1982)

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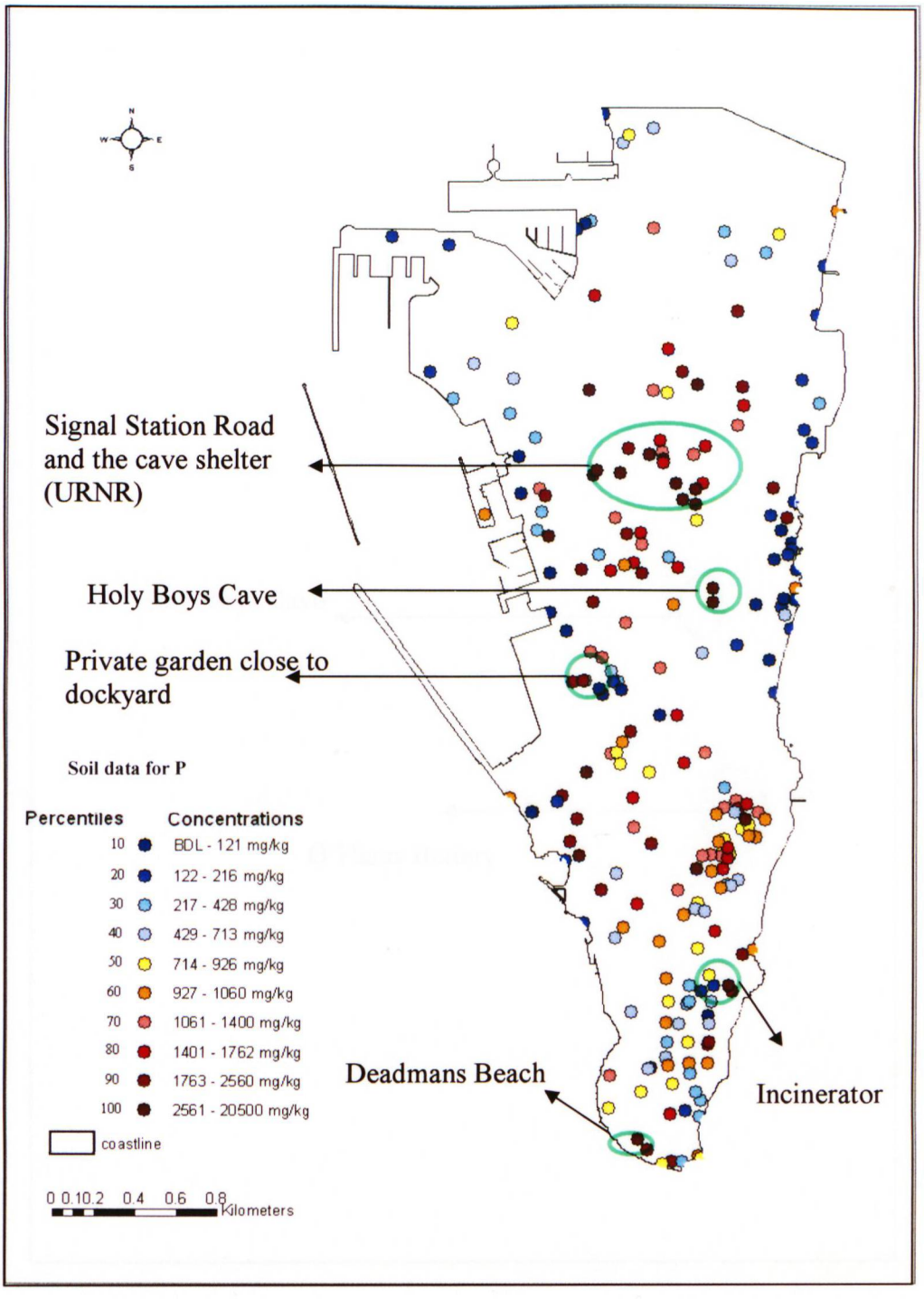

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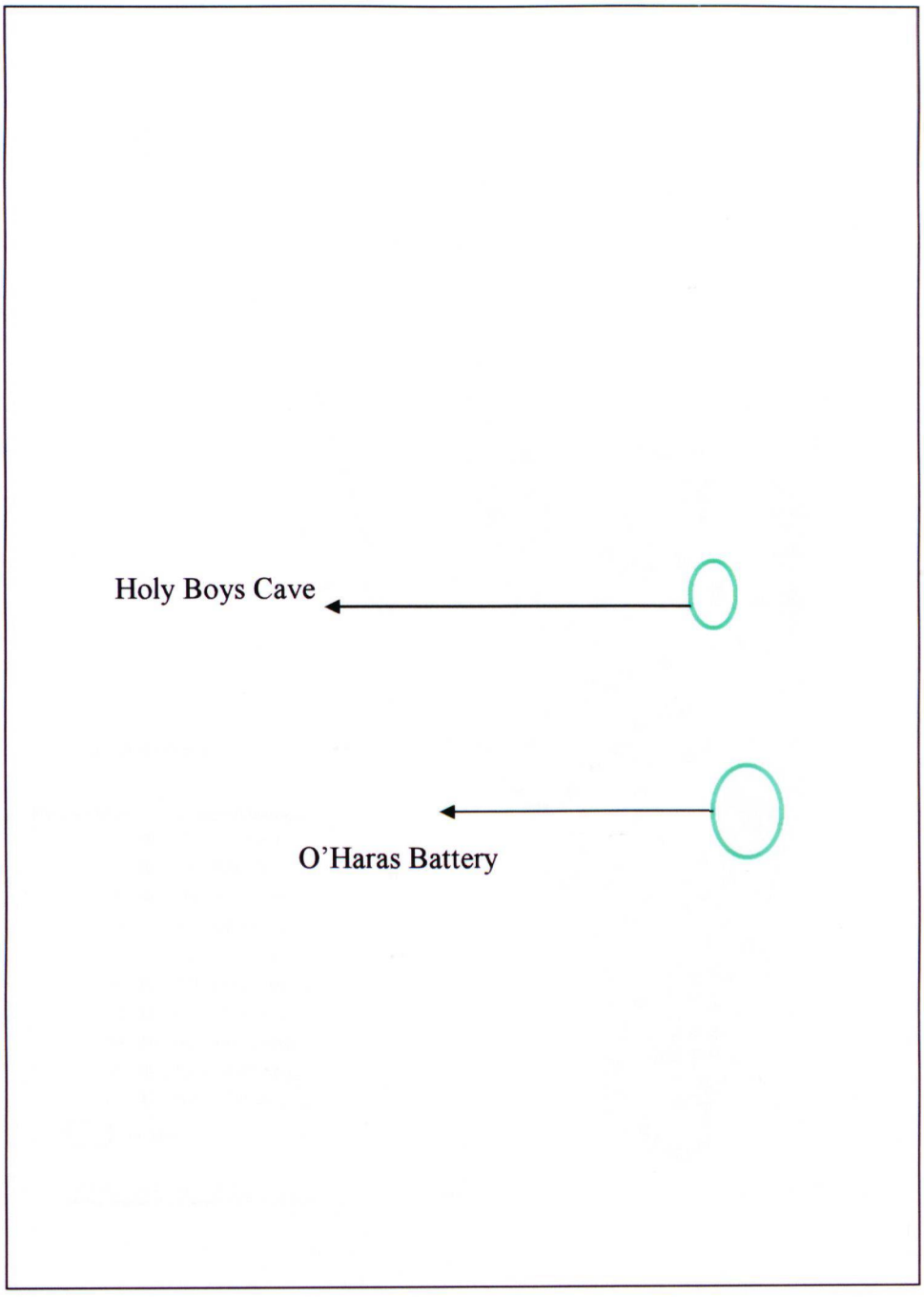

Holy Boys Cave
O'Haras Battery

of 334-527 mg/kg for P. The 95th percentile value for P in Gibraltar soils is 3300 mg/kg.

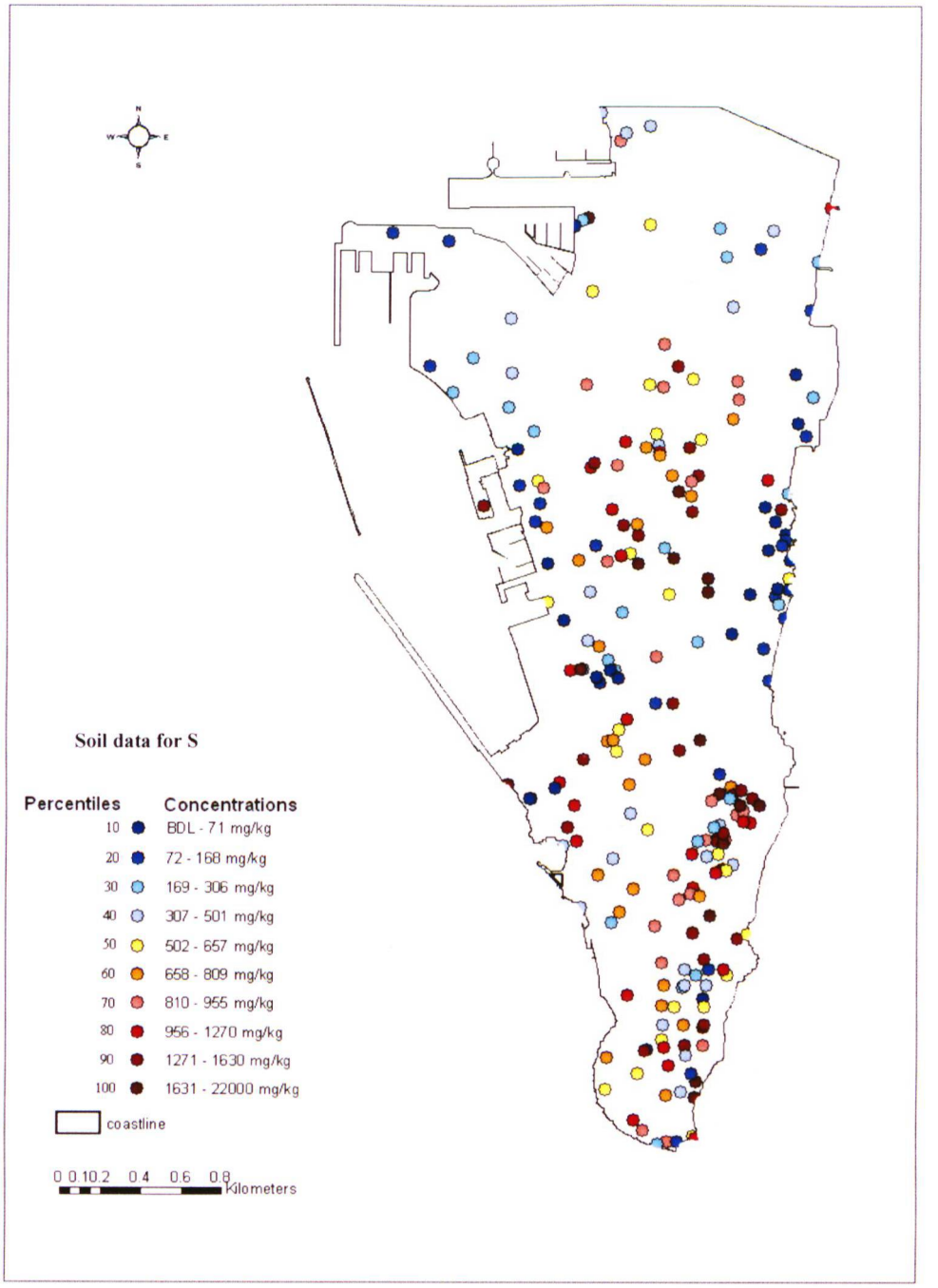


Figure 7.26 S concentrations in soils (0-15 cms) from Gibraltar. (n-238)

Out of the eight sites with concentrations exceeding this value, six are found in the URNR and are clustered around Signal Station Road. The other three sites include O'Hara's Battery, Holy Boys cave and a private garden. The high concentrations in

of 334-527 mg/kg for P. The 95th percentile value for P in Gibraltar soils is 3300 mg/kg.

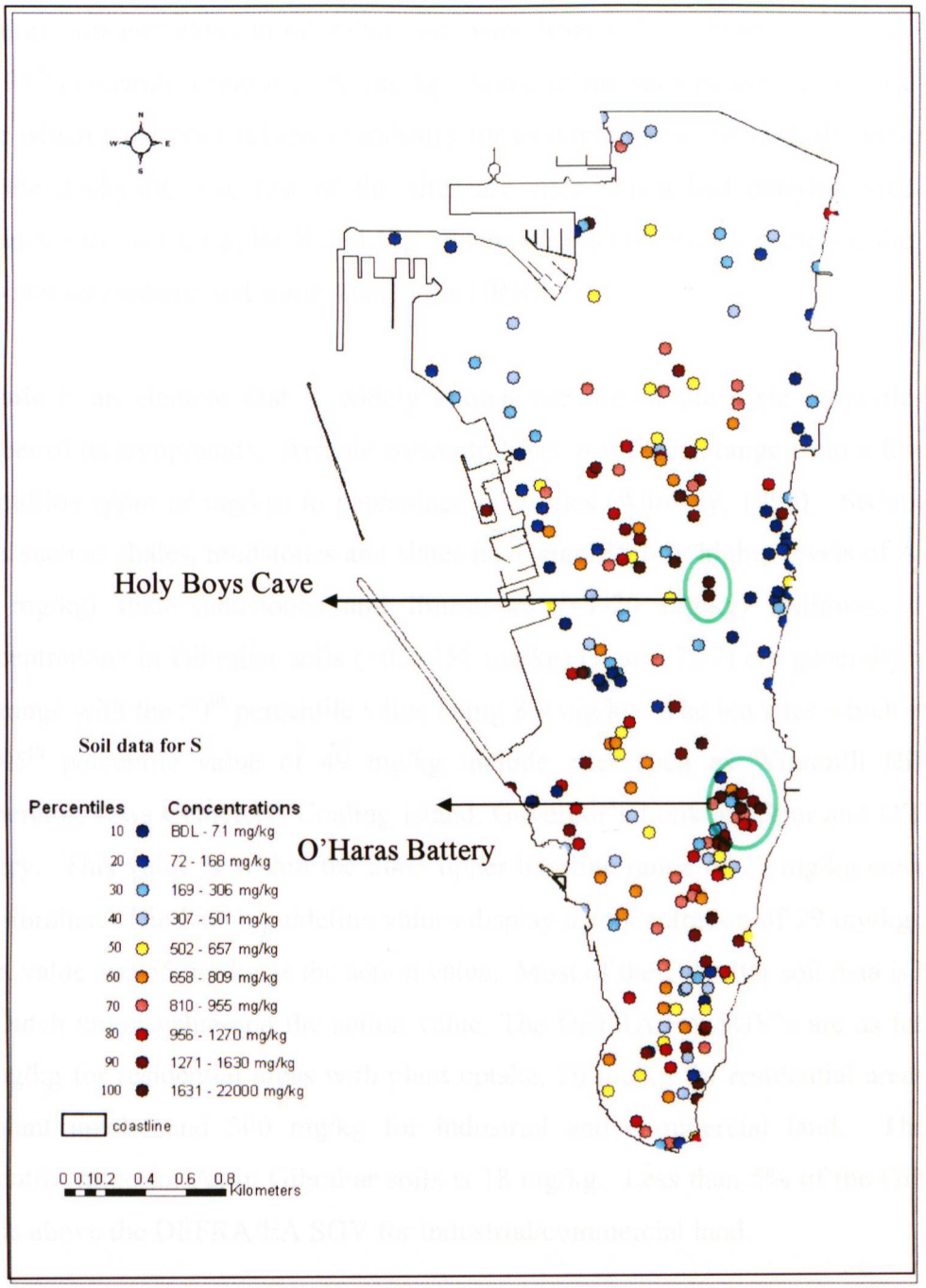


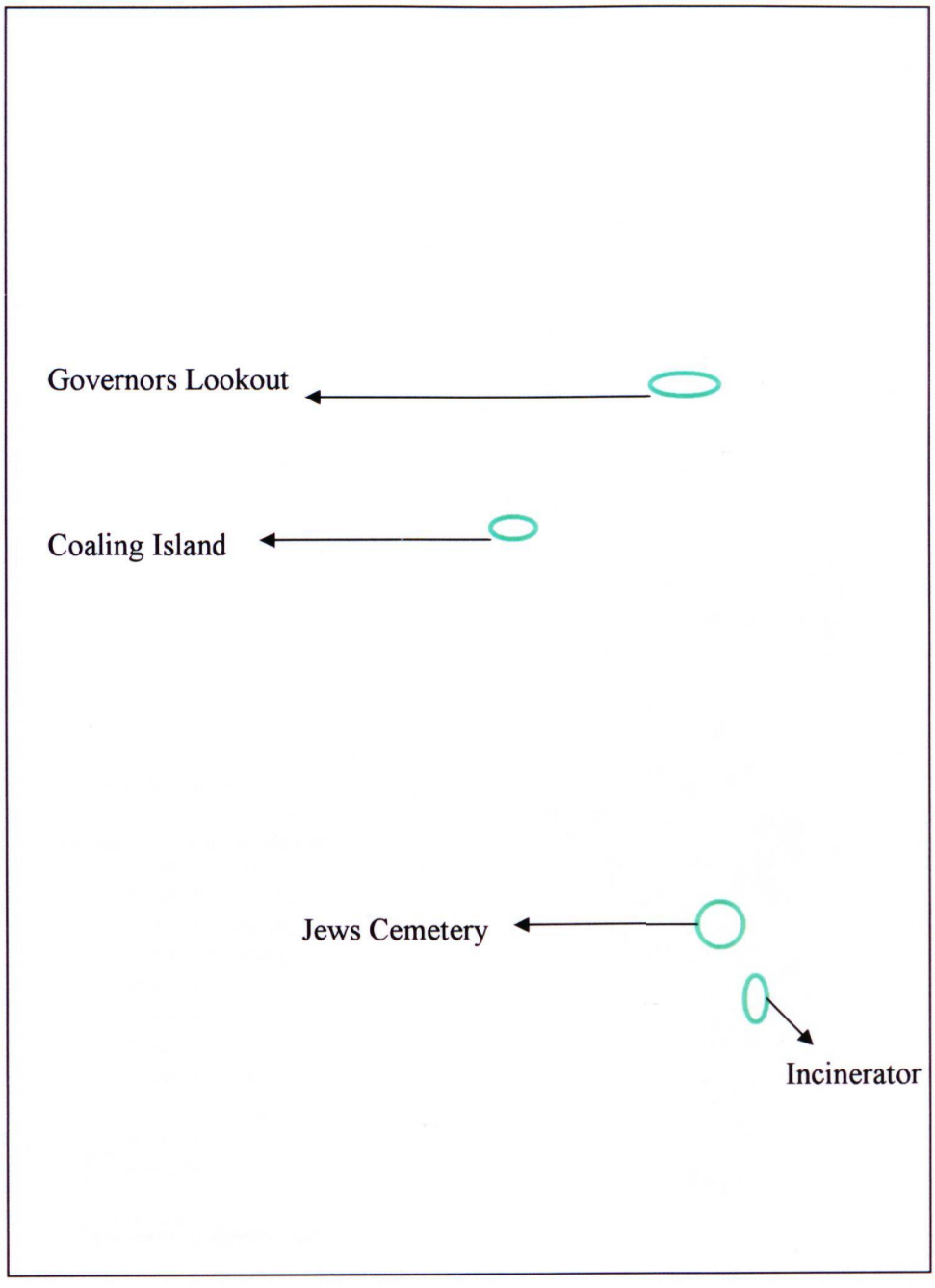
Figure 7.26 S concentrations in soils (0-15 cms) from Gibraltar. (n-238)

Out of the eight sites with concentrations exceeding this value, six are found in the URNR and are clustered around Signal Station Road. The other three sites include O'Hara's Battery, Holy Boys cave and a private garden. The high concentrations in

the latter site could possibly be due to the addition of inorganic fertiliser phosphorous to the soils.

Sulphur concentrations in Gibraltar soils vary from 0.2-22000 mg/kg (figure 7.26). The 95th percentile value is 2290 mg/kg. Some of the sites exceeding this value are those which have been related to industry for example the scrap yard, the incinerator and the dockyard. The rest of the sites are sites which had outlying values for elements such as Li, Ca, Be K and Mg. Such sites include the cave shelter, the top of the water catchments and some sites in the URNR.

Arsenic is an element that is widely known because of the toxic properties of a number of its compounds. Arsenic concentrations in soils can range from a few parts per million (ppm or mg/kg) to percentage quantities (Alloway, 1995). Sedimentary rocks such as shales, mudstones and slates have significantly higher levels of As (<1-900 mg/kg) than sandstones and limestones (<1-20 mg/kg) (Alloway, 1991). Concentrations in Gibraltar soils (<0.2-351 mg/kg) (figure 7.27) are generally within this range with the 50th percentile value being 8.9 mg/kg. The ten sites which exceed the 95th percentile value of 49 mg/kg include sites such as Windmill Hill, the Incinerator, Jews Cemetery, Coaling Island, Governor's Lookout, Spur and O'Hara's Battery. This value is within the 2003 upper baseline range of 77 mg/kg calculated for Gibraltar. The Dutch guideline values display a concentration of 29 mg/kg as the target value and 55 mg/kg as the action value. Most of the Gibraltar soil data is below the Dutch target value and the action value. The DEFRA/EA SGV's are as follows: 20 mg/kg for residential areas with plant uptake, 20 mg/kg for residential areas with no plant uptake and 500 mg/kg for industrial and commercial land. The 75th percentile value for As in Gibraltar soils is 18 mg/kg. Less than 5% of the Gibraltar data is above the DEFRA/EA SGV for industrial/commercial land.


Governors Lookout
Coaling Island
Jews Cemetery
Incinerator

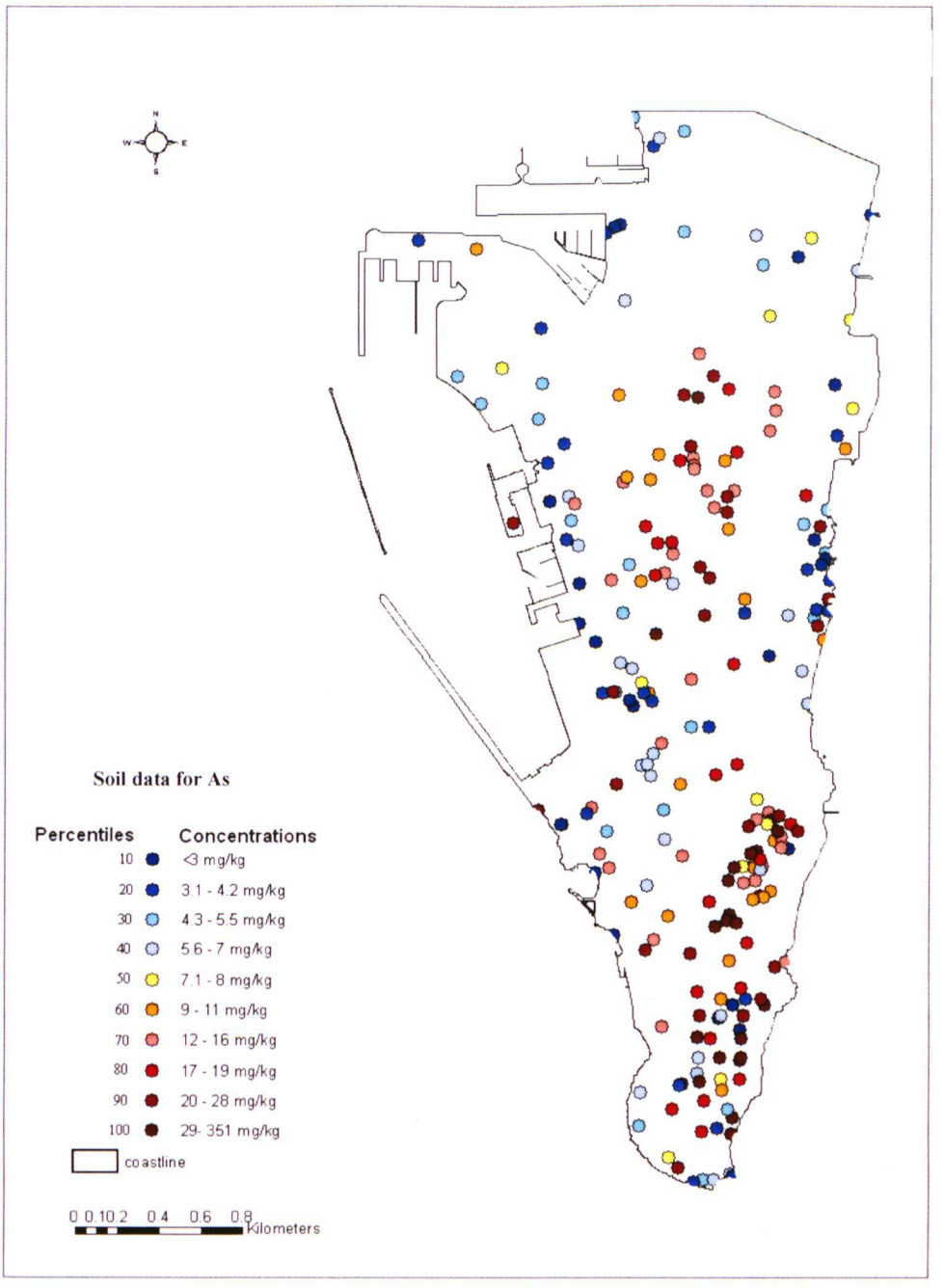
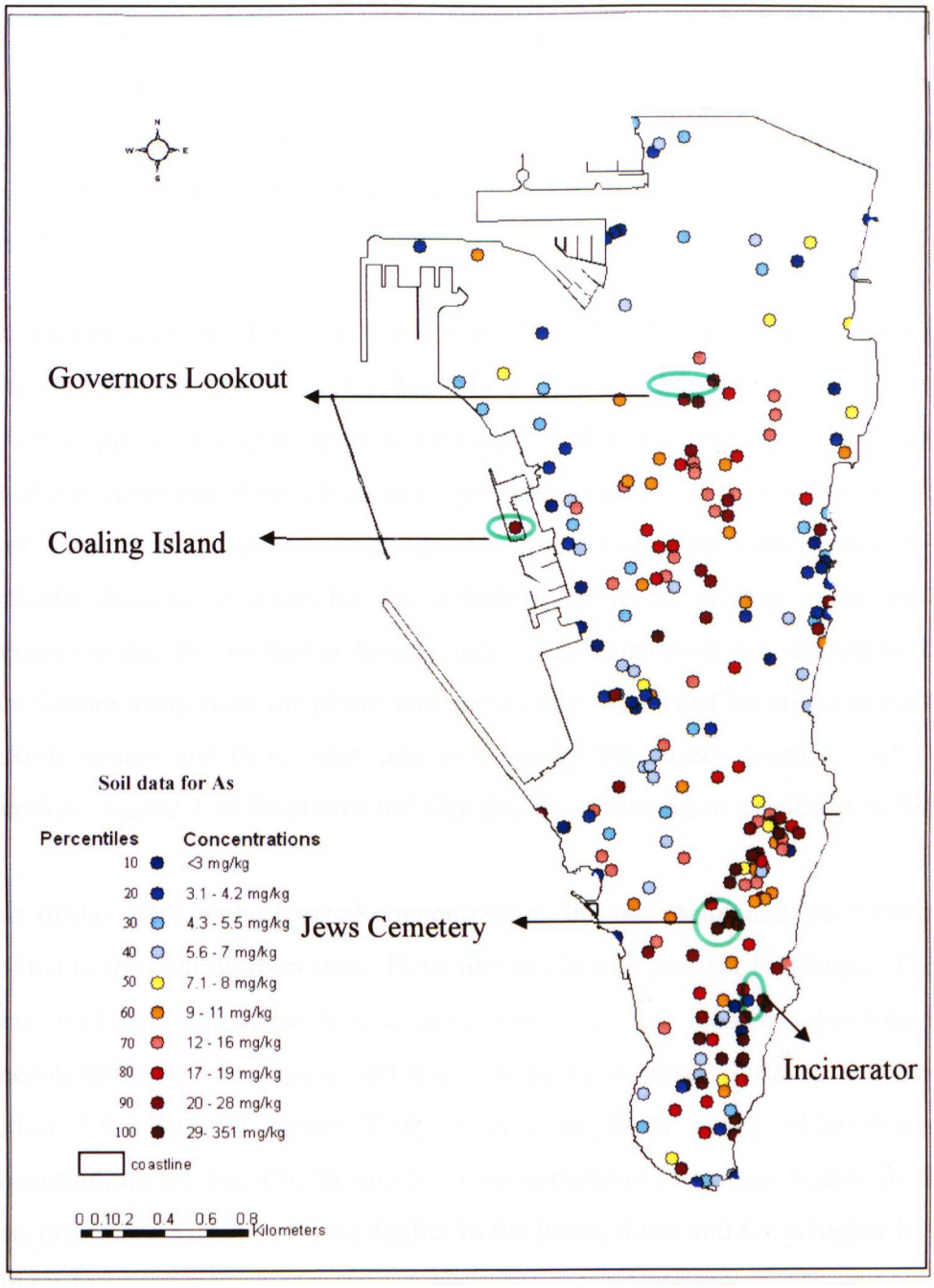


Figure 7.27 As concentrations in soils (0-15 cms) from Gibraltar

7.4 Spatial presentation and discussion of element concentrations in house dusts

The concentration of trace metals in dust from urban homes can originate from both internal (within the home) and external (outside the home, e.g. garden) sources. The spatial distribution of element concentrations in dusts from Gibraltar is such that it is difficult to identify possible sources. Twelve sites have outlying values which exceed



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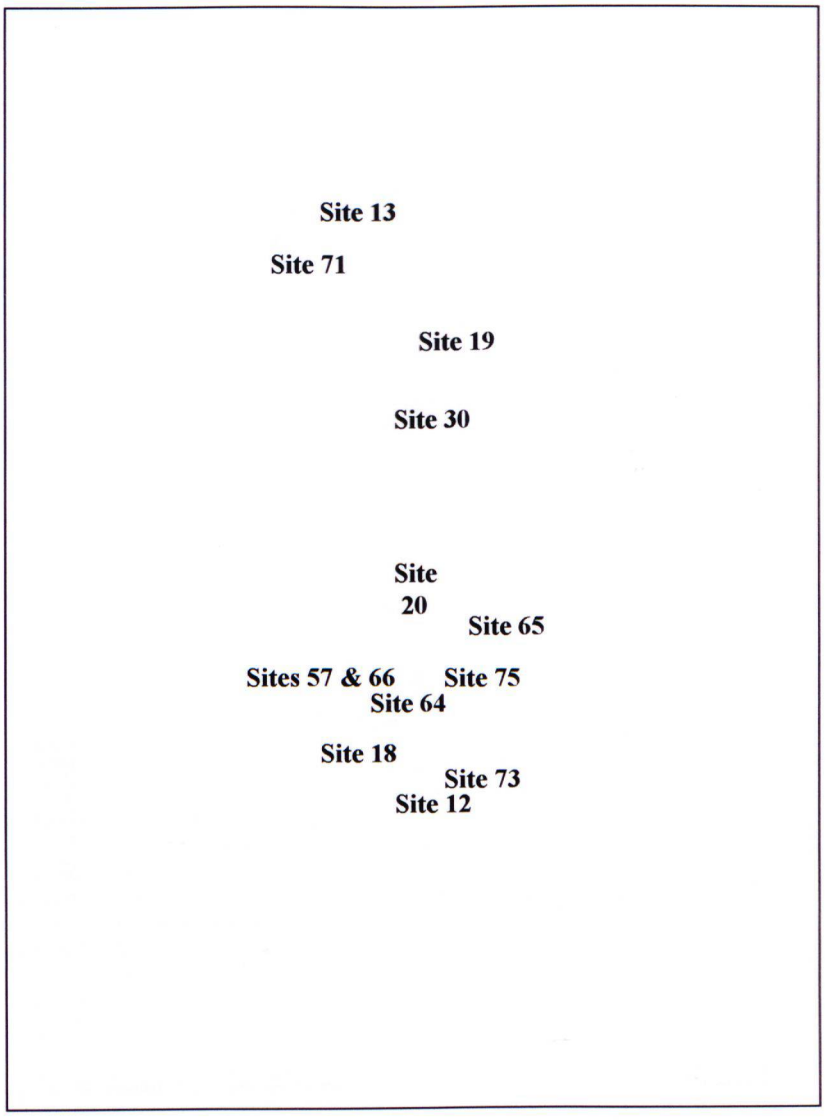
the 95th percentile for a range of elements. The locations of these sites are shown in figure 7.28. There are four distinct locations, three of which are in close proximity to an industrial area. Two sites are close to the electricity generating station in the north of Gibraltar, and the other two sites are located south of the dockyard in the southern part of town.

The sites in area one (Europort), near the electricity generating station have outlying values for the elements Na, V, Cr, Mg, Mn, Ni and S. Plate 7.1 was taken from one of the sites opposite the generating station and desalination plant and shows the smoke which can come out of the desalination plant at "start up" in the mornings. There are other sites in this vicinity which do not contain elevated concentrations for any particular element. Reasons for this include the urban topography of the area and the direction which the particular houses face. The remaining households in that area were further away from the plants and had a large number of buildings in between the possible source and these sites, and additionally the houses faced a south westerly direction. Figure 7.29 illustrates the high density of the urban dwellings in the area.

Two further sites with elevated concentrations in both major and trace elements are situated in the central town area. Both sites are in old, pre-war buildings. The central town, including the areas where these two sites are located, also has elevated concentrations of both major and trace elements in street dusts as can be seen in section 7.5. Site 30 (figure 7.28) is an example of a site which has elevated concentrations for Na, Ca, Sr and S. Concentrations of Na are higher in the street dusts (section 7.5), Ca and S are higher in the house dusts and Ca is higher in the soils (table 7.1).

Site 19, also in the town, is situated in an area of high urban density with a lot of old pre war buildings and narrow streets. It has elevated concentrations for Ti, V, Cr, Mn, Fe, Ni, Cd, S and As. This site has elevated concentrations of anthropogenically related elements as opposed to site 30 which did not. The questionnaire completed by households (see appendix B) taken at the sites does not reveal any definitive clues as to why the concentrations for these elements are high.


Site 13
Site 71
Site 19
Site 30
Site
20
Site 65
Sites 57 & 66
Site 75
Site 64
Site 18
Site 73
Site 12

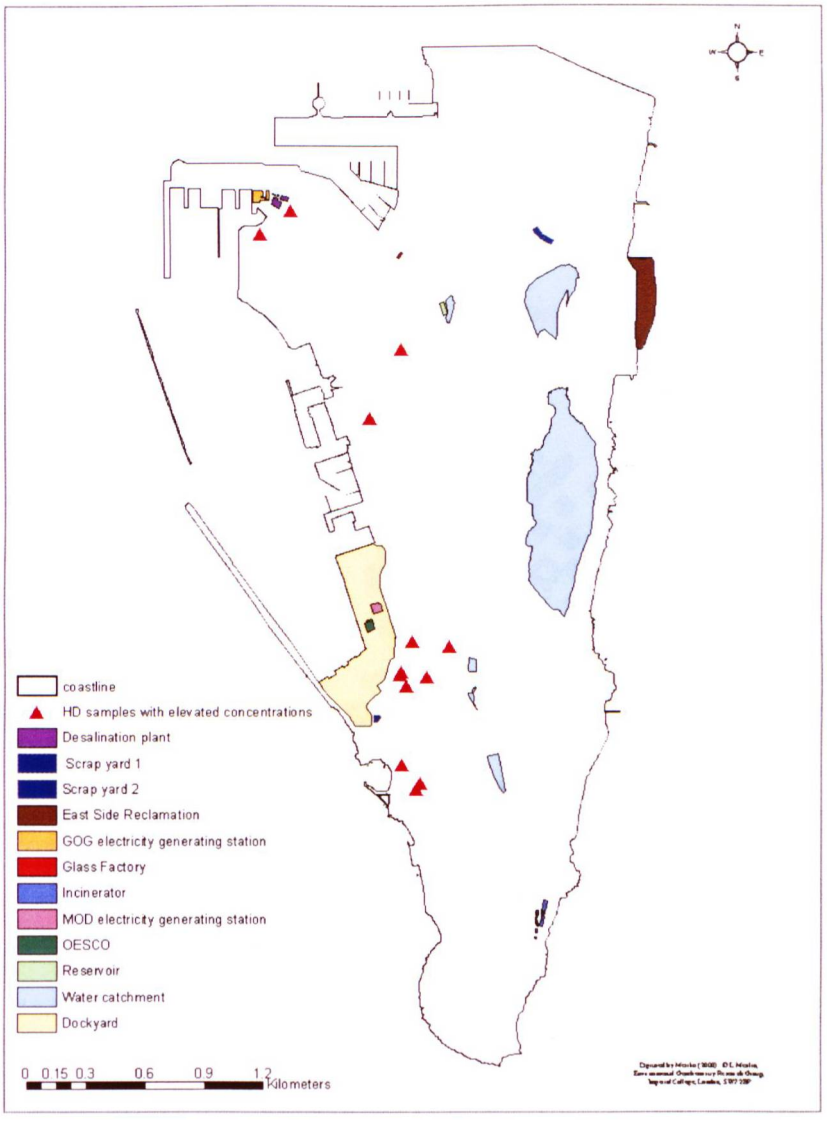
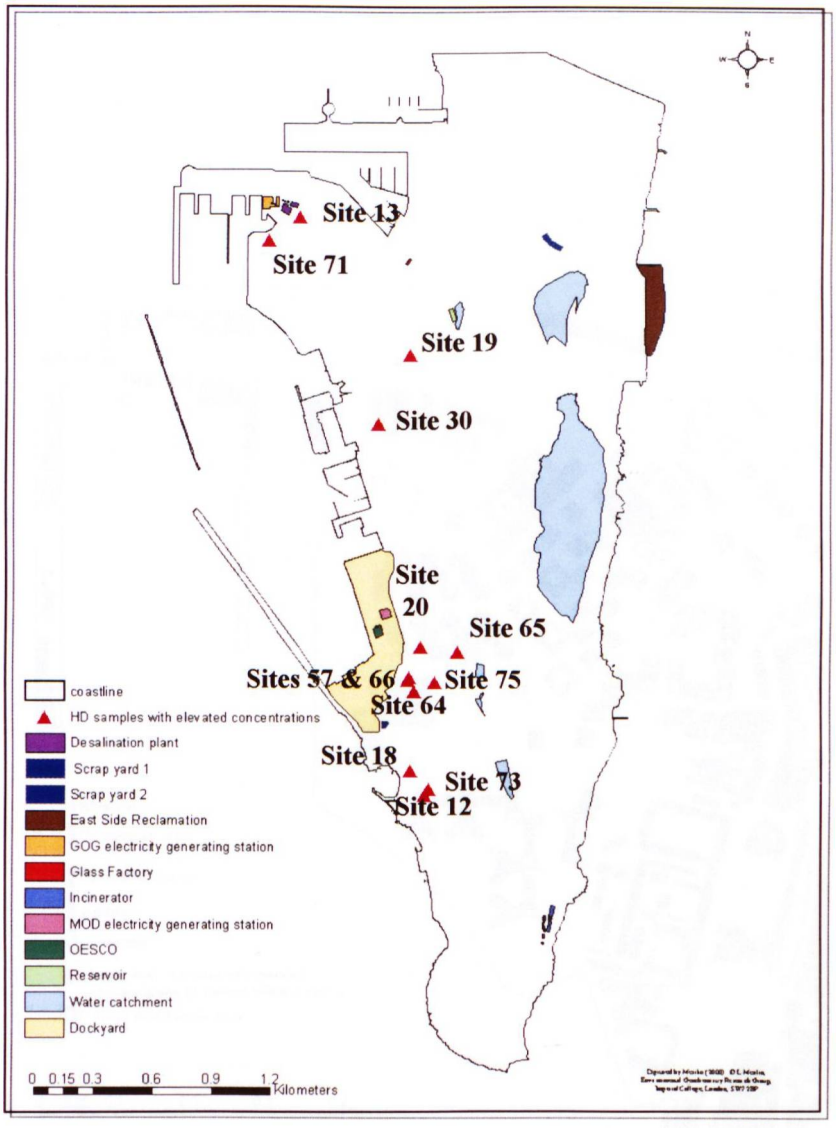


Figure 7.28 House dust (HD) samples with outlying values for various elements concentrations from Gibraltar.

Table 7.1 Selected element concentrations in different media at site 30 in the town area. (mg/kg)

Elements	Street dust	House dust	Garden soil
Na	2640	1890	395
Ca	12100	18300	76100
Sr	199	847	107
S	7280	45200	955



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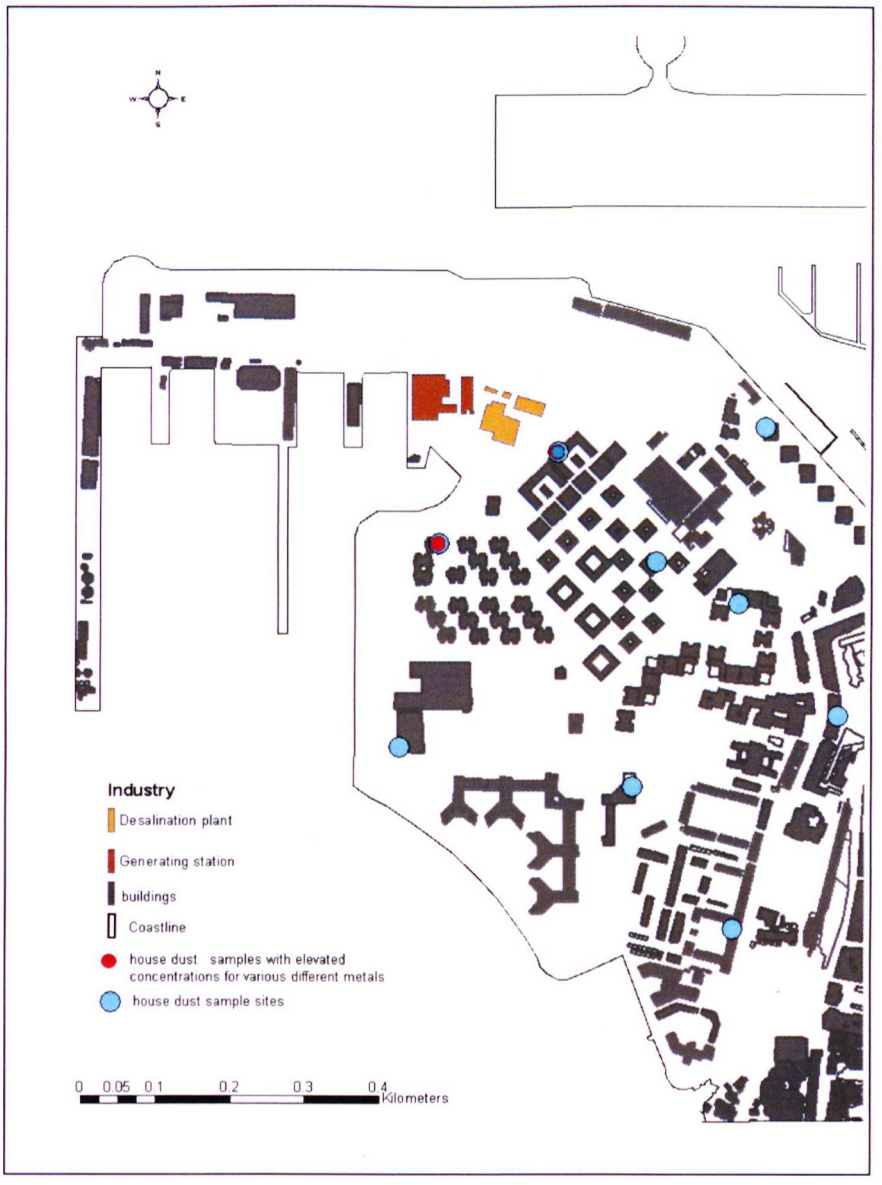


Figure 7.29 Density of households and commercial property in the Europort area.

The houses were not redecorated in the past year prior to the samples being taken and the occupations of the residents were not of an industrial nature. There was no correlation between element concentrations and the age of the properties, the number of times the site was cleaned, the type of heating and flooring or any of the other site factors. Concentrations of elements in house dusts in this area cannot definitively be compared with the concentrations in street dusts in the immediate area due to the increased urban density and the nature of the topography. The spatial heterogeneity of an urban environment within the town area and the short term temporal variability of elemental concentrations in dusts do not justify a comparison of concentrations between different media at this site.

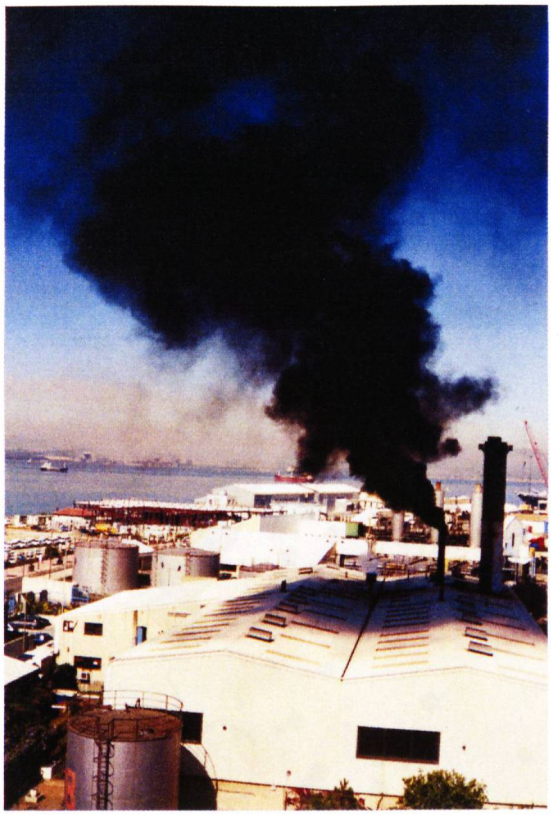


Plate 7.1. Desalination plant at start up.

The other two clusters of element concentrations in house dusts with outlying values are found to the south of Gibraltar, south of the dockyard. The two areas (clusters) in this district had samples with concentrations greater than those reported by Fergusson and Kim (1991) for trace elements in house dusts in the following range of elements: Cu, Cd, As, Zn, Cd, Pb, Sr, Ti, Mn, Fe and Ba. Not all the sites necessarily were elevated in all these elements. Figure 7.30 shows the sample locations for soils and dusts in this area. There were other households in the same vicinity which did not display elevated concentrations. The sand blasting of ships used to occur (and still does occasionally) in the dockyard and there have been numerous reports from the district south of the dockyard relating to a black dust which settled on cars, buildings and inside homes on a regular basis. Soils with a high content of this black dust (found in the area whenever the sand blasting occurred) had higher concentrations for the above named elements (samples identified in section 7.3, south of the dockyard) compared with the rest of the dataset. Black dust was not visually present in the remaining households in the area when the samples were taken. It should be noted that not all the house dust samples in this area were taken on the same day. This is an

important factor which when combined with the cleaning schedules of each of the premises in this area could explain why certain households displayed higher concentrations of metals than others.

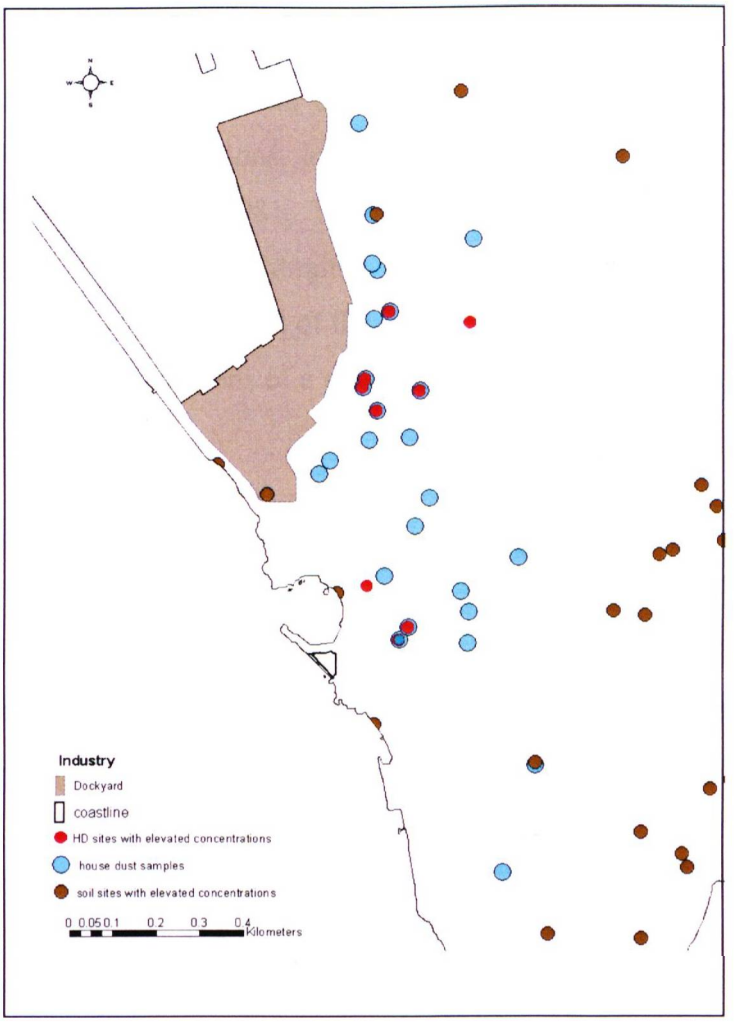


Figure 7.30 Soil and house dusts samples in the dockyard area.

The soil samples taken in this area do however display elevated concentrations in the same range of elements. The point to take note of here is that soils can be considered as "longer term" indicators of possible contamination, whereas dusts samples are a reflection of short term or recent activities. The difficulty in interpreting element concentrations in house dusts includes the vast number of factors which need to be considered, ranging from factors relating to inside the home (type of flooring, heating system used, smokers in the premises etc), to factors such as industry in the area, the urban density in the area, the direction which a site might be facing, wind direction just before and during the time when the samples were taken etc. Reconnaissance studies such as these are however very useful in identifying areas where evidence

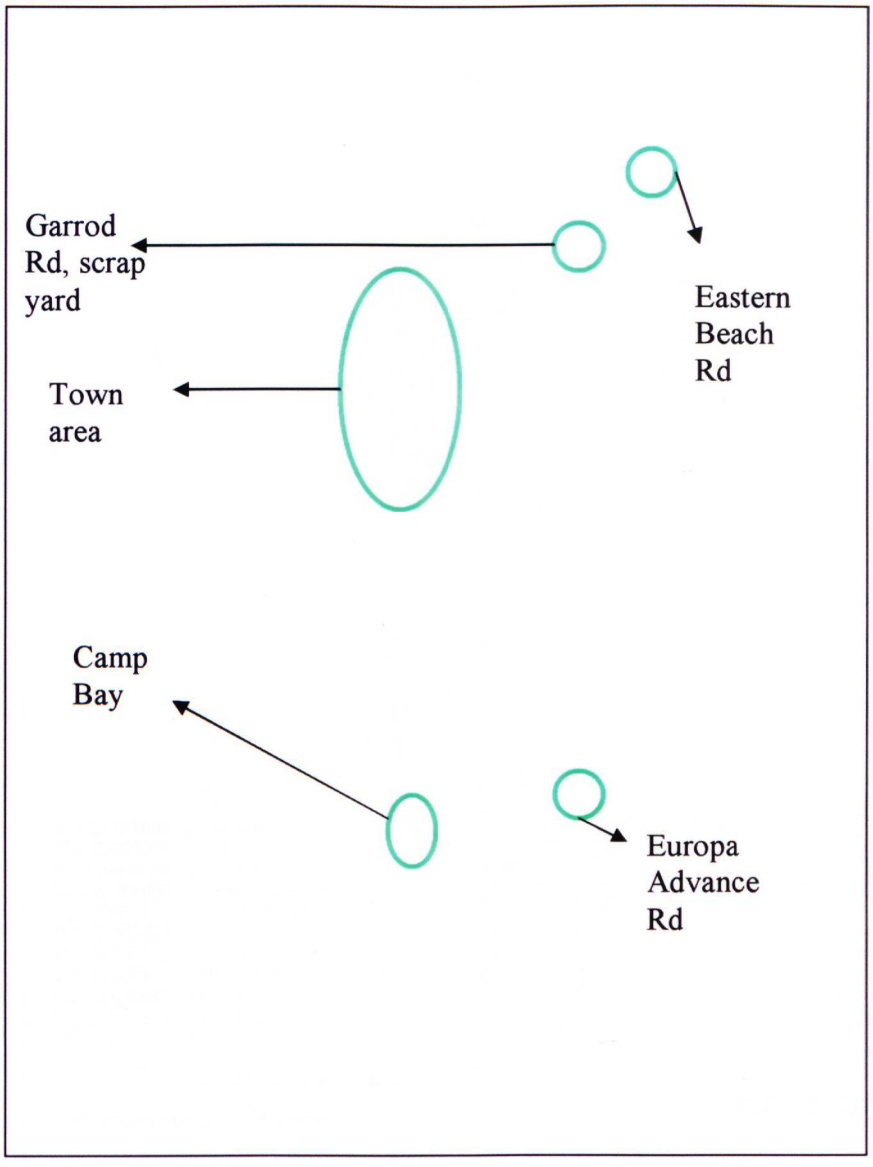
suggests possible sources of contamination, thereby indicating areas where further longer term monitoring is necessary.

7.5 Spatial presentation and discussion of element concentrations in street dusts

Heavy metals in dusts in the urban environment come from a variety of sources including traffic, vehicle emissions, industrial sources, building materials and even the weather (Harrison *et al.*, 1981, Thornton, 1991). The spatial distribution of elements in street dusts in Gibraltar shows distinct areas where elevated concentrations (in relation to the rest of the dataset) are found. Figure 7.31 shows the areas with elevated concentrations of a range of elements (e.g. Pb, Cu, As, Zn, Ca, Ni etc) in street dusts.

The most noticeable area is the cluster in the town. The district which is referred to as the "town area" has a high density of urban dwellings, often with old pre-war buildings, narrow streets and a large volume of traffic. Plates E3 and E4 in appendix E is an aerial photograph showing the town area. Eighty three samples were taken from major, secondary and pedestrianised roads within the town area. Element concentrations in the town area are high for most if not all elements analysed compared with samples taken in the east side, southern district or URNR. The town area is largely commercial and residential. The traffic density, combined with the urban topology, namely the narrow roads, the lack of wind flow and the age of the buildings) are the main reasons attributed here to the elevated concentrations.

A second area with elevated concentrations is found to the north of Gibraltar in close proximity to the airport and runway. One site is on Winston Churchill Avenue close to the border with Spain and the second is just south of the runway at Eastern Beach Road. Both sites are on major roads and have a very high volume of traffic. These two sites displayed elevated concentrations when compared to the rest of the dataset for the elements Al, As, Ba, Ca, Cr, Fe, K, La, Mn, Na, Ni, Pb, P, Sr, S, Ti and V. The increased Pb and Ba levels in dusts could relate to the emissions from fuels motor vehicles (as already stated). However further research using source apportionment techniques possibly SEM would be needed to verify this.


Garrod
Rd, scrap
yard
Eastern
Beach
Rd
Town
area
Camp
Bay
Europa
Advance
Rd

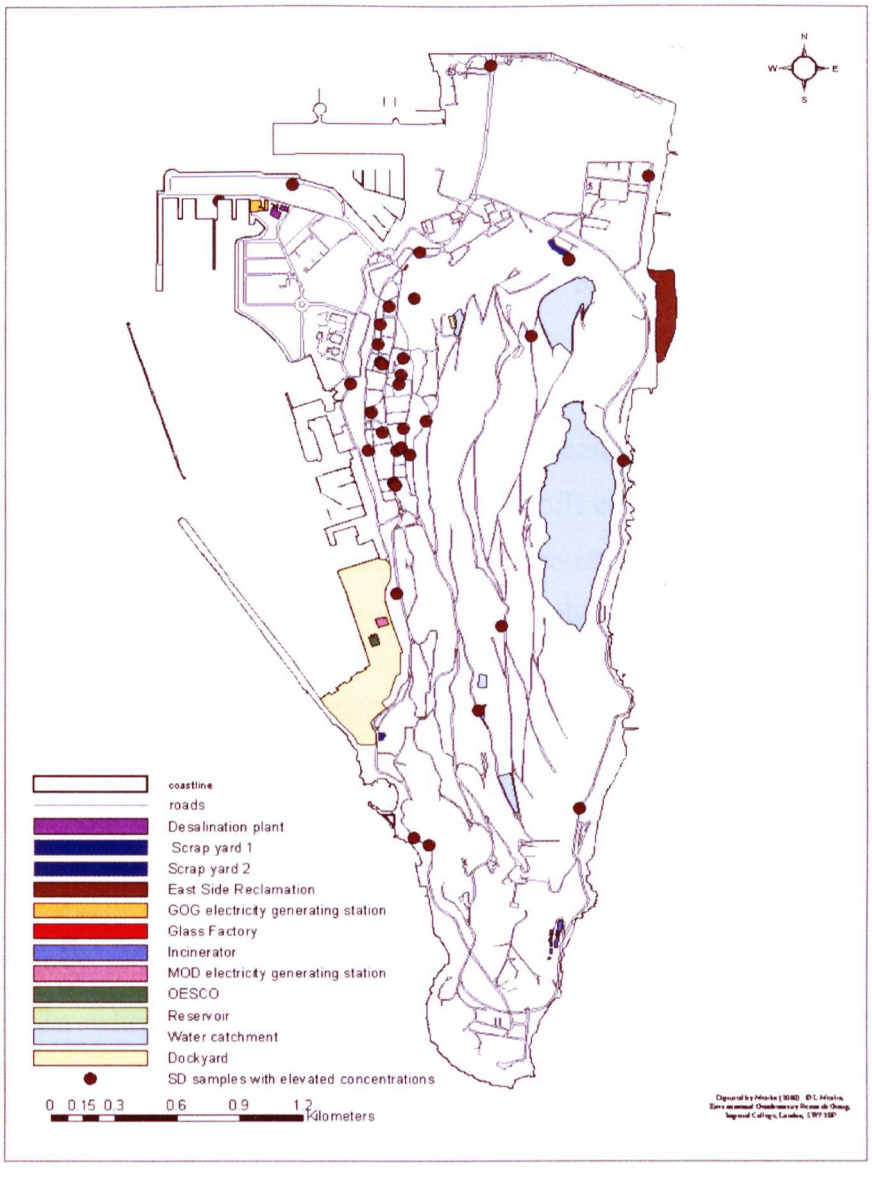
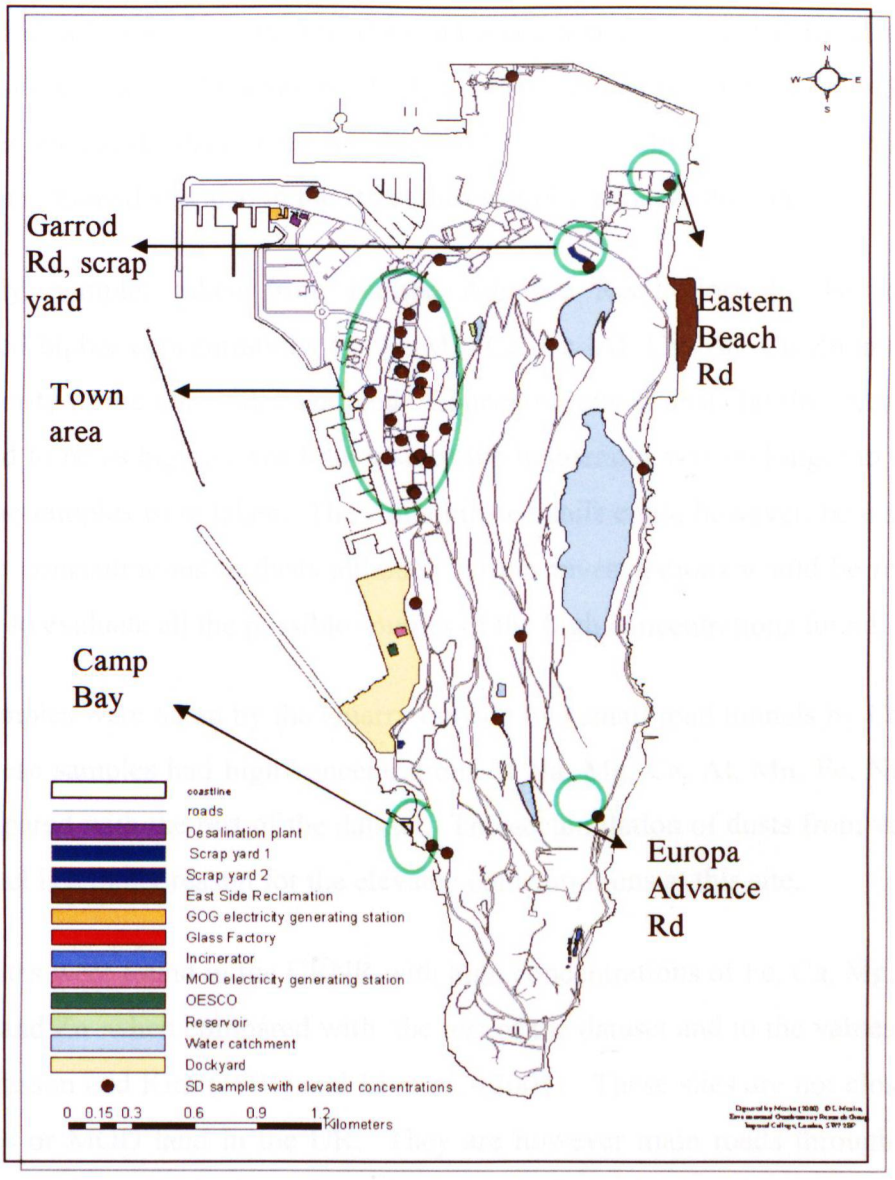


Figure 7.31 Street dust (SD) samples with outlying values for various element concentrations from Gibraltar.

Another area with high concentrations as compared with the rest of the dataset was found near the harbour. Two samples were taken in this area, one on North Mole Road and the other on Mons Calpe Road. These sites had elevated concentrations of As, Ca, Cd, Fe, K, La, Mn, Na, Pb, P, S, Sr and V. The high levels of Ca, Mn, Fe, Na and S could be related to the reclamation site. North Mole Road is in the port area where some maintenance of ships docking in the area occurs, such as underwater hull cleaning etc. In addition the electricity generating station and the desalination plant are both located on this road.



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A site which is very closely linked to industrial activity is Garrod Road where the scrap yard is located. This site has higher concentrations in comparison with most of the other sites in the dataset for As, Ba, Cd, Co, Cu, Fe Mn, Pb and Zn in the soils as already mentioned and also in the street dust samples taken at this site.

Similarly, samples taken from Europa Advance Road close to the incinerator displayed higher concentrations of Na, Mg, Ca, Ba, Al, Cr, Mn, Cu Zn and Pb than the majority of the other sites sampled. Concentrations in dusts (at this site) were not expected to be as high as was found, since the incinerator was no longer in operation when the samples were taken. The contaminated soils could however, be a source for the high concentrations in dusts although further investigations would be required at this site to evaluate all the possible sources of the high concentrations found.

Two samples were taken by the Quarry outside two small road tunnels by Camp Bay. Both these samples had high concentrations of Na, Mg, Ca, Al, Mn, Fe, Ni, Cu and Zn compared with the rest of the dataset. The accumulation of dusts from vehicles in the tunnel is a likely reason for the elevated concentrations at this site.

Three sites were found in the URNR with high concentrations of Fe, Ca, Mg, Mn, Cu, Co, Pb and Zn when compared with the rest of the dataset and to the values reported by Fergusson and Kim (1991) and Li *et al.*, (2001). These sites are not close to Gun Batteries or MOD land in the UR. They are however main roads through which a huge traffic flow travels throughout the year mainly in the form of coaches and taxis which take tourists around the nature reserve.

Lastly a site near Catalan Bay on Sir Herbert Miles Road displayed high concentrations for Al, As, Be, Cr, K, Li, Mn, P and Sr. This site is close to the east side reclamation although the reclamation site was filled when the dust samples were taken. The site is also close to MOD tunnels which go right through the Rock. Once again further research would be needed to apportion the high concentrations at this site.

7.6 Sequential extractions in soils and street dusts

The results from the sequential extractions on soils and dusts were incorporated into the GIS database. Two sets of sequential extractions were carried out on soils and one set on the street dusts. Each set allows 36 samples to be analysed. Each sample is displayed as a pie chart. Each pie illustrates the relative partitioning into each step. With the sequential extraction data there again do not appear to be any immediately discernible spatial patterns concerning the spatial distribution of the partitioning of elements into the different steps. The examples of Pb, Cu, Zn and Fe in soils and street dusts are shown here. As stated in section 4.4.1, the samples analysed by this method were chosen to reflect processes in the urban and natural environment. For example, samples were pre-selected for this experiment according to site location criteria and "total" concentrations obtained for the heavy metals from the ICP-AES analysis. Samples were chosen from sites which were known to have either no history of industrial land use or specific industrial land use, either at present or previously. Similarly, samples, which displayed elevated concentrations (refer to definitions provided in chapter 1) or concentrations which were classed as outlying values when the data were plotted in histograms and box plots (i.e. samples more than 2 SD's from the mean) were selected for this analysis.

Figure 7.32 illustrates the partitioning of Pb in soils (a) and Pb in street dusts (b) in Gibraltar. The maps verify, as was stated in section 6.2.2 that Pb in soils is mainly partitioned into step 5 followed by steps 2 and 3[3]. A cluster can be seen in the town area where at least half of the Pb is partitioned into step 5, the residual phase. This could suggest that the Pb in the soils in the town area is present in a different chemical form and is not very mobile or potentially bioavailable. Apart from this there are no other spatial patterns as regards the partitioning of Pb in soils. Lead in street dusts (b) is mainly partitioned into steps 2 and 3 with step 1 of lesser importance. No immediately discernible patterns can be found in the map. The main difference between Pb in soils and street dusts is that Pb is potentially more mobile and bioavailable in street dusts as opposed to soils where it is largely partitioned into the organic/sulphide and residual fraction. This could be due to the different physical and

[3] Step 1 = Soluble and Exchangeable phase, Step 2 = Carbonate phase, Step 3 = Bound to Fe-Mn oxide fraction, Step 4 = Bounds to organic/sulphide fraction, Step 5 = Residual fraction. (for further details refer to page 98).

chemical process/reactions which occur within the soil matrix that are not found in the dust matrices.

Zinc in soils in mainly partitioned into steps 3 and 5 (figure 7.33 a). The only cluster which can be found is again in the town area where a group of samples are found in which most of the partitioning of the Zn is in step 3. Zinc in street dusts (b) is largely partitioned into steps 2 and 3. No spatially related patterns can be found. As with Pb, the main difference between Zn in soils and street dusts is that Zn is potentially more mobile in street dusts than soils.

Figure 7.34 illustrates the partitioning of Cu in soils (a) and street dusts (b). Copper is largely partitioned into steps 5, 4 and 3. The three samples taken from Europort partition predominantly into step 5 and there again appears to be a small cluster in the town area where the samples partition largely into step 4. These are the only patterns found. Most of the Cu in soils is partitioned into steps 4 and 5 and so not very mobile or potentially bioavailable. Copper in street dusts is partitioned largely into steps 4 and 5 with step 3 of secondary importance. This is similar to the partitioning in soils. No spatial patterns can be discerned however, in the spatial distribution of the partitioning of Cu in dusts.

Iron in soils as well as street dusts (figure 7.35) is mostly partitioned into step 5 throughout Gibraltar, with the occasional samples partitioning largely into step 3. A larger degree of partitioning into step 3 occurs in street dusts than in soils. However, both media are dominated by the partitioning into the residual phase (step 5). No spatial patterns can be discerned for Fe in soils or dusts.

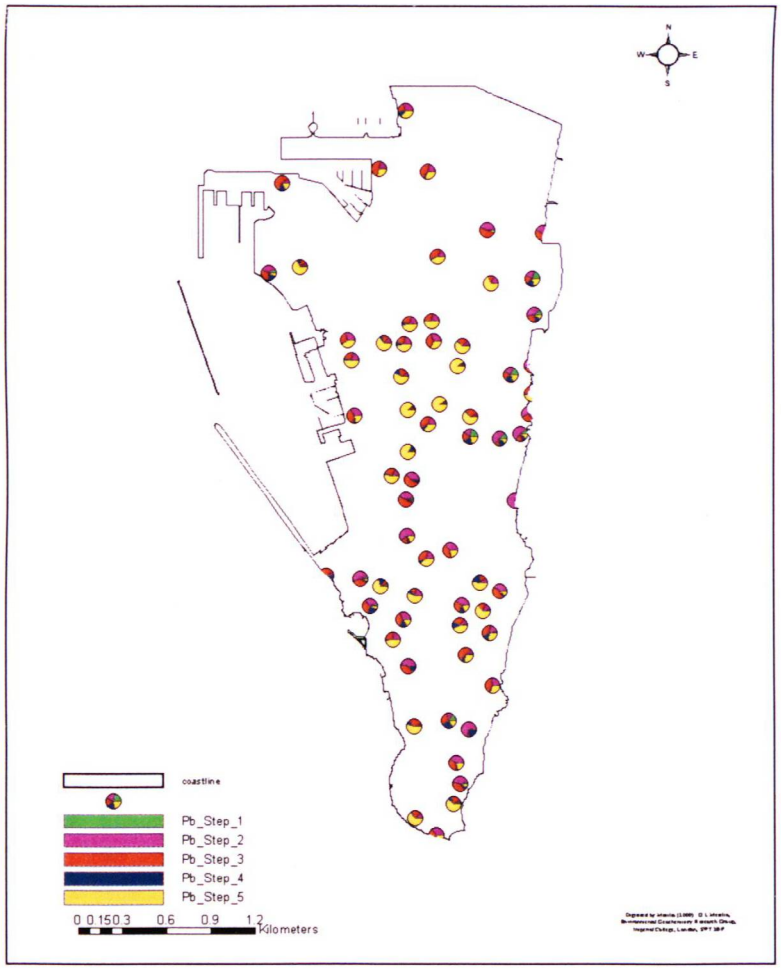
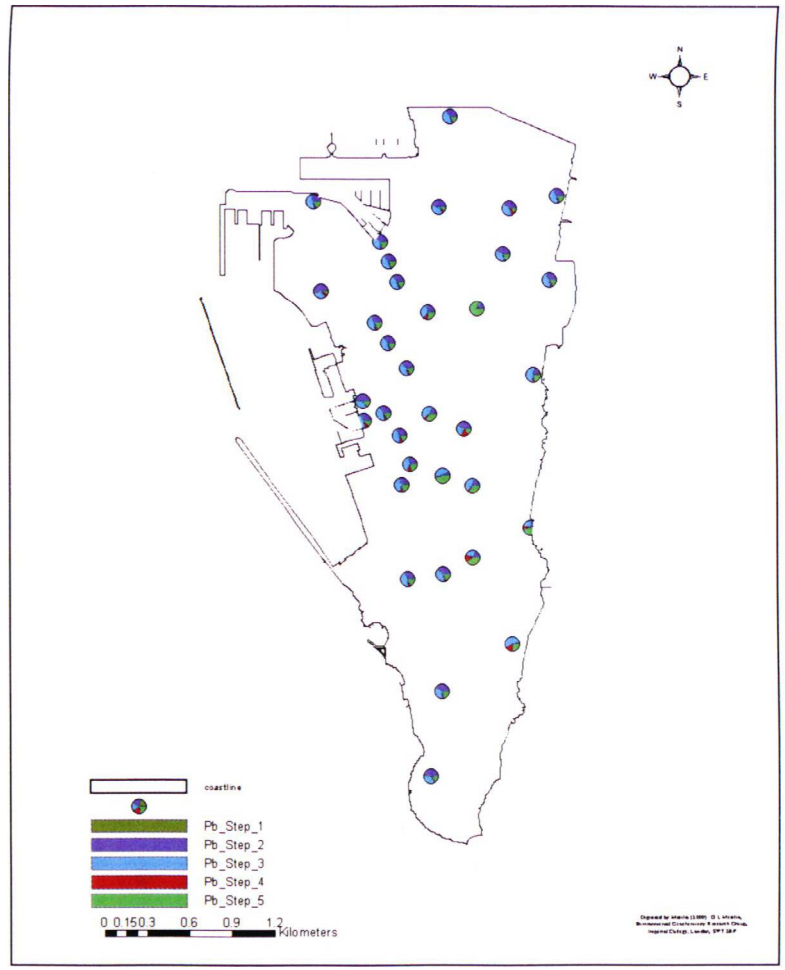


Figure 7.32 (a) Partitioning of Pb in surface (0-15 cms) soils. (n=66)



(b) Partitioning of Pb in street dusts from Gibraltar (n=33)

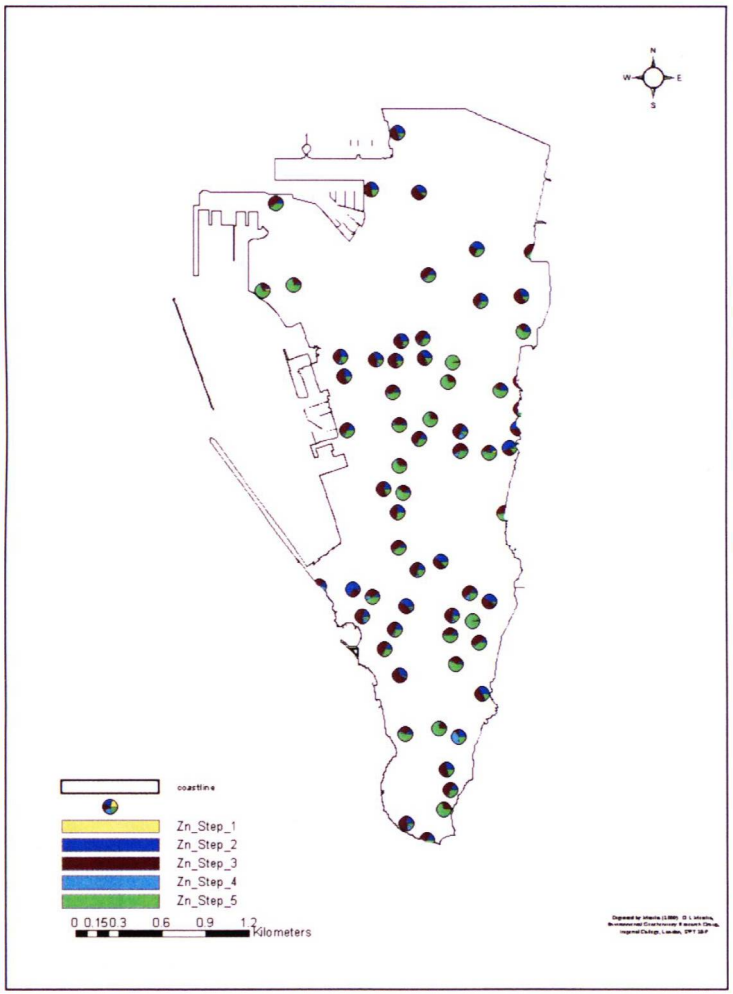
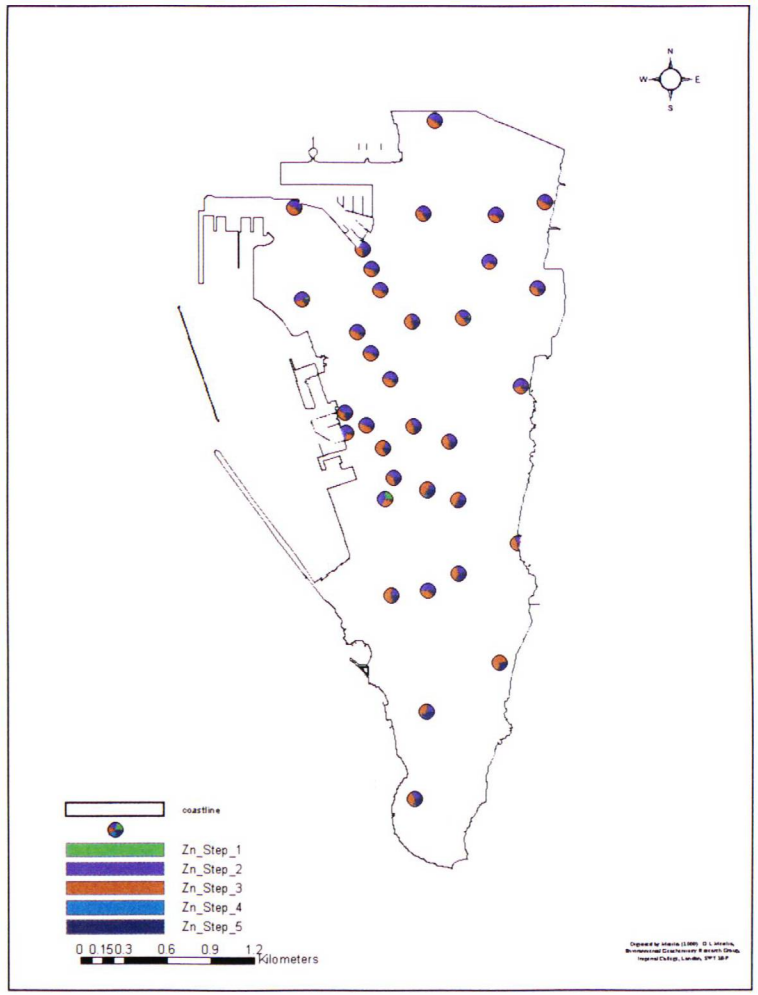


Figure 7.33 (a) Partitioning of Zn in surface soils (0-15 cms)(n=66)



(b) Partitioning of Zn in street dusts from Gibraltar (n=33)

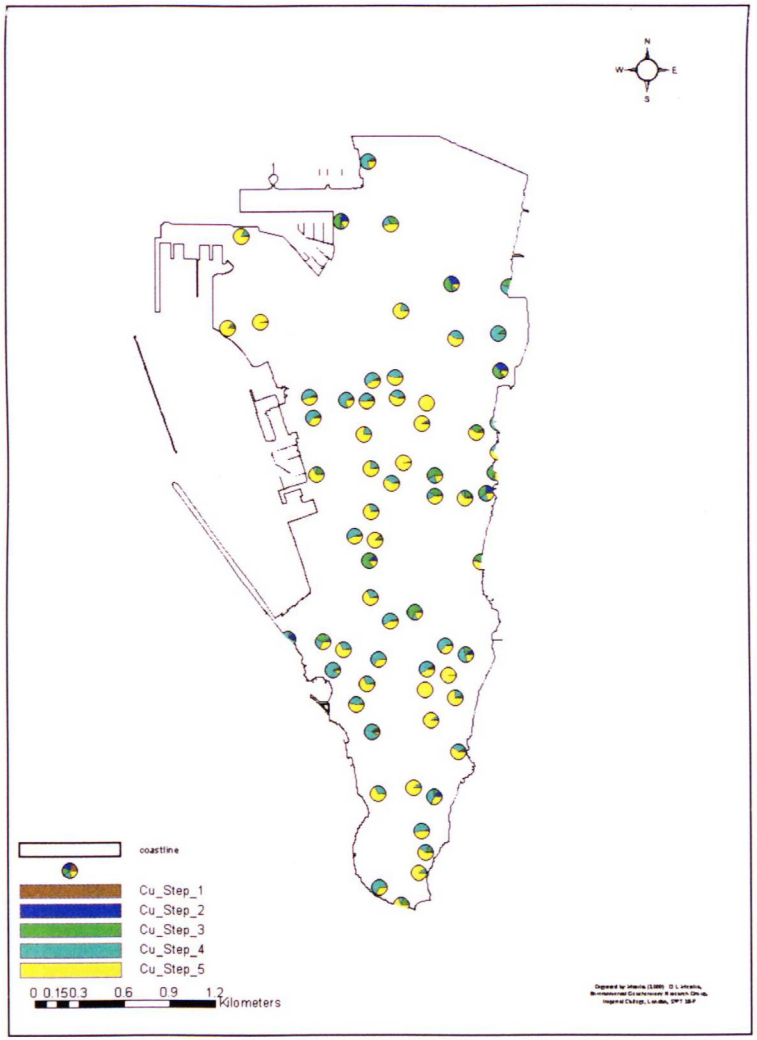
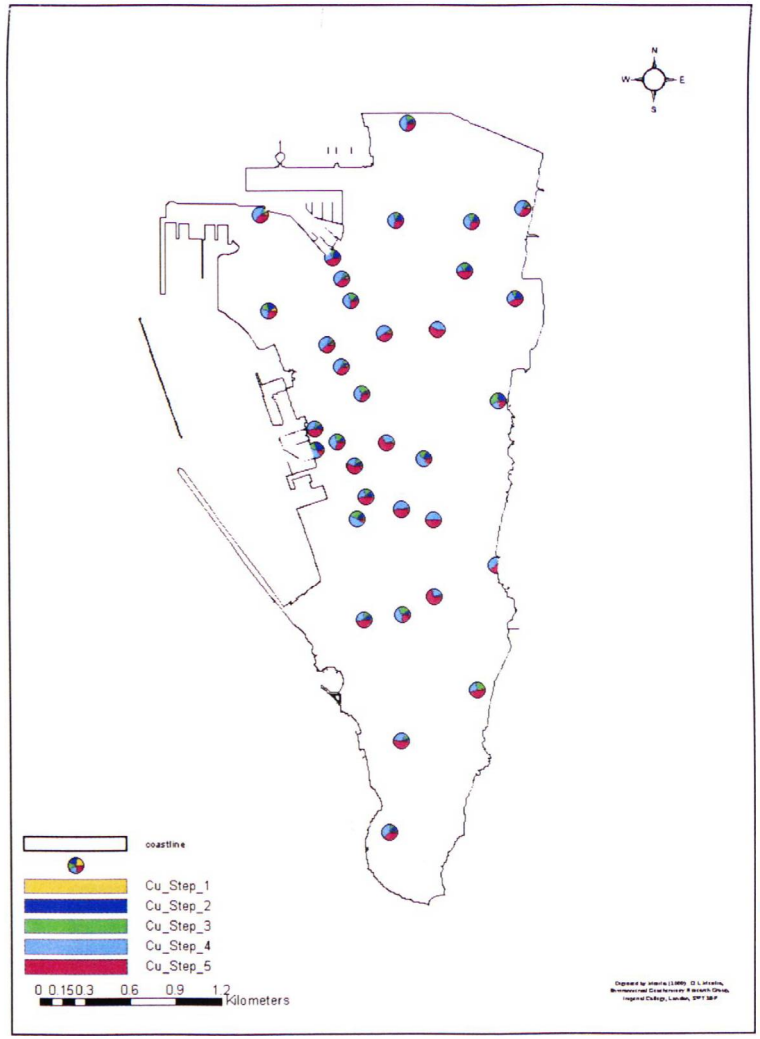


Figure 7.34 (a) Partitioning of Cu in surface soils (0-15 cms)(n=66)



(b) Partitioning of Cu in street dusts from Gibraltar (n=33)

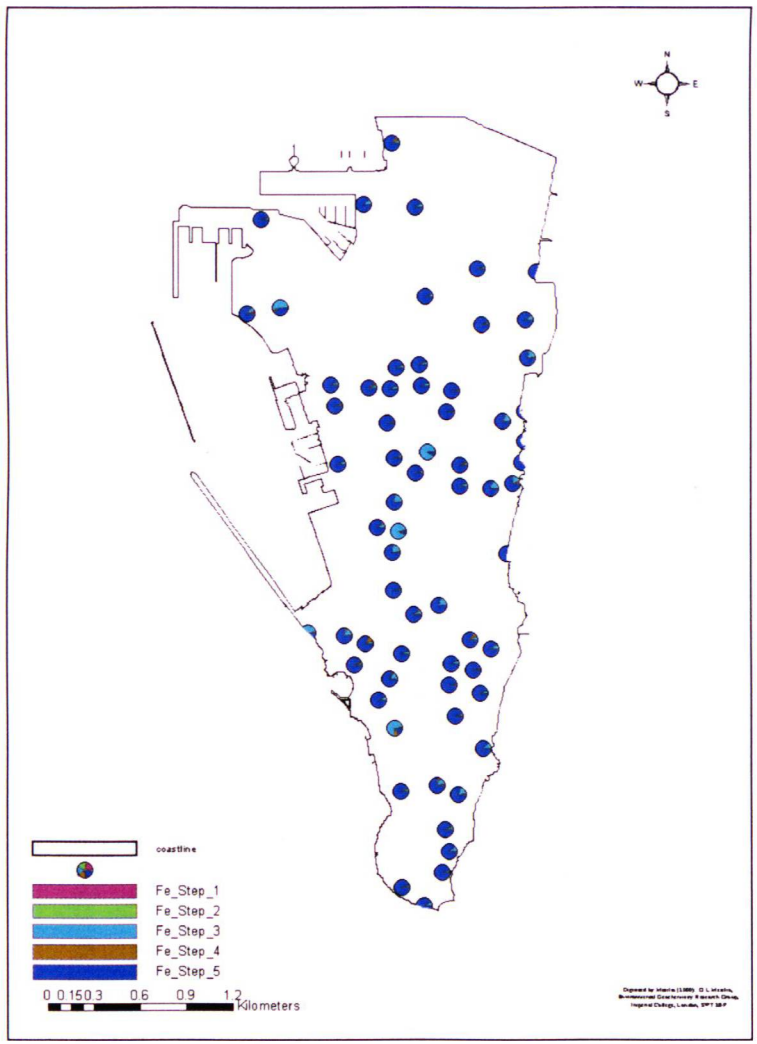
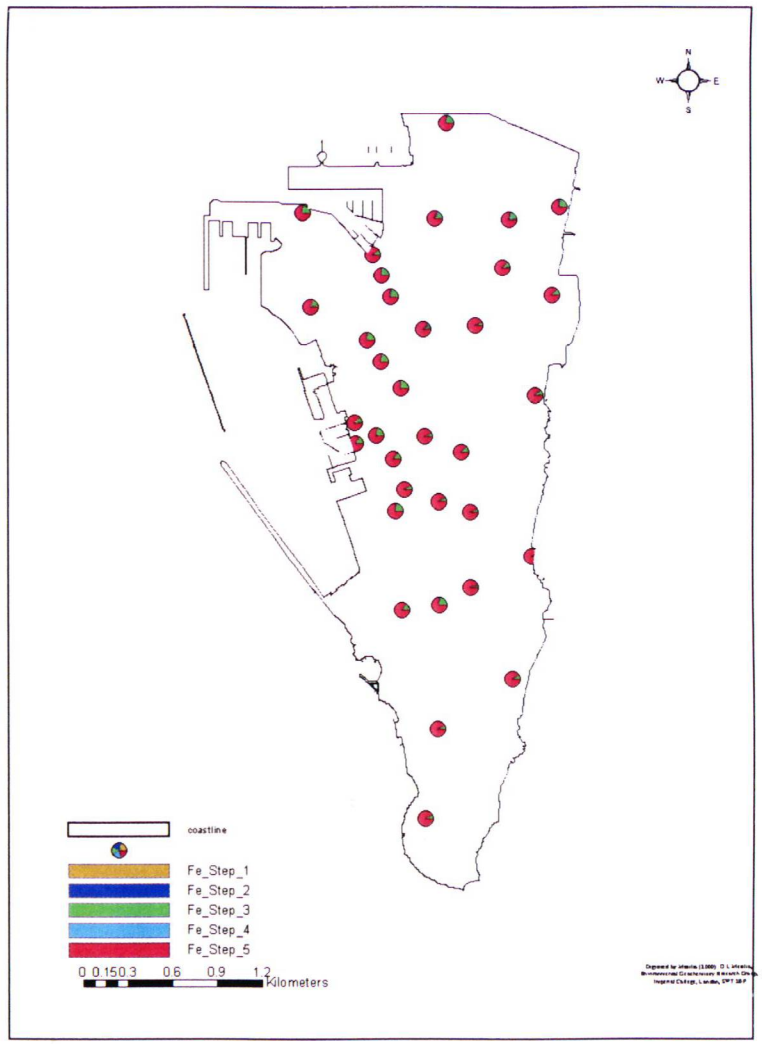


Figure 7.35 (a) Partitioning of Fe in surface soils (0-15 cms)(n=66)



(b) Partitioning of Fe in street dusts from Gibraltar (n=33)

7.7 Chapter Conclusions

There are various techniques which can be used in GIS to display and analyse data. The most important issue is using the appropriate technique for the type of data and the environment under investigation. Kriging is a well established method used widely for predicting concentrations in unsampled locations. However, methods of surface interpolation are not generally suitable for areas such as Gibraltar where urban density and topology do not allow the use of sampling techniques based on a grid. These are better suited to model surface interpolations. Similarly in any urban environment where a large portion of the landscape is paved and where there is a marked spatial heterogeneity over very short distances, interpolating large areas is unreasonable because the presence of the urban landscape has converted what would ordinarily be continuous data into discrete data. This occurs because the urban landscape (roads, buildings, scattered green areas) fragments the measurement (natural) landscape. When concentrations of elements are modelled throughout an area primarily because a sampling strategy which is too dense may be non-cost effective, it is recommended that the use of surface interpolation techniques be used on a site specific basis. Such sites should have a constant type of topology (in other words different types of natural landscapes) through a large portion if not most of the site.

It is interesting to note how there appears to be two distinct sets of range outliers. These are those sites which have high (outlying) concentrations for certain major and trace elements and another group of sites which have high concentrations for the more anthropogenically related elements such as Pb, Zn, Cu, Cd and As.

There are certain areas in Gibraltar with high (outlying) concentrations (as compared to the rest of the dataset, and/or published world means) in either soils and/or dusts. These sites have high concentrations of a range of different elements including; As, Ca, Cd, Fe, K, La, Mn, Na, Pb, P, S, Sr, Pb, Cu, Zn, As and V. The anthropogenic sources in Gibraltar which could lead to high concentrations of heavy metals in soils include the scrap yard, the incinerator, traffic, the electricity generating station and the desalination plant, the sand blasting of ships at the dockyard, the rifles ranges and the MOD.

The spatial distribution of element concentrations in house dusts from Gibraltar is such that it is difficult to identify possible sources. Twelve sites have outlying values for a range of elements, with the locations of these sites (section 7.3) within four distinct areas. Three of these are in close proximity to an industrial area; two are close to the electricity generating station in the north of Gibraltar, and the other two sites are located south of the dockyard in the southern part of town. The spatial distribution of street dusts in Gibraltar also shows distinct areas where elevated concentrations (in relation to the rest of the dataset) are found (section 7.5). Figure 7.31 shows the areas with elevated concentrations of a range of elements (e.g. Pb, Cu, As, Zn, Ca, Ni etc) in street dusts.

Spatial patterns found of element concentrations in soils show the likely influence of the sand blasting of ships, traffic, the effects left from the incinerator as well as the underlying geology. Similarly, areas with very low element concentrations and possible deficiencies of nutrient trace elements have been found in Gibraltar. These areas include on the east side: Sir Herbert Miles Road, the wind blown sands (WBS) in the water catchments and the east side sand slopes. This area consists largely of sands which are comprised of 70% quartz with subordinate lithic fragments of schist and speleothem, and shell fragments and benthic foraminifera (Rose and Rosenbaum, 1991). On the western side the sites include the Alameda sands, Jumpers Bastion and Europort. The Alameda sands underlie most of the town area and like the Catalan Bay sands are comprised mainly of quartz, but contain some lithic sandstone fragments, which the latter sands do not possess. The grains are more rounded than the Catalan Bay sands and the red colour seems to represent well-developed pedogenesis (Rose and Rosenbaum, 1991). Windmill Hill in the south of Gibraltar, the north of Gibraltar near the border and some sites in the URNR also contain very low concentrations.

Windmill Hill is on the Southern Plateaux. It consists of rock platforms, which then meet the sea at the bottom of a vertical steep cliff. The higher of the two platforms is called Windmill Hill. The area in Europort where the samples were taken consisted of a large flat grass patch next to the sea. This area has recently undergone a change in land use (in the year 2002-2003) and housing developments have commenced. Table 7.2 lists these areas together with the elements showing very low concentrations

of some elements at each of these sites. Some of the possible nutrient deficiencies found in areas such as the East side, the Alameda sands, Windmill Hill and the URNR could be the result of the underlying geology as samples taken in these areas were taken on natural soils on different geological parent materials.

Table 7.2 Areas of low concentrations and possible deficiencies of nutrient trace elements in soils from Gibraltar.

Areas	Elements
East side – Sir Herbert Miles Road, WBS, East side sand slopes	Li, Na, K, Be, Mg, Ba, Al, La, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, P, S As
Alameda sands, Jumpers Bastion	Li, Na, K, Be, Mg, Ca, Sr, Al, La, Ti, V, Mn, Fe, Co, Ni, Cu, As
Europort	Mg, Ca, Sr, Ba, V, Cu, Zn, Pb, P, S
Windmill Hill	Na, Be, Ti, V, Cr, P
North of Gibraltar	Li, K, Ba, Al, V, Fe, Co, As
Upper Rock Nature Reserve	Na, K, Mg, Ca, Sr, Ba, Zn, Cu, Cd, Pb,

Results for Ag, Cd and to a lesser extent La, Co, Cr and Mn need to be interpreted with caution due to high numbers of samples falling below or close to detection limit.

The GIS maps produced in chapters six and seven illustrate how results from statistical techniques can be incorporated into a GIS. They also display environmental data across the whole of Gibraltar. These maps can then be integrated with data related to geology, land use, transportation techniques etc. This aids in the identification of sites or areas which require further research, as well as helping in the verification or rejection of hypotheses regarding spatial patterns within the dataset. One of the key tools of a GIS is its data handling capabilities. Once the features have been captured into a GIS it can be analysed and modified to suit the requirements of the project.

Figure 7.36 illustrates how statistical analyses can be incorporated with geochemical mapping and displayed in simple but visually, very effective diagrams. The diagram depicts in **blue** samples with Pb concentrations greater than 1000 mg/kg which exceed guideline values for lead in soil and where a potential hazard to human health may exist. These samples are shown on a map, a histogram and a Q-Q plot. Such

diagrams allow the researcher to evaluate whether the samples highlighted on the map are displayed as outlying values in the histogram. The location of these samples in terms of the overall graphical distribution of the data can be assessed. In this case, the sites of interest encompass around 2.5% of the dataset and are outlying values according to the rules of a Gaussian (bell shaped curve) distribution. Diagrams such as this one can be used to illustrate very effectively the location of samples on a map with very low or high concentrations as shown by statistical as well as mapping techniques.

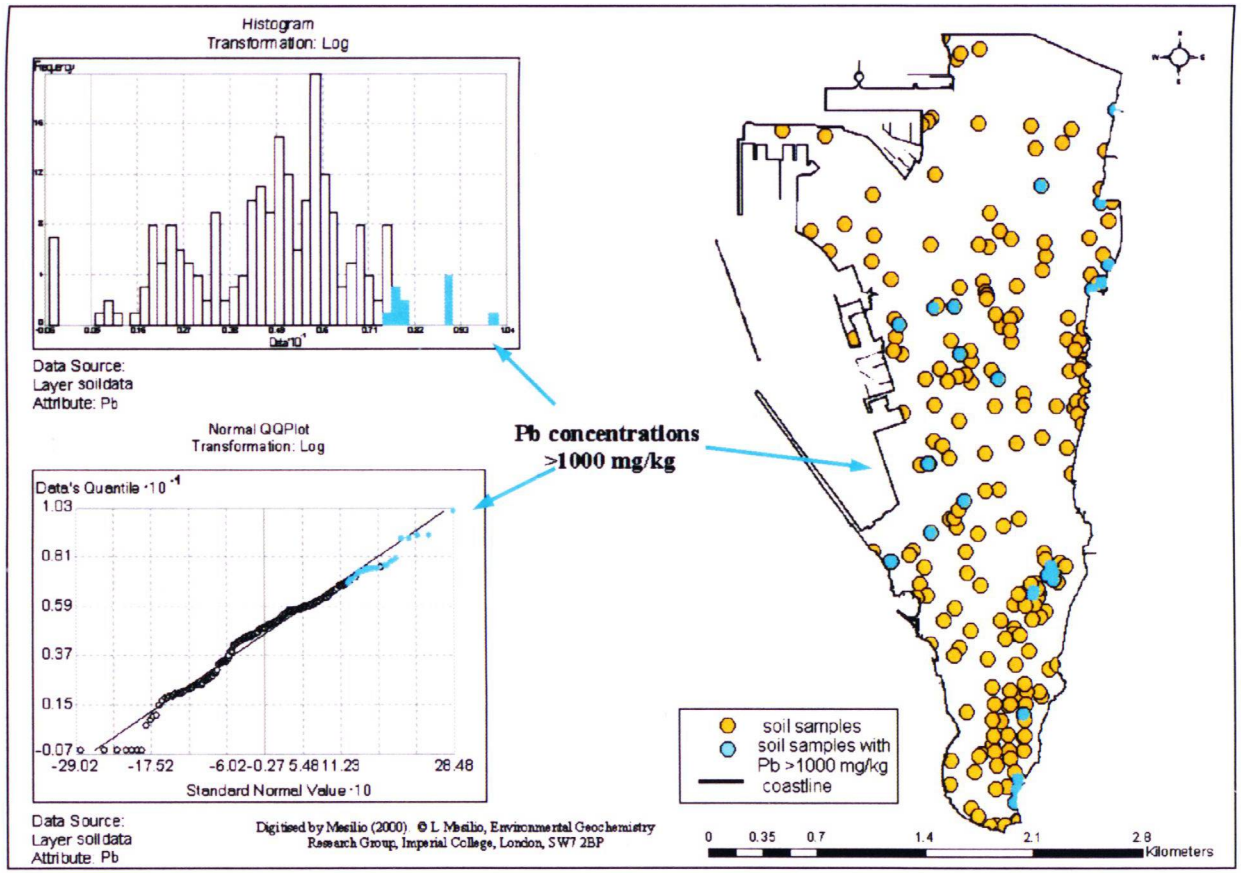


Figure 7.36 Presentation of spatial data analysis for Pb concentrations in Gibraltar surface (0-15 cms) soils. n=238 (mg/kg)

CHAPTER 8

Urban geochemistry and the effects of natural and anthropogenic inputs on the sustainability of urban development

8.1 Introduction

Metals are present as natural components in all environmental media (section 2.5.1). However it is the transfer of metals to the inhabited environment from urban development and industrial activities that has aroused the interest of scientists, stimulated the emotions of the public and attracted the attention of politicians and regulatory authorities.

Physical degradation of the soil is one of the main environmental issues being addressed today. Concern that human activities are unsustainable, has resulted in reports such as "Our Common Future" by the World Commission on Environment and Development (1987) and "Sustainable Use of Soil" a Draft Soil Strategy for England published by the Department for Environment (DEFRA, 2001), following a report with the same title from the Royal Commission on Environmental Pollution (2001). Despite these and many other similar reports worldwide, relatively little research has been conducted on investigating the sustainability of ecosystems and the land they live on.

The presence and distribution of elements in the urban environment reflects both the influence of bedrock geochemistry and soil forming processes as well as contamination of land arising from traffic, building materials and demolition as well as many industrial practices (Thornton, 1991; 1995). This has led to deposition of substances in, on or under the land, such as heavy metals, petrochemical and organic compounds, soluble salts, mining materials and from the land filling of wastes. This has often happened without adequate precautions against leaching or the escape of landfill gases. One of the main issues when dealing with land contamination is that

current and future pollution is generally tackled by other legislative means, but the legacy of past contamination has not been fully addressed in national or international legislation. In addition uncertainties about remediation requirements (both scientific and legislative) and liability for them can cause blight; this deters development of land and adds to pressures on greenfield sites, thus affecting urban regeneration (DETR, 2000).

8.2 Land use and policy issues in Gibraltar

One of the main issues of concern in Gibraltar which needs to be properly addressed is the influence of the previous/historical land use on element concentrations in soils and dusts. The historical evolution of land use in Gibraltar has been dominated by its role as a site of strategic military importance. Fortifications on the rock date from 1160 through to World War II. These fortifications were at the hands of the Moors, Spaniards and the British respectively (Rose, 2000). Evidence of this military based progression can be seen from the stone walls, the bastions, the towers and the numerous artillery positions on the Rock. Built to enhance the natural defences of this location, they now serve as tourist attractions which constrain the "natural" development of the modern city (Rose, 2000). In 1994 the disbandment of the 1st (Fortress) Specialist Team RE brought to an end over two centuries of British military engineering in Gibraltar. This left behind a legacy of works and land now largely inherited by civilian bodies responsible to the Gibraltar government. There is now a need to balance increasing urbanization with appropriate conservation (Rose, 2000).

There is currently no legislation in Gibraltar in the form of an Environmental Protection Act regarding the contamination of soils or land. The Town Planning Ordinance does contain regulation regarding Environmental Impact Assessments on a site, but it is more in relation to the nature of development of the site as opposed to a pre-requisite investigation of the site. There is no guidance, legislative or otherwise regarding land quality assessments of soils at sites as an initial investigatory procedure. The MOD has recently begun a land quality assessment on their sites in Gibraltar. Regarding the releases of substances to land, section VA the Public Health Ordinance (Government of Gibraltar, 2002) in Gibraltar establishes a system of integrated waste management whereby the Government is responsible for ensuring that pollution of the environment due to the release of substances to any

environmental medium is prevented or minimised. It is an implied general condition that the person carrying on the process must use the best available technique not entailing excessive cost:

a) for preventing the release of substances prescribed for any environmental medium into that medium or, where that is not practicable by such means, for reducing the release of such substances to a minimum and for rendering harmless any such substances which are so released and:
b) for rendering harmless any other substances which might cause harm if released into any environmental medium

Furthermore, where the process is likely to involve release of substances to more than one environmental medium, the techniques used must minimise the pollution to the environment taken as a whole, having regard to the best practicable environmental option for the substances concerned (Government of Gibraltar, 2002).

The small size of Gibraltar combined with its high urban density means that proximity to roads and/or industrial activity is always a major factor when considering the influence of anthropogenic activities on possible contamination. The issue of sustainability and the sustainable management of soils in Gibraltar does not just concern issues about contamination; factors such as overcrowding of the land and soil loss through changing land uses should also be considered. Unfortunately the aims and objectives of this work as well as the word limit imposed do not allow these issues to be addressed in length. The proximity factor brought about because of the small land area of Gibraltar combined with past (and present) land use is potentially the key controlling factor that influences the spatial distribution of element concentrations found. Traffic is also an important factor which affects elemental concentrations in soils and dusts. Many brownfield[1] sites exist in Gibraltar and land after denudation (mainly through the removal of the soil and surface material) is almost always reused. Once the MOD has finished working on a site, it is passed onto the Government of Gibraltar for either housing development or other commercial or industrial projects. Usually this is done with little scientific investigative work into the condition of the site, although this now appears to be gradually changing.

[1] *Brownfield land is a term used to describe urban land which has a history of industrial use but which still has some potential for re-development*

8.3 Assessing the risks

One of the key points when addressing the issue of site management and contaminated land is an understanding of the impacts and risks posed from potentially contaminated sites. The risks on each site need to be assessed and controls triggered only where there is significant harm, or a significant possibility of it, or actual or likely pollution of controlled waters. Risk assessment (RA) can be defined as a scientific evaluation of the likelihood and uncertainty of environmental hazards being present in a product, system, or plan (USEPA[2], 1994; Wang *et al.*, 1997) (see section 2.7.2). RA should be a neutral, independent and academic judgement for an adverse effect or an unwanted event. The classification of what represents a risk should not be influenced solely by public perception. Sound science is needed before social responses such as public interests and political priorities are considered in the risk or site management process.

The extent of the risk on any particular land depends upon a number of factors including the following (DETR, 2000):

- the characteristics of the substances in the land;
- the local geology and hydrogeology;
- the nature and presence of receptors;
- the use of the land, or of adjacent land;
- the nature of the land in terms of whether pathways might exist or be created;
- measures that exist, if any, to reduce or limit the risk.

Additional risks might result from the redevelopment of the land, as often occurs in Gibraltar, for example if housing replaces industrial or military use. The level of risk should be assessed both to human health and to surrounding ecosystems. Potential future risks of this kind can become the subject of controls under the Town Planning Ordinance.

Urban regeneration and local economic growth can suffer as a result of contamination. This can occur through general industrial dereliction, derelict spoil

[2] United States Environmental Protection Agency

heaps and former waste disposal sites. Such land will often have been contaminated to varying degrees and furthermore can lead to the contamination of other lands or waters. In addition to the direct costs of dealing with any contamination, there may be considerable reservations as to what (if any) regulatory requirements for remediation may be imposed, as well as possible liability for such work. Reservations such as these can deter development and become major causal factors in land remaining derelict. In addition to adverse localised social and economic effects the growing lack of confidence in brownfield sites arising from contamination and its associated uncertainties, can also lead to increased and unwanted pressures for new development on greenfield[3] sites (DETR, 2000). A statutory guidance would be needed within the Gibraltar legislation to help to address all these risks by providing a clear framework for dealing with contamination. In the UK Part IIA of the 1990 Environmental Protection Act (EPA) legislation establishes a specific contaminated land power, including a definition of contaminated land and a procedure for securing remediation when such land is identified. This definition states that *any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on or under the land, that:*

a) *significant harm is being caused or there is a significant possibility of such harm being caused; or*

b) *pollution of controlled waters is being, or is likely to be caused*

(section 78A(2) of Part IIA of the Environmental Protection Act 1990, DEFRA 2000b).

The statutory guidance covers five distinct aspects of the regime. These are the definition of contaminated land as stated above, its identification, its remediation, the exclusion from and apportionment of liabilities for the cost of remediation and the recovery of the cost of remediation (DETR, 2000).

There is currently no existing code of practice or legislation as regards contaminated land in Gibraltar. The existing UK EPA legislation would need to be amended so as to ensure its suitability for the environment in Gibraltar. Additionally local authorities in the UK have encountered problems regarding the interpretation of the

[3] Greenfield sites are defined as land which has never been developed

legislation, as the phrasing used is rather general and non-specific at times. Amendments to, for example, the explanation of contaminated land would avoid such problems from occurring in Gibraltar. The implementation of such legislation in Gibraltar would require the training of personnel in the local environment agency to ensure the efficient undertaking of this code of practice. It is suggested here that a "suitable for use" approach be adopted when dealing with areas which have element concentrations that exceed baseline or guideline values. In the UK, Part IIA of the EPA (1990) was inserted into that Act by Section 57 of the Environment Act 1995. It provides a new regulatory regime for the identification and remediation of contaminated land. In addition to the requirements contained in the primary legislation, operation of the regime is subject to regulations and statutory guidance (DEFRA, 2000a). Determination of site status should be through a risk assessment and at its heart a consideration of source-pathway-target relationships. EPA (1990) Part IIA states "Whilst a risk assessment may indicate that on the balance of probabilities the assessed area of land appears not to be contaminated, it is still possible that the land is contaminated land" (DEFRA 2000b).

Land contamination, if not dealt with adequately can pose a serious threat to human health and/or the environment, specifically on surrounding ecosystems. One of the main principles for environmental policies is that decisions or actions that could have an adverse effect on the environment should be based on the best possible information and analysis of risks (DETR, 2000).

8.4 Assessment of contamination

The purpose behind establishing baseline values in soils with lower and upper threshold values is largely for the identification of any anomalous values belonging to outlying populations. These outlying populations refer to potentially elevated or contaminated sites. Baseline values represent elemental concentrations specific for a *given region* and *time period* (Salminen and Tarvainen, 1997). They are ideal for the assessment of possible contamination in urban environments where the result of the urbanization process has often lead to "naturally" slightly elevated concentrations of metals referred to here as "ambient baseline concentrations". One of the first assessments of contamination or pollution should then be to compare the dataset and

its baseline range to established guideline values. The two most commonly used soil guideline values in the UK and Europe are given in Table 8.1. These are the Dutch and DEFRA/EA SGV values.

Table 8.1 Summary of soil guideline values for toxic trace metals (values reported in mg/kg)

Metal	*Dutch Values*[1]		*DEFRA/EA SGV*[2]		
	Target	Intervention	Residential plant uptake	Residential no plant uptake	Industrial and commercial land
As	29	55	20	20	500
Cd	0.8	12	(pH <6) 1 (pH 6-7) 2 (pH >7) 8	30	1,400
Cu	36	190	-	-	-
Ni	35	210	50	75	5,000
Zn	140	720	-	-	-
Pb	85	530	450	450	750

References: 1 Zero Environment, 2001 2 DEFRA and Environment Agency, 2002a-e,

Soil guideline values (SGV) are almost exclusively used during the redevelopment of former industrial or brownfield land and are based on the potential hazard to human health using either children or adults as the receptors. Different countries have developed their own guideline values; however the Dutch values are quoted and used by a large number of countries. The Dutch values apply to land intended for any potential use (Zero Environment, 2001). The DEFRA/EA SGV values have been calculated from an exposure based risk assessment and are intended for use by Local Authorities in the UK to support Part IIA of the Environmental Protection Act 1990 (DEFRA 2002a-e). The legislations main objective of the legislation is:

"..to provide an improved system for the identification and remediation of land where contamination is causing an unacceptable risk to human health or the wider environment assessed in the context of the current use and circumstances of the land" (DEFRA, 2002a).

All guideline values are based on total concentration in the soil. The DEFRA-EA SGV have been derived on the basis of a particular land-use. Currently there are three types of land-use for which SGV have been developed: residential, allotments and commercial/industrial. In some countries the assessment of sites may be in relation to the amount of contamination above some predetermined background concentration, or up to some pre-set "critical load". In the UK this is most commonly considered relevant for assessing "new" or additional contamination and may be complemented by assessment of effects on more specific receptors (DETR, 2000).

The CLEA model and ensuing guideline values are suited to "site-specific risk assessment". The model allows the input of factors such as oral, inhalation and dermal exposure, soil type, pH, soil organic matter, and other site-specific factors. The CLEA model: technical basis and algorithms document published by DEFRA and the EA (2002a-e) states that it is a conceptual model derived not for a specific site but for a broad range of sites within a land-use category. Precautionary assumptions ensure that the model is protective of most if not all sites within the category. The standard land-uses take into account human behaviour and the professional judgment of policy-makers to provide a conceptual model suitable for a range of generic site conditions and land-uses. They are not intended to reflect accurately either the conditions of a specific site or the behavior of a specific site-user.

As stated in the previous paragraph, with careful consideration as to the limits of the model, it is suggested here that such a model can be used in Gibraltar on an individual site basis. This could enhance the applicability of the model because the input parameters would be based on an actual site thereby taking account of specific circumstances and more targeted data collection. The reported outcomes can be used as an overall guide when compared to the current baseline values for Gibraltar. Therefore a more adequate and informed decision can be made regarding the level of contamination present at a site.

8.5 Metal variations in Gibraltar

The elemental data gathered in soils and dusts through this survey has allowed the identification of areas with elevated concentrations of the heavy metals where there may be a possible risk to the human population or to flora and fauna. Similarly

industrial processes have been identified (such as the sand blasting of ships in the dockyard, the incinerator, the electricity generating station and the desalination plant) which could lead to exposure of the local population to potentially toxic metals. Five areas in Gibraltar have been identified with elevated concentrations in soils and/or dusts that exceed guideline values for one or more metals. Some of these sites can be related to anthropogenic activity, others require further investigation in order to assess where the elevated concentrations originate from unknown factors at that site. For example the elevated element concentrations of K, Mg, Ca, Al, Ti, Mn, Fe, Cu, Zn, Pb and S in soils and dusts at the scrap yard can generally be attributed to the land usage of that site. Additionally an incinerator used to be situated adjacent to this site. When this incinerator was in operation it burnt domestic refuse but there was no separation of materials at source (refer to figure 7.3 for site locations). Similarly the elevated concentrations of the metals named above found in house dusts opposite the electricity generating station and desalination plant may be influenced by the proximity to these industrial activities.

Indications of the possible effects of previous industrial activity or land use can be inferred from the elevated concentrations in the Rosia area (figure 7,3, and figures 7.4-7.27), the site of an earlier gas works plant. Similarly the elevated concentrations of metals at Spur Battery in the URNR might be related to the use of Spur battery during the Second World War. The elevated concentrations at this site could also be from discarded waste materials found at this site or from wind deposition originating from O'Hara's Battery (situated about Spur Battery) which was also used during the second world war. The topography of the area suggests the possible likelihood of the latter: however further research would be needed to validate any of these statements.

The spatial extent of the current variations in major and trace elements in soils and dusts have been investigated through GIS analysis as well as the influences of current and previous land uses (chapter 7). This influence has been identified but not proved conclusively. The spatial distribution of metals in soils and dusts in Gibraltar is heterogeneous and site specific, therefore a portion of the variability found between different sites is not always believed to be spatially related. This enhanced the likelihood of errors when predicting concentration surfaces using GIS. Interpolation

techniques are generally not suited to areas with distinctly varying topologies such as those found in Gibraltar.

Investigations into the speciation of the elements found, when combined with the use of SEM or isotope analysis as source apportionment techniques will assist in the assessment of the influence of previous activities on element concentrations in soils and dusts.

Sustainable development in Gibraltar can only be achieved when scientific research is used to compliment land use management and policy implementation as regards all aspects of Gibraltar's future cultural and economic growth. For example tourism is one of the key industries in Gibraltar. The nature reserve is one of the main attractions for the tourist industry in Gibraltar. It is also an area of scientific and ecological importance. The effects of tourism and general development in this area need to be assessed in order to ensure that the atypical flora and fauna are disturbed or affected as little as possible if at all.

Table 8.2 and 8.3 compares element concentrations between the Upper Rock Nature Reserve (URNR) and the town area in soils and street dusts respectively. Table 8.2 shows that most elements display larger concentrations in the URNR as opposed to the town area. The anthropogenically related elements however, namely Ag, Ba, Cu, Pb and Zn have higher concentrations in the town area. Once again Pb and Ba illustrating the influence of increased traffic flow in the town as opposed to the URNR. The elements which were associated with the lithogenic/pedogenic factor (F1) and the geologically related factor (F3) in the factor analysis on soils (section 6.6.4.1) are found to have higher concentrations in the URNR. These elements include: Li, K, Be, Mg, Ca, Sr Al, Ti, V, Cr and Ni. This shows the influence of the underlying geology and pedogenic processes operating in the relatively undisturbed soils of the nature reserve.

The street dust data show a slightly different pattern to the soil data. Lithium, Be, Ca and Al display higher concentrations in the URNR. The following elements all have higher values in the samples taken in the town area; Na, Sr, V, Mo, Mn, Ni, Cu, Ag, Zn, Cd, Pb, S and As. Cadmium, Cu, Pb and Zn are good indicators of pollution in

dusts and soils because they are found in petrol, car components, oil lubricants, industrial and incinerator emissions (Alloway, 1995) (section 2.5.3). Element concentrations in dusts in the urban environment come from a variety of sources including traffic, vehicle emissions, industrial sources, building materials and even the weather; for example temperature and relative humidity can affect the chemistry of soils and dusts, thereby influencing the possible migration of elements between different environmental media. In addition, rainfall can transport the contaminated dusts into the urban drainage system and consequently into sewage treatment works and rivers (Harrison *et al.*, 1981; Thornton, 1991). The effects of wind blown dusts and rainout deposition from the Spanish hinterland could also be a contributing factor which needs to be assessed. The physical (and chemical) environment of cities is profoundly affected by almost every kind of human activity, from deliberate acts of construction, management or vandalism, to accidental or incidental pollution. The history of land use in urban areas is difficult to ascertain, for example major industrial sources from the last century may be masked by the presence of post World War II housing (Thornton, 1991).

Elements such as K, Mg, Ba, La, Ti, Cr, Fe, Co and P display higher mean values in soils of the town area but have a higher maximum value in the URNR (table 8.2). The higher mean (both AM and GM) and median values in town samples probably reflect the short-term contamination of dusts on samples as influenced by the sources listed in the latter paragraph, found within an urban environment. The high maximum values found in the URNR for these same elements could in turn reflect a few samples representing the lithogenic and pedogenic processes predominating in this natural setting. The comparisons of soils and street dusts between these two areas of Gibraltar illustrate the differences encountered between two environmental media as affected by proximity to different types of anthropogenic activity. The soil data illustrate this more clearly than the street dust data and also compliments the results of the factor analysis. Further research using scanning electron microscopy would aid in conclusively identifying the different effects on element distribution of anthropogenic activities such as incineration of waste, traffic etc on the soils and street dusts between these two very different environments.

Table 8.2 Descriptive statistics comparing Gibraltar surface (0-15 cms) soils in the Upper Rock Nature Reserve and Town area

	Uncontaminated soils in the Upper Rock Nature Reserve. mg/kg (n=60)						Uncontaminated soils in the town area. mg/kg (n=23)					
	AM	Median	SD	GM	Min	Max	AM	Median	SD	GM	Min	Max
Li	33	28	22	27	1	113	13	13	4	12	7	20
Na	448	355	305	388	138	2060	322	358	96	308	173	498
K	9048	7353	6425	7549	2420	32000	4156	4170	1203	3991	2220	6800
Be	1.32	1.30	0.70	1.13	0.03	3.73	0.76	0.79	0.17	0.74	0.46	1.08
Mg	12211	8435	11103	9485	3091	74000	7761	6780	4316	6692	2120	19000
Ca	53636	45036	42821	34888	1950	179000	41409	37600	27969	29533	4420	79900
Sr	84	77	42	74	24	205	70	58	40	59	18	159
Ba	166	155	74	148	8	407	270	143	257	194	74	1040
Al	37797	34000	23793	31233	847	131000	18349	17845	4315	17840	10700	25971
La	21	19	10	19	1	56	13	13	4	11	0	18
Ti	636	646	181	595	32	1070	560	488	190	531	315	869
V	82	69	61	65	2	319	38	33	12	36	26	64
Cr	151	153	75	130	24	326	139	136	54	128	43	269
Mn	410	382	164	375	37	1020	286	287	84	273	114	450
Fe	24959	23100	12840	22144	1787	80900	15870	15878	4073	15398	10000	27900
Co	9	9	4	8	2	22	7	7	2	7	4	11
Ni	50	44	21	46	22	127	43	43	13	42	27	74
Cu	45	41	24	38	6	110	75	41	97	38	6	437
Ag	0.37	0.38	0.22	0.27	0.04	1.00	0.54	0.40	0.44	0.00	0.00	1.30
Zn	227	142	236	154	17	1150	290	201	316	161	27	1350
Cd	2	1	1	0.02	0.02	6	1	1	1	0.20	0.02	2
Pb	162	97	174	97	3	952	491	302	623	142	8	2110
P	1500	1220	1228	1216	107	8710	1432	1300	1047	995	205	3190
S	1025	822	901	786	76	6500	583	409	399	438	103	1400
As	19	16	16	15	1	80	8	7	3	7	4	16

(Please note Cd and Ag data to assessed with caution due to number of samples below IDL and proximity of most sample concentrations to IDL Cadmium concentrations below 2 mg/kg to be assessed with caution).

Table 8.3 Descriptive statistics comparing Gibraltar street dust samples in the Upper Rock Nature Reserve and Town area

	Street dusts samples in the Upper Rock Nature Reserve mg/kg (n=19)						Street dusts samples in the town area mg/kg (n=33)					
	AM	Median	SD	GM	Min	Max	AM	Median	SD	GM	Min	Max
Li	13	11	9	10	2	41	13	14	3	12	3	15
Na	292	245	211	238	58	895	1926	1870	776	1623	189	2650
K	3153	2740	1880	2573	492	7610	4697	5310	1521	4220	876	5610
Be	1	0.46	0.32	0.46	0.20	2	0.48	1	0.12	0.46	0.17	1
Mg	12793	12400	10025	8550	460	35900	15950	16300	3307	15440	5020	26300
Ca	61352	54200	42530	50000	9620	203000	113755	121000	22998	110093	35400	132000
Sr	61	60	26	56	21	118	174	192	47	163	42	210
Ba	85	77	41	76	25	194	112	113	21	110	52	157
Al	14447	13000	9747	11607	3170	40100	13739	15000	3532	13030	4290	16200
La	9	9	5	8	2	24	12	13	4	12	5	19
Ti	499	406	308	428	126	1340	513	548	81	505	264	584
V	38	39	22	31	7	82	85	71	38	73	11	138
Cr	171	153	140	113	14	498	176	188	45	167	40	235
Mn	246	247	85	228	84	383	490	507	134	463	125	614
Fe	17333	15288	8610	14894	3230	34300	28336	29900	4838	27726	10200	31900
Co	5	5	3	4	1	11	9	10	2	8	2	10
Ni	34	37	16	29	3	61	101	107	31	94	20	135
Cu	84	58	83	55	5	309	379	430	181	332	63	876
Ag	0.20	0.16	0.15	0.13	0.03	0.44	2	2	1	2	0.04	4
Zn	252	198	231	188	26	1050	1234	1300	357	1138	215	1610
Cd	1	1	0.36	0.40	0.10	1	1	2	1	1	0.10	3
Pb	147	98	125	104	17	451	1759	1960	611	1506	104	2270
P	724	536	471	589	80	2150	1496	1660	517	1311	206	1920
S	995	980	504	833	129	1810	5676	6220	2190	4671	503	7360
As	7	8	4	6	1	17	11	11	4	10	3	17

(Please note Cd and Ag data to assessed with caution due to number of samples below IDL and proximity of most sample concentrations to IDL Cadmium concentrations below 2 mg/kg to be assessed with caution).

8.6 Applications of the dataset for sustainable development and scenario analysis

The challenge when trying to focus on issues relating to sustainable development such as the sustainable management of land and soils lies in trying to integrate the datasets with scientific tools of analysis and with the environmental policy making and management processes.

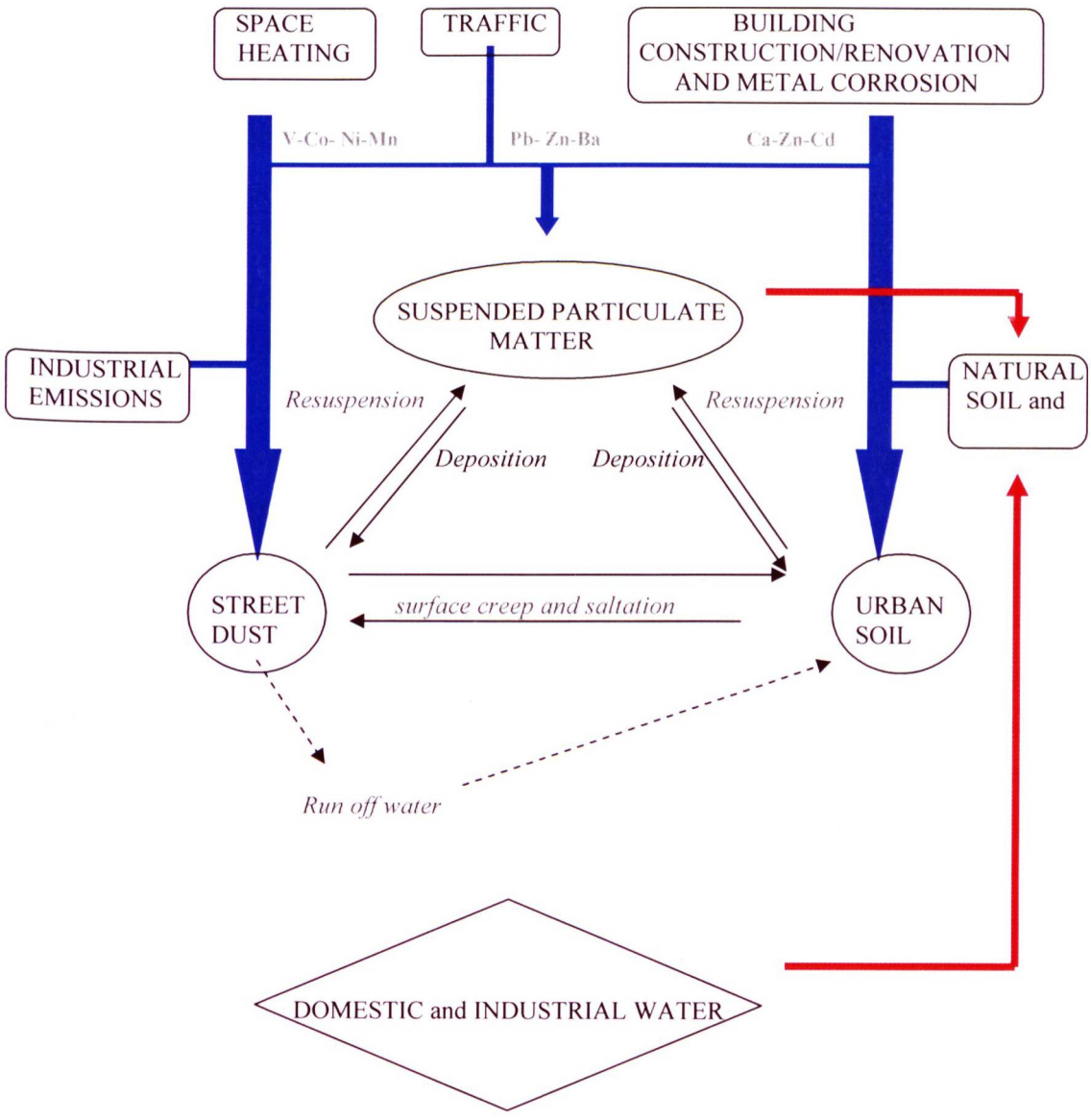


Figure 8.1 The urban cycle of particulate matter.

Source: modified from DeMiguel *et al.* (1999)

Urban locations consist of different interrelated environmental media namely soils, street dusts, house dusts and suspended particles through which particulate matter circulates (DeMiguel *et al.*, 1999). Figure 8.1 has been modified from DeMiguel (1999) and illustrates the circulation of particulate matter within a city. From this analysis urban environments can be geochemically modelled in the same way as the natural environment.

The range of elements generated in the urban environment is subject to change. This happens as elements migrate through the different media and before the particles finally accumulate in soils (urban sinks) or house dusts within the urban area. When assessing the impact of elements on given media such as soils or dusts, it is important to be aware of the processes both natural and anthropogenic, which operate within that environment. Similarly in order to evaluate the concentration of elements within each media, in addition to the rate of mass transfer among them, a simplified qualitative model should first be put forward.

The use of such models, when combined with the statistical and spatial evaluation techniques as used and discussed in previous chapters, can help in source identification and apportionment. For example in certain areas within a city the association of Pb-Cu-Zn-Ba can be used to evaluate the contribution of traffic more reliably, as was done in this work using factor analysis (section 6.6.4.1). Zn-Cd associations in dusts can show the effect of the corrosion of building materials. The combination of V-Ni-Mn-Co in soils and dusts in certain locations such as residential areas can be linked to emissions from domestic heating systems (DeMiguel *et al.*, 1999).

Urban geochemistry is concerned with the identification of elemental sources in towns and cities and the degree, to which they compliment, mask or change natural geochemical signatures in the surface environment (Kelly *et al.*, 1996). In urban soils. (Section 2.5), the effects of the geological parent material and pedogenic processes are overshadowed by the anthropogenic input and disruption from industrial and urban activity. It is the latter which exerts the most influence on the distribution of trace metals. The history of an urban region can and usually does include a series of land use changes, including natural resource exploitation, industrial activities, post

war housing and transportation of fill material (Thornton, 1991). When the effects of present day urbanisation are added to this, the resultant impact on local soils can be critical in terms of contamination with heavy metals from a variety of sources.

Another important application of an urban geochemical dataset lies in assessing pathways of human exposure, such as inhalation through air or particulates, ingestion via food, water or beverages and dermal via dust exposure. This exposure assessment is commonly being carried out through the use of models such as the Integrated Exposure Uptake Biokinetic (IEUBK) model and the Contaminated Land Exposure Assessment (CLEA) model (section 2.7.2). Regulators are now turning to risk assessment based principles in an attempt to reinforce "command and control" mechanisms as more effective methods of environmental protection. Exposure assessment and risk characterisation involves the examination and application of data gathered from urban datasets, the application of uncertainty analysis to make uncertainties explicit, and finally the integration of scientific risk assessment and public perception to make cost-effective policy and regulatory response. Risk characterisation combines information on toxicity and exposure estimates into an integrated expression of human health risk. It also identifies the uncertainties in risk estimates. The chemical-specific risks are estimated for each exposure pathway. Then these chemical specific risks are added to estimate cumulative pathways specific risk. Finally, risks are added across all chemicals and relevant pathways to estimate a total human health risk to individuals exposed to contaminants at a site (USEPA, 1994).

A GIS consists of hardware and software, with procedures automated data, designed to support the capture, management, manipulation, analysis, as well as the modelling and display of spatially referenced data for solving complex planning, management and research problems. Analysis using a GIS is important because: it integrates spatial as well as other types of information, provides a consistent analysis framework for geographically referenced data, provides new and insightful ways of manipulating and displaying data as well as allowing the viewing and analyses of data based on geographical proximity and relationships.

The application of GIS in this work has been developed as a decision support system which will convey environmental information that will assist various Government departments in Gibraltar. A GIS allows strategic planning, development control and pre-application assessment (Grossinho, 2001). The GIS project will assist in the modelling of urban regeneration based on the "suitable-for-use" approach adopted by various EU governments. The different layers incorporated in the GIS include the coastline, roads and paths, buildings, recreational areas, MOD areas, industrial locations, the underlying geology, the Upper Rock Nature Reserve as well as the collection and analyses (both statistical and spatial) of the geochemical data for the soils and dusts. The GIS database allows spatial operations as well as statistical analysis to be made on the dataset whilst delivering the results in an "easy to use" graphical user interface. The individual layers can be modified as and when needed. Modelling techniques such as geometric modelling and query analysis provide an interactive framework whereby the data can be manipulated to reveal spatial patterns and aid in decision making. As a result, the system thereby allows various options of interest to be assessed which will in turn assist government departments in the integration of EU directives with the Gibraltar regulatory system.

8.7 Chapter Conclusions

Increasingly a great deal of attention is being focused on understanding the chemical nature of the urban environment. Despite the existence of a large body of environmental legislation at both the national and EU levels, it is now generally acknowledged that it has not acted to prevent environmental deterioration (Kramer, 1992; Thornton, 1995). Some of the difficulties experienced by environmental agencies lie in the efforts to provide the legal controls with a scientific basis through standards. This is because existing institutional and administrative mechanisms do not easily incorporate scientific principles into legislation. European legislation has been particularly criticised in this respect (Thornton, 1995: Makuch, 2000) and an attempt is being made to tackle this problem through expert working groups and greater consultation at an earlier stage in the legislative drafting (Thornton, 1995). The basis upon which the standards have been set is always plagued with problems relating to scientific uncertainty which are not always well documented or understood

by future users. Thus, authorities are not always clear about the limitations of the standards or the circumstances in which they should be applied (Thornton, 1995).

The contamination of soils and dusts in Gibraltar is not considerable. Element concentrations are elevated above guideline values when compared to the calculated baseline values in a few sites. These sites as well as possible sources for the elevated elemental concentrations have been identified. The main inputs of metals to soils and dusts in Gibraltar appear to come from a variety of sources including vehicle exhausts, industrial emissions, paint, fossil fuel burning and the historic activity from incinerators, gas works and scrap metal yards. The exact influence of the underlying bedrock has not been ascertained. The extent of each source as a contributing factor has yet to be assessed. Recommendations have been made regarding the path and strategies which future land use management in Gibraltar should take. This is necessary if Gibraltar is to overcome the constraints which it faces in terms further socio-economic development. Sustainable development must first begin with sustainable use of the land. The "suitable for use" approach provides the best means of reconciling the governments various environmental, social and economic needs in relation to contaminated land. Contaminated land requires well-thought-out and cost-effective measures to contain, control or eliminate the risks.

In the past few decades, the natural input of particular elements to soils due to pedogenesis has been exceeded by anthropogenic input. It is thereby necessary to understand the extent, association and environmental availability of the elements that are harmful to the health of the flora, fauna and people.

CHAPTER 9

Conclusions

9.1 Introduction

The underlying principle of the current investigation is to obtain baseline data for a number of different elements, so that the relative importance of indoor and outdoor sources of exposure may be investigated and reported accurately. Each of the analytical techniques applied in this research can be used as effective tools for the generation of data. However, when any tool or method is used in isolation, the results obtained may not truly reflect all the different aspects which influence and function within a particular environment. In this work, chemical and numerical analysis tools have been combined with multivariate statistics and GIS mapping, providing a very powerful instrument for the quantitative description of the variables in question in terms of spread and volume, factors controlling the variability and spread of geochemical data and relating the results to non-numeric spatial information. Confirming and refining hypotheses related to geochemical interpretations from statistical outputs is best achieved when several methods are used to compliment each other.

This chapter summarises the main findings and conclusions of this research. The wider implications and uses of the research are indicated. A summary of the limitations of this work and recommendations for further research are also included in this chapter.

9.2 Summary of data collection and organisation

The starting point of any environmental investigation should always be a comprehensive and thorough desktop study (collection and review of all available information) for the study area. For this research a general review of the site history of military and civilian areas and a review of the geology was carried out. Potentially contaminative uses (past and present) of the land were investigated by reading the existing literature and interviewing people within various government departments.

Also interviewed were members of the public such as academics, historians and people who worked in certain types of industry such as the old gasworks plant. A site reconnaissance was also conducted to identify any site hazards such as derelict buildings or naturally unsafe areas such as cliffs. This information was used to form an initial working hypothesis and to aid the sampling strategy which was adopted. Other sources of information used in this investigation include historical accounts of industrial, waste disposal and MOD activities.

The basic aim of the sampling strategy was to provide current levels of element concentrations in soils and dusts that accurately reflect the mean value of the environmental variables being measured. Further aims were to determine spatial and temporal distributions of the variables. The overall sampling strategy was based on a loose grid and stratified random pattern. It was also based as closely as possible on the European Soil Sampling guidelines (ESSG) (section 4.2.2). A total of 246 soil samples (0-15 cm) and 162 dusts samples (80 house dusts and 82 street dusts) were collected. All samples were analysed using a nitric/perchloric acid digestion for "total" elemental concentrations of 26 elements (Li, Na, K, Be, Mg, Ca, Sr, Ba, Al, La, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb, P, S, As), as well as total organic carbon content (LOI) and pH. Molybdenum has not been included in the statistical analysis due to unacceptable levels of precision in the reference materials. Results for Ag, Cd, and to a lesser extent La, Co, Cr and Mn (in soils, rocks, house and street dusts) need to be interpreted with caution due to high numbers of samples falling below detection limit (appendix C contains the IDL for the SEQ analysis) and leading to an unacceptable precision. The IDL for Cd is set at 0.2 mg/kg, however, any data below 2 mg/kg is often considered to be questionable and warrants caution in the analysis. This was done in all the statistical and GIS techniques used throughout this study. Selected samples were then chosen for sequential chemical extractions. The results of the sequential extraction analysis also need to be analysed with caution, as the results of the precision and accuracy were not fully satisfactory.

The numerical analyses of the data commenced with simple statistical analysis. This involved the screening of the data to ensure correctness, plausibility, quality and reliability of the information before further statistical and spatial analysis methods were employed. This was achieved using a sampling and analytical quality control

scheme as well as exploratory statistical tools. Once this was done and the data conformed to the requirements necessary for further statistical analyses, factor analysis was applied to the data set. The objective here was to reveal a pattern or structure of the data which related the variables that are controlled by the same processes. If these variables then relate to concentrations levels of possible pollutants the groups then relate to the nature of the pollutants and can also minimise the list of possible pollution sources. This analysis creates a new set of latent variables that describe the original variable groupings. The integration of GIS mapping with the results of multivariate statistics adds a geographic dimensionality to the acquired information (Korre, 1997). The exploration of the geographic distribution of the variables allows evaluation of the spatial properties of the data, representing the soil and dust data in the different areas of Gibraltar. It should be noted however that the ability to associate variables with each other and with non-numeric geographic information is sometimes limited and can sometimes be subjective to visual interpretation.

9.3 Assessment of data in Gibraltar soils

There are certain areas in Gibraltar with elevated concentrations in either soils and/or dusts. These sites have elevated concentrations of a range of different elements including; Ag, As, Ca, Cd (Ag and Cd analysed and interpreted with caution), Fe, K, La, Mn, Na, Pb, P, S, Sr, Pb, Cu, Zn, As and V. The anthropogenic sources in Gibraltar which possibly lead to elevated concentrations of heavy metals in soils include the scrap yard, the incinerator, traffic, the electricity generating station and the desalination plant, the sand blasting of ships at the dockyard, the rifles ranges and activities of the MOD.

The elements Li, V, La, Ti and Co were highly partitioned in step 5, the residual fraction. Elements associated with this fraction are bound to the primary rock forming minerals, ore minerals and organic matter and are not bioaccessible. This is attributed to their occurrence in the stable phases. Lithium is mobile in pedogenic processes and so becomes associated with the clay fraction. The elements such as Na, Ca and Sr have a more variable partitioning pattern. These elements are released from the primary mineralogy and are distributed into various soil phases during the

soil forming processes. The concentrations of these elements in soils and dusts are believed to be influenced by the geological parent material and redistribution during pedogenesis. Iron and Co were partitioned into steps 3 and 5 showing a strong association with the formation of Fe-Mn oxides (step 3) and clay minerals (step 5). Sulphur was largely partitioned into step 4, reflecting the strong association S has with organic matter (Kabata Pendias, 1992). Phosphorous was largely partitioned into the residual fraction, possibly reflecting insoluble phosphate species. The partitioning of the heavy metals shows a high variability. Cadmium was partitioned throughout the five steps. The majority of Cu, Zn, Pb, Cr and Ni in soils were associated with step 5 with smaller amounts fractionated into step 3 and step 4. The mobility of these metals in soils is therefore low (p161, 162). Zinc and Pb in dusts however partitioned largely into steps 3 and 2.

The concentration of metals in soils and dusts in Gibraltar is heterogeneous and site specific, therefore a portion of the variability found between different sites is not spatially related. The soil data were classified according to the following land use categories; residential, commercial, industrial areas and open spaces. The concentrations of Cr, Ni, Cu, Zn Cd, Ca, K, Na, Fe and As in soils, were found to be slightly elevated in the industrial areas and open spaces but this difference was not found to be statistically significant. Certain sites in close proximity to industrial areas as well as open spaces with a former history of industrial use did display elevated concentrations as related to the rest of the data set. The ANOVA analysis showed that there are significant differences between some of the element concentrations in the varying land use categories (table 6.18). Lead and Ba had a significant difference in concentrations taken from soils on open spaces and residential areas. Additionally significant differences were found between the element concentrations in the different geological parent materials. Samples taken on the Catalan sands (table 6.17) have a statistically significant difference in concentrations of Li, K, Ba, Al, La, Ti, Mn, Na, Mg, V, Cu, Cd, Pb, P and S to samples taken on other geological materials.

T-tests were carried out to test element concentrations between soils concentrations taken from civilian and military sites and similarly between natural and garden soils. The difference noticed between these two groups was found to be statistically significant for the elements Ba, Ti and Cr in planted verses natural soils.

Baseline concentrations are a good measure of the variation in trace element concentrations. Their use as an aid in the identification of areas with elevated metal concentrations will allow risk assessments to be conducted and future policy regulations to be implemented. It must be noted however, that these baseline values are for Gibraltar at this point in time, for the years 2001-2003. Ongoing development, the everyday activities of people and changes in land uses will probably affect these values in the not to distant future. It is suggested however, that the baseline values calculated in this work be used as indicative guideline values for element concentrations in soils until such time as further geochemical surveys are undertaken.

Multivariate factor analysis was used to extract factors explaining the majority of the variance in the data set. Three main factors were extracted; anthropogenic, lithogenic/pedogenic and geologically related. Factor 1, the lithogenic/pedogenic factor, represents 55% of the total variation and had high loadings on the elements Li, K, Be, La, Ti, V, Cr and Ni. The concentration of these elements in soil was in all probability inherited from the parent material. The second factor, the anthropogenic factor, accounts for 10% of the total variation in the dataset. It has high loading scores on the anthropogenic elements Co, Cu, Zn, Cd, Pb, S and As. The metals Co, Cu, Zn, Cd and Pb are largely introduced to soils and dusts by anthropogenic processes. The third factor, the geologically related factor accounts for 8% of the total variation. It is characterised by the elements Ca, Sr and Mg. The parent material of an area (calcite $CaCO_3$ and dolomite $CaMg(CO_3)_2$ in Gibraltar) controls the occurrence of Sr and Mg in soils and their cation size is similar to Ca^{2+} therefore substituted for Ca in minerals (Kabata-Pendias and Pendias, 1992).

9.4 Assessment of data in house dusts from Gibraltar

The concentration of trace metals in dust from urban homes can originate from both internal (within the home) and external (outside the home, e.g. garden) sources. House dust data, as was the case with the soil data, have large standard deviations. There are some outlying values which originate from a few households and these are discussed in section 7.4. The relative contribution of different indoor and outdoor factors to these high outlying values has not been verified. The descriptive statistics show that as with the soil data, most elements have a large range of concentrations. Elements including Na, K, Mg, Ca, Al, Fe, Cu, Zn, Pb, P and S have very large standard deviations suggesting a large scatter about the arithmetic mean. Most

elements have a positive skew and show a non-normal distribution. Once the data underwent logarithmic transformation, a lognormal distribution was achieved.

The spatial distribution of element concentrations in dusts from Gibraltar is such that it is difficult to identify possible sources. Twelve sites have outlying values for a range of elements, the locations of these sites (section 7.4) within four distinct areas. Three of these are in close proximity to an industrial area; two are close to the electricity generating station in the north of Gibraltar, and the other two sites are located south of the dockyard in the southern part of town.

The house dust data conformed to the requirements necessary for FA. Four factors were extracted accounting for 77% of the total variation. The first factor can be described as the household or industrial factor. It accounted for 54% of the total variance and had high loadings for the elements V, Cr, Mn, Fe and As. The second factor is interpreted as the industrial or heavy metal factor. It accounted for 21% of the total variance and displayed high loadings for the elements Co, Cu, Zn, Cd and Pb. The third factor was defined by the lithogenic/pedogenically related elements and represents the soil factor in house dust. It accounted for 8% of the total variance. The elements associated with this factor were Li, Na, K, La, Ti, P and S. The fourth factor is identified as the geologically related factor and illustrates the influence of the geology of Gibraltar on the composition of house dusts. The elements associated with this factor were Ca, Sr and Mg and accounted for 5% of the total variance found.

9.5 Assessment of data in street dusts from Gibraltar

The data shown in section 6.5 displays large standard deviations for most elements (Co, Cd excluded[1]). Some elements such as As have a normal distribution, other elements including Cu, Zn and Cd (and to a lesser extent Pb) display a normal distribution only when the data undergo logarithmic transformation. The spread of the distribution of elements such as Na, K, P, S, V, Sr, V, Sr, Ni, Zn and Pb clearly indicates a bimodal distribution, meaning that the variance of some of these elements come from two or more populations which would indicate two or more distinct

[1] Data for these two elements to be assessed with caution due to unacceptable precision resulting form the large number of values below detection limit.

sources, again either geological, anthropogenic or both. Outlying values are present in the distribution of La, Ba, Mn, Fe, Cr, Cu and Zn. The spatial distribution of elements in street dusts in Gibraltar shows distinct areas where elevated concentrations (in relation to the rest of the dataset) of a range of elements (e.g. Pb, Cu, As, Zn, Ca, Ni etc) are found.

The patterns found in street dusts are very similar to those found in soils for the major elements (section 6.5.1). The elements La, Ti, Be, Co, V, Ba, Fe, Cr, Ni, Cu, Cd and As are partitioned largely (>50%) into step 5, the residual fraction, and so are presumed to have a low mobility in street dusts.

The FA on the street dust data revealed four factors which accounted for 87% of the total variance in the data set. The first factor has a combination of elements related to the underling geology such as Ca, Sr and Mg (Factor 3, the geologically related factor, section 6.8) as well as elements relating to anthropogenic inputs. The second factor contains elements which are related to lithogenic and soil forming processes. The presence of Pb and Ba in the third factor indicates a traffic source. The fourth factor is defined by Co, Cu, Cd and Ti representing a heavy metal source, possibly originating from scrap yards.

9.6 Comparison of soils and dusts datasets and general findings

The urban environment is affected by a wide variety of anthropogenic activities, which can increase metal concentrations in soils and dusts. The results presented in this study do not permit any firm or definitive conclusions to be made on the exact nature of indoor and outdoor sources of contamination. They do indicate however that dusts generated within the house itself can be an important source of exposure for certain elements. It is important to note that indoor/outdoor concentration ratios vary widely from one element to another and from one residence to another within an area (Rasmussen *et al.*, 2001). These variations, when compared with exterior soil and dusts in Gibraltar (or any other urban environment), combined with the distinct multi-element signature of house dust can make it difficult to predict accurately the contribution that of each of these factors would have in exposure assessment studies.

The mean concentrations of Li, K, Be, Ba, Al, La and As were found to be higher in soils than in house and street dusts. These elements are naturally present within soils as they relate to lithogenic and soil forming processes. This could also be due to the longer residence time of these elements in the soil matrix as well as to factors relating to the underlying geology. It could also be attributed to the anthropogenic addition through atmospheric dispersion, to direct deposition of these elements and to waste products containing these elements to soil. Sodium, Sr, Ti, Ni, Cu, Ag, Zn, Cd, P and S were higher in house dusts and Mg, Ca, V, Cr, Mn, Fe, Co and Pb were higher in street dusts than in soils (section 6.9). The high GM and 95th percentile values of Cu, Cd, Pb and Zn in house dust compared with soils and street dust could reflect factors associated with metal deposition. For example the area of residence within Gibraltar (town area versus southern district), the level of traffic near the home, the use of lead-based paint, and solders and plumbing materials within the home. These factors could result in higher concentrations of elements in the enclosed house environment as opposed to street dusts. High element values in street dusts as compared to roadside soils reflect the short-term contamination of dusts from vehicle exhaust emissions and component wearing. The high Mg and Ca concentrations could reflect the geology as well as anthropogenic factors such as cement. Chromium, Mn, Fe, Co and Pb could arise from refractory bricks, leaded petrol, roofing, guttering, pipe work and plating of car parts. It was not possible to run AVOVA analysis, correlation analysis or regression analysis or make direct comparisons between the house dust data and garden soil data because very few homes (<5) had gardens (83 house dust samples, 5 garden soil samples). The majority of the soils sampled were from amenity areas, derelict land, MOD land and the nature reserve.

The results of the sequential extractions in soils and street dusts are comparable. On occasion, elements such as Pb and Zn partition largely into the more mobile phases in street dusts as opposed to soils. This could be due to the different chemical forms of the elements present in soils as opposed to street dusts. This could also be due to the different physical and chemical process/reactions which occur within the soil matrix that are not found in the dust matrices.

The type of urban land use and industrial location has been known to exert geographically related "controls" on the concentration and spatial distribution of

metals in urban soils (Mielke, 1991; Birke and Rauch, 2000). Some trends have been identified for the soil and dusts data in Gibraltar. In this work, geostatistical methods have been used to assess the spatial distribution of element concentrations across Gibraltar. Different techniques of spatial data analyses were assessed in terms of their applicability and accurate representation of the processes occurring within the environment under investigation. The basic hypothesis behind geostatistical methods that *things* (be it objects or element concentrations in soils) *that are closer together are more alike than things that are further apart* is rejected on the basis of two variables. Firstly the spatial heterogeneity found within very small distances in urban areas, and also rural areas (due to the presence of mineral deposits and natural geochemical anomalies); and secondly, the temporal variability of element input from anthropogenic sources to the natural environment. Gibraltar is a very small heterogeneous area. The common errors of under- and over-estimating high and low values associated with kriging models are the result of the marked spatial heterogeneity found within very short distances in many urban areas. This is a problem that can lead to the misinterpretation of the data and result in serious consequences for land use management. Interpolation techniques are generally not suited to large areas with distinctly varying topologies. The geostatistical methods of Inverse Distance Weighting and kriging are more applicable on an individual site basis which has a more homogenous type of topology. Additionally changes in land use such as those documented in East side reclamation in Gibraltar between the years 2001 and 2003 mean that if such maps are produced, they need to be interpreted with caution and amended regularly.

The spatial presentation of element concentrations in soils and dusts shows that there are certain areas in Gibraltar with elevated concentrations of metals and other elements in either or both of these environmental media. Figure 7.3 identifies several sites that are discussed throughout this chapter with concentrations of Ag, As, Ca, Cd, Fe, K, La, Mn, Na, Pb, P, S, Sr, Pb, Cu, Zn, As and V in these media exceeding guideline values and/or world means. These sites are discussed in detail in section 7.3. These types of maps (point source concentration) allow the identification of sites, which require further investigation. They can also aid in the initial identification of possible sources of elevated concentrations; for example sites with elevated concentrations can be displayed with industrial locations, or proximity to major roads.

The anthropogenic sources in Gibraltar which could lead to elevated concentrations of heavy metals in soils include the scrap yard, the recent but now unused incinerator, traffic, the electricity generating station, the desalination plant, the sand blasting of ships at the dockyard and the rifles ranges.

Twelve sites (section 7.4) have outlying values for a range of elements in house dusts. The locations of these sites are shown in figure 7.28. There are four distinct locations, three of which are in close proximity to an industrial area. Two sites are close to the electricity generating station in the north of Gibraltar, and the other two sites are located south of the dockyard in the southern part of town. The difficulty in assessing sources of elements in house dusts includes the vast number of factors which need to be considered, ranging from factors relating to inside the home (type of flooring, heating system used, smokers in the premises etc), to factors such as nearby industry in the area, the urban density in the area, the direction which a site might be facing, wind direction just before and during the time when the samples were taken etc. Reconnaissance or baseline studies such as these are however very useful in identifying areas where evidence suggests possible sources of contamination, thereby indicating areas where further longer term monitoring is necessary. The spatial distribution of street dusts in Gibraltar also shows distinct areas where elevated concentrations (in relation to the rest of the dataset) are found (section 7.5). Figure 7.31 shows the areas with elevated concentrations of a range of elements (e.g. Pb, Cu, As, Zn, Ca, Ni etc) in street dusts.

The results from the factor analysis were incorporated into the GIS database. Three main factors were extracted to explain the majority of the variance in the Gibraltar geochemical soil dataset (described above). The factors were saved as new variables into the original dataset. Each soil sample has a coefficient score for each corresponding factor and this has been plotted as a layer on a GIS. Samples with high loadings in the lithogenic/pedogenic factor (F1) and the geologically related factor (F3) corresponded sites in the Upper Rock Nature Reserve (URNR), open spaces and sites of exposed soil outcrops (figure 6.25, 6.26).

The factor maps produced for the house and street dust datasets do not display immediately obvious spatially related patterns, however the samples identified with

high scores for the anthropogenic and household/metal factors in the house dust dataset correspond to the samples described as outlying sites discussed in section 7.4. Figure 6.28 does not show any immediately discernible spatial pattern as regards the geographic distribution of the four factors found for house dusts across Gibraltar. Sites with high loadings in the household and anthropogenic factors (F1 and F2) are identified and discussed in section 7.4 but they are not always necessarily found in close proximity to industrial areas. Spatially related patterns are found in section 7.4 as regards elevated concentrations of a variety of elements in house dusts across different areas of Gibraltar. These patterns however are not portrayed with the factor maps produced. This reflects the large variety of sources and/or factors that makeup the composition of house dust.

The factor map for the street dust data (figure 6.29) show one geographical area as displaying a cluster of samples all having high loadings for factors F1 (soil related/anthropogenic) and F2 (lithogenic/pedogenic). This area is the central and upper town area, which is described in section 7.5, as the town area. This area has elevated concentrations for the anthropogenically related elements found in F1 and F2. Samples taken in the URNR did not display a similar pattern, as was initially anticipated. No other definitive geographically related patterns can be discerned from figure 6.29. Samples with high loadings in the industrial or traffic factors aren't necessarily close to industrial areas or busy roads. Once again, the spatially related patterns are noted in section 7.5 as regards concentrations of a variety of elements in street dusts across different areas of Gibraltar, are not portrayed with the factor maps produced.

There do not appear to be any metal anomalies in soils or dusts in Gibraltar that exceed SGV or world means to such an extent that they would pose a threat to human health or to the flora and fauna. Gibraltar, despite being one of the most densely populated areas in the world, has relatively low levels of toxic metals. Gibraltar was isolated from the rest of Europe for many years (1969-1985). This combined with its role as a military base meant that resources were brought into Gibraltar by sea and later land. The development of heavy industry that could have resulted in increased element concentrations in soils was therefore not necessary. Spatial patterns found of element concentrations in soils show the likely influence of the sand blasting of ships,

traffic, and the effects left from the incinerator as well as the underlying geology. Despite the fact that Gibraltar is an enclosed environment, military occupation for many years and a very high traffic density, the concentrations of elements found do not show any cause for concern for either the environment or the people (Thornton, cited in THES, 2004). Areas with very low element concentrations and deficiencies of nutrient trace elements have been found in Gibraltar. These areas include on the east side: Sir Herbert Miles Road, the wind blown sands (WBS) in the water catchments and the east side sand slopes. On the western side the sites include the Alameda sands, Jumpers Bastion and Europort. Windmill Hill in the south of Gibraltar, the north of Gibraltar near the border and some sites in the URNR also contain very low concentrations. Table 7.2 lists these areas together with the elements showing very low concentrations at each of these sites.

The GIS maps produced illustrate how results from statistical techniques can be incorporated into a GIS. These maps can be integrated with data related to geology, land use and transportation techniques. This can then allow the identification of sites or areas which require further research, as well as aiding in the verification of hypotheses regarding spatial patterns within the dataset. One of the key tools of a GIS is its data handling capabilities. Once the features have been captured into a GIS it can be analysed and modified to suit the requirements of the project.

As already stated, from a methodological perspective, each of the analytical techniques applied in this work can be used as effective tools for the interpretation of data, as long as the limitations to each method are noted and carefully considered. However, when any tool or method is used in isolation, the results obtained may not truly reflect all the different aspects which influence and function within a particular environment. Confirming and refining hypotheses related to geochemical interpretations from statistical outputs is best achieved when several methods are used to compliment each other.

9.7 Limitations encountered and recommendations for further research

9.7.1 Limitations of the work

The assessment of the methodology applied in this research revealed a few areas of potential weaknesses. The restriction as to the number of samples taken together with the topography of the area meant that a stratified random fashion sampling strategy had to be adopted. The sampling strategy used may have missed out areas where elemental concentrations are high and similarly areas where concentrations may have revealed further patterns for the spatial distribution, aiding the identification of potential sources.

Increasing the number of samples on specific land use categories, such as industrial sites could aid in the identification of possible sources and could have lead to more conclusive results from the factor analysis. The factor analysis highlighted sites that had been classified as sites with outlying values. The loadings for certain factors at some sites verified the influence of nearby industrial locations, but this was not always the case. During redevelopment the top 1-2 meters of soil is usually disrupted, removed or compacted and so sampling from further down the soil profile (>15 cms) could provide some useful insights into the element distributions within the soil profile as well as providing a clearer picture as to the true concentrations at a particular site.

There is no universal protocol which meets the requirements of every analytical investigation. A number of problems exist when sampling in urban areas which are linked with the built up environment. Adhering to a pre-defined sampling strategy can often be difficult due to restrained access to private property or MOD areas, and the lack of suitable sampling sites in heavily developed areas close to the city centre. A number of uncertainties also exist regarding the history of land use at particular sites, and the actual origin of the topsoil which has been sampled. Limitations of the ICP-AES analysis lie in sample dissolution problems and in its inability to distinguish between different species of the same element. Limitations of this instrument include the detection of trace metals below a concentration of 1 mg/kg; inert gasses, oxygen, nitrogen and carbon cannot be measured (Walsh, 1997). Examples of limitations encountered in the sequential extractions include incomplete dissolution of the

targeted phase which results in subsequent re-precipitation during the method. Also the loss of material is almost unavoidable when washing the sample and whilst decanting the solution after each step. This then leads to a recovery of less than 100%. The recovery of Al is unacceptably low due to the resistance of aluminosilicates to chemical attack. The concentration of Cd in soils falls close to or below the detection limit especially in the sequential extraction scheme, making the interpretation and use of the results somewhat difficult, and warranting caution.

Although the methodology used addresses the problem of quantitative assessment of soil variables and assesses the relationship with other spatial information recorded in the GIS database, the identification and quantification of the pollution sources is not complete. The identification and spatial distribution of the possible sources of contamination was identified through GIS and FA however, the relative amount of the effect that each source attributes at any given area is not quantified. The geochemical datasets were found to be appropriate for the application of factor analysis, but there were limitations to the interpretation of the factors derived because geochemical data sets are very heterogeneous. In homogenous data sets, the first 2 or 3 extracted factors explain up to 90 to 95% of the total variance (Davis and Thornton, 1987a; Manly, 1994). In this research, up to 87% of the total variance was explained by the first three or four factors extracted from the Gibraltar geochemical datasets. The remaining percentages are regarded as "noise". This may be considered a high proportion by some analysts but enforces the factors of temporal variability and spatial heterogeneity which are so important when analysing urban geochemical data. Another limitation to the use of all statistical methods particularly multivariate statistics is that the results are highly sensitive to the input parameters. Reimann *et al.* (2002) concluded that the variable inputs into a factor analysis were very often constrained by the elements analysed by a certain analytical technique, or by the elements that fall below the analytical detection limit. Thus, the results produced must be interpreted with caution.

9.7.2 Recommendations for further research

Further more detailed geochemical surveys of Gibraltar will help to assess the impact of development on the landscape and how best to ensure that future development does not place unnecessary strains on the already limited resources, such as the land. The

further addition of contaminating elements to urban soils and dusts will undoubtedly continue as Gibraltar continues to develop and progress. The long-term assessment of metal speciation and bioavailability in soils and dusts needs to be assessed by some form of periodic assessment and monitoring (perhaps every 5-10 yrs) into the extent, physico-chemical form and bioavailability of metals.

Increasing the sampling density in certain areas such as the Upper Rock Nature Reserve as well as other areas of natural land, and all brown field sites will ensure an effective land use management scheme. Similarly, adopting another sampling strategy in certain areas such as a systematic or herringbone sampling pattern may ensure greater detail and accuracy of elemental distribution in the areas covered.

In terms of laboratory analysis, using different digestion techniques such as digestion in aqua regia or with hydrofluoric acid (HF) would ensure that certain metals are completely dissolved and the results obtained are a true representation of the concentrations in those soils. An extensive biogeochemical survey is needed on crops grown on private gardens to assess potential human exposure to toxic metals and to assess plant uptake of metals in natural areas. Verifying the speciation and isotopic nature of metals will help to assess the bioavailability and potential toxicity and the source of these metals.

In order to stay within the boundaries of the title, the aims and the objectives and also taking into account the time factor associated with this work, this has resulted in restrictions on this thesis which did not permit certain statistical and GIS analysis to take place. Further statistical treatment of the data could help to reveal underlying patterns within the data set. For example regression analysis can be used to model the factors influencing metal concentrations in soils and dusts. Also, correlation analysis can be used to illustrate the relationship between metal partitioning in steps 1 to 5 and the soil properties pH and loss on ignition (total organic carbon content).

Probability mapping within the GIS database can be used to define areas that exceed a threshold value. Geometric modelling and query analysis can also be used within the GIS database to further interpret any spatial patterns which are present. Past and present land use maps could be digitised and added to the database, to assess the

influence of previous land uses on current element concentrations in soils. Risk assessment analysis in the form of the Integrated Exposure Uptake Biokinetic (IEUBK) model for Pb in children developed for the U.S. Environmental Protection Agency can be used to estimate the blood lead (PbB) levels in children exposed to Pb contamination from several sources (IEUBK, 1999). Similarly, the Contaminated Land Exposure Assessment (CLEA) model can be used to assess current levels of exposure to Pb in children through different exposure pathways. Scanning Electron Microscopy would prove very useful for characterising and apportioning the sources of particulate matter in the samples collected.

Further analysis of Gibraltar soils and urban dusts is required to determine the most suitable types of remediation to be used. The changing use of the urban landscape means (new developments on natural, disused and former MOD sites) that a categorisation of soils based on geochemical criteria needs to be developed. The degree of contamination was proposed by Hollis (1991) as a property in the classification scheme for anthropogenic soils.

9.8 Summary and Conclusions

The detailed aims and objectives of the project are set out below:

1. To undertake a detailed geochemical survey of Gibraltar and to examine total metal concentrations using a variety of soils from urban, rural and military areas.

This aim was accomplished and element concentrations were obtained for different land uses throughout Gibraltar.

2. To establish baseline values.

Baseline values were calculated for this point in time for Gibraltar soils. They were calculated using the method described by Dudka *et al.* (1995) and Chen *et al.* (1999) of the GM/GSD^2 (lower baseline) and $GM*GSD^2$ (upper baseline).

3. To establish the extent and magnitude of the variations in major and trace elements in soils and dusts (street and house dusts) in order to assess the impact of industrial, commercial and urban development on the geochemical landscape.

The use of GIS mapping and multivariate statistics aided in the identification of areas with elevated concentrations and the spread of the data was assessed. Anthropogenic, lithogenic/pedogenic and geologically related factors were extracted from the soil and dust surveys. The difference found between element concentrations in the different land use categories although important, was not statistically significant.

4. To identify the principal factors affecting trace metal mobility and availability in the urban soils using the sequential chemical extraction method, developed by Tessier *et al.* (1979) and modified by Li *et al.* (1994a).

The solubility of metals in soils is discussed in section 6.2.2 and 6.5.1 and summarised in section 9.3. Factors relating to the trace metal mobility and availability of elements in soils and dusts are discussed but have not been firmly established.

5. To carry out Factor Analysis on the complete dataset. Factor analysis attempts to identify underlying variables that explain the pattern of correlations within a set of observed factors. It is employed in an attempt to identify pollution sources and to apportion natural versus anthropogenic contributions.

Factor analysis was applied to the soil dataset and three main factors were extracted explaining up to 87% of the variability. Four factors were extracted in the house and street dust data sets explaining 77% and 87% of the variance encountered. The natural and anthropogenic contributions were generally distinguished with ease in all three data sets and some successful attempts were made to identify pollution sources.

6. To develop a GIS database so as to assess the spatial distributions of elements. This will be done by comparing the geochemical maps produced to features

such as the underlying geology, topography, historical and present land use as well as in relation to elemental associations.

The GIS database for Gibraltar was created. All the various topographical layers were digitised except previous and current land use. This information was obtained however in regards to the different sites where samples were taken. The analytical data were then incorporated into the GIS database and the maps in chapter 7 were produced.

7. To deliver a GIS database to the Government of Gibraltar, which they can use to assess land use changes in different locations and to investigate sources of contamination to the environment and to assist with future land use planning.

The GIS database will be delivered to the Gibraltar government on completion of this research.

8. To investigate how the urban geochemistry of Gibraltar relates to issues concerning land use management and sustainable development.

Chapters eight and nine discuss this topic. Chapter eight discusses the need for legislation and ordinances to be adopted in Gibraltar to ensure effective future sustainable development. These issues are also discussed in the following section.

9.9 Sustainable land use in Gibraltar

Soil is a non-renewable resource. In order to achieve sustainability, soils and the environment in general require in-depth and sophisticated management, within the framework of a comprehensive and explicit Government policy for environmental protection (Royal Commission on Environmental Pollution, 19th report, 1996). The issue of sustainability however, encompasses much more than just soil or land use management.

Gibraltar covers a very small land area with limited natural resources. Sustainable development in Gibraltar in the past has always been governed by its role as a site of

strategic and military importance. This view has now largely changed and tourism for example, is a big part of the Gibraltar economy. The effects of current day tourist practices need to be investigated in terms of effects on the natural landscape, particularly so in the upper rock nature reserve. The preservation of the natural areas, the pollution from the increasing numbers of vehicles circulating in Gibraltar all affect the future sustainable development of Gibraltar as well as land use management and preservation of soils.

In the past sustainability was not foremost in people's minds, particularly those of the military. Projects that have recently been undertaken in Gibraltar which illustrate a change in this respect include the pedestrianisation of Main Street in the city centre, the land quality assessment being carried out by the MOD on military sites in Gibraltar, the introduction of Environmental Impact Assessments (EIAs) before any major developments and the reseeding of the disused water catchments. These latter sites were reseeded with natural vegetation in the hope of bringing back the indigenous floral species which were present before the site was turned into water catchments. Development is an ongoing process. In the three years of this research, land use changes to sites have occurred which affected the subsequent interpretation of the data collected. The main example is the completion of the east side reclamation project, a reclamation site used as a landfill. The incinerator was closed down, sites have been vacated by the military and handed back to government for further use and plans to build a sewage treatment works in Gibraltar have commenced. These are but a few examples which prove that development, sustainable development and environmental monitoring *are not static processes.*

This baseline survey provides an indication into current levels of element concentrations in soils and dusts from Gibraltar and promotes the need for further ongoing studies not just in this field of research, but also in other areas of the natural and urban environment which affect and are intrinsically linked to sustainability. The monitoring of contemporary releases and remobilisation of metals in the urban environment is an important component in sustainable practices. The awareness of the potential damage that industrial operations and related human activities may cause to our natural environment has resulted in the close monitoring of industrial installations.

Modern environmental legislation requires the monitoring and assessment of environmental (soil, air, water) quality right from the start of planning of an industrial process, during the operational life of the plant and through to the rehabilitation or closure of the site. In other words, a review of the life cycle of that (industrial) process.

Sustainability will only be achieved if there is a sound foundation of knowledge and understanding to inform and inspire the management of our resource (Royal Commission on Environmental Pollution, 19th report, 1996).

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THE NEW CONTAMINATED LAND REGIME

Part IIA of the 1990 Act establishes a specific contaminated land power, including a definition of contaminated land and a procedure for securing remediation when such land is identified. The regime can be summarised, very briefly, as follows:

- local authorities will cause their areas to be inspected to identify contaminated land;
- enforcing authorities (i.e. the local authority or the Environment Agency, depending on the case) will establish the appropriate person(s) to bear responsibility for remediation;
- enforcing authorities will decide what remediation is required in any individual case and ensure that such remediation takes place, either through agreement with those responsible or, where necessary, and after consultation, by serving a remediation notice or, in certain circumstances, through themselves carrying out the work; and
- enforcing authorities will record information on a public register about their actions;
- contaminated land will be identified on the basis of risk assessment. Land is only "contaminated land" where it appears, by reason of substances in, on or under the land, that:
- significant harm is being caused or there is a significant possibility of such harm being caused; or
- pollution of controlled waters is being, or is likely to be, caused.
- under the provisions concerning liability, responsibility for paying for remediation required by a remediation notice will, where feasible, follow the "Polluter Pays" principle. In the first instance, persons who caused or knowingly permitted the substances to be in, on or under the land will be liable. If none can be found, responsibility will pass to the current owner or occupier (except where the problem is solely one of water pollution). Responsibility will be subject to limitations set out in Part IIA and the guidance.

The Contaminated Land Regulations will prescribe

- descriptions of land which, if contaminated land, are required to be designated as a "special site. Once designated as such, the Environment Agency becomes the enforcing authority for that site rather than the local authority. Designation is unlikely to impose costs on businesses, except possibly for those who wish to check whether the designation is appropriate. Indeed additional costs may be avoided, where the site is already being regulated by the Agency in another context such as integrated pollution control, since operators can continue to deal with a single regulatory body instead of two.
- the material to be included in the remediation notices which authorities are required to serve in certain circumstances.

- the particulars which are to be placed on the public registers to be maintained by the enforcing authority under Part IIA, and other detailed matters. Businesses wishing to purchase land may benefit by the availability on public registers of a comprehensive record in respect of that land of all the regulatory actions which have been taken by authorities under Part IIA. The Act makes provision for cases involving commercial confidentiality.
- the grounds for appeals against remediation notices. The proposed grounds are be widely framed so as to include explicitly all the reasonable grounds on which an appeal might be made. Although there are costs associated with making an appeal, these do not derive from the regulations.
- the arrangements for persons to claim compensation from those to whom they have been required by Part IIA to grant rights (eg rights of access), in order for the requirements of a remediation notice to be carried out. Compensation will cover primarily depreciation in land, loss and disturbance, and economic loss. While this basis of compensation may increase the costs to a business required to carry out remediation compared to some other basis, it reflects other existing compensation arrangements. In most cases, any cost attributable to this basis of compensation compared to any other is likely to be a small part of the overall cost of carrying out the required remediation.

The statutory guidance covers five distinct aspects of the regime
- the definition of contaminated land
- its identification
- its remediation
- exclusion from and apportionment of liabilities for the cost of remediation
- recovery of the cost of remediation.

The intended effect of this statutory guidance remains as indicated in the CCA prepared for the Bill. That assessment explained that, in comparison to existing controls to deal with land contamination, the new measures would provide greater consistency across the country as the regulating authorities would be required to operate within a framework of guidance from the Secretary of State for which there was previously no provision. It also noted that the extent of any remedial or preventative works would be restricted, through guidance from the Secretary of State, to those necessary having regard to the use of the site, its location and its physical characteristics (the "suitable for use" approach); and that enforcing authorities would also have

to have regard to the cost which was likely to be involved in any given case, and to the seriousness of the harm or water pollution being addressed.

THE RISK POSED BY CONTAMINATED LAND

Contamination of land and pollution of waters arises principally from industrial practices which have led to deposition in, on or under land of substances such as oils and tars, heavy metals, organic compounds and soluble salts, and mining materials; and from the landfilling of waste without adequate precautions against leaching or the escape of landfill gases.

HAZARDS RESULTING FROM CONTAMINATED LAND

Land contamination can create hazards where pollutants in, on or under land reach a target or receptor, through any one or more of the following pathways:

- vapour or gas path to the surface, directly or via adjoining land;
- by leachate or erosion (eg to surface waters, to drainage, or to deeper aquifers);
- by direct uptake (eg to the food chain, or other parts of the ecosystem);
- by direct ingestion, contact or inhalation (eg by humans, animals or other organisms);
- by other contact (eg contact with building materials).

HARMS

The hazards outlined above may lead to

a) Harm to the health of users and occupiers of land, for example because of the presence of asbestos fibres, toxic metals or carcinogenic compounds. While the potential for harm from many other substances exists, little is known of any actual adverse effects on health among people living on or near contaminated land.

b) Harm to the environment which may have implications for ecosystems.

c) Harm to water quality. This includes both surface water, and also groundwater, abstraction of which makes up 35% of the total public supply. Groundwater also provides the baseflow for many surface water systems, some of which are used for potable supplies, and for fishing and other recreational uses.

d) Direct physical harm to human beings, for example through explosion of landfill gas. Explosions and fires have occurred under houses built close by former landfills at Loscoe (Derbyshire) in 1986, and Kenilworth (Warwickshire) in 1989. There can be a fire hazard where combustible material is present below ground, and underground fires can release toxic

and asphyxiating gases which can travel extensive distances below ground. Harm might also arise from contamination of food, for example if dairy animals grazed on contaminated soil.

e) Harm to structures, for example through chemical attack on building materials.

Harms to health and the environment arise not from the mere presence of contaminating substances, but their movement along a pathway to where they can cause damage to a receptor. The controls represented by Part IIA and its associated statutory guidance recognise that there is no need to remediate all land with contamination present. The introduction of either new pathways, or new receptors can also give rise to hazards. Where this might arise through development, the planning system provides the necessary controls, which in effect complement those provided by Part IIA.

ASSESSING THE RISKS

The risks on each site are to be assessed, and the controls are triggered only where there is significant harm, or a significant possibility of it, or actual or likely pollution of controlled waters. The extent of the risk on any particular land depends upon a number of factors including the following:

- the characteristics of the substances in the land;
- the local geology and hydrogeology;
- the nature and presence of receptors;
- the use of the land, or of adjacent land;
- the nature of the land , in terms of whether pathways might exist or be created;
- what measures exist, if any, to reduce or limit the risk.

Additional risks might result from the redevelopment of the land, for example if housing replaces industrial use. However, potential future risks of that kind are the subject of controls under the planning and building control regimes and not under Part IIA.

RISKS TO INVESTMENT AND REGENERATION

In addition, urban regeneration and local economic growth can be put at risk by contamination. As at 1 April 1993, a total of 39,600 hectares of derelict land on 10,400 sites was recorded in England. This included general industrial dereliction, derelict spoil heaps, former dock and railway land and former waste disposal sites. Such land will often have been contaminated to varying degrees, and may also pollute other land or waters.

Apart from the direct costs of dealing with the contamination, there may often be considerable

uncertainties about what regulatory requirements for remediation may be imposed, and about liability for such work. Such uncertainties have been major contributory factors in land remaining derelict, by reducing investment confidence, and deterring development. This can be demonstrated by the fact that land in these circumstances frequently has a negative value, and may have been abandoned by its owners. Government regeneration programmes, including English Partnerships, spend considerable sums in securing reclamation of such blighted land. For example, about a third of sites reclaimed by English Partnerships involve the treatment of contamination. In 1997/1998, some 1220 hectares of land in England were reclaimed or improved through the Single Regeneration Budget. Nearly £911 million of private sector investment was secured. These figures help to illustrate the importance of minimizing the risk to investment confidence arising from land contamination. As well as adverse localised social and economic effects, the lack of confidence in brownfield sites arising from contamination and its associated uncertainties can also lead to increased and unwanted pressures for new development on greenfield sites. Part IIA and in particular the statutory guidance will help to address all these risks by providing a clear framework for dealing with contamination.

Field notes street dusts PhD March 2001

Sample 7 - **Sir Herbert Miles Rd 1 (cliff to sea)** *28-05-00* (40 018 00 N, 2 894 00 E)
- ✓ soils in place long time
- ✓ sandy soils as in catchments, no colour variation in core
- ✓ christanthenons, greater soft storksbill

Sample 8 - **Sir Herbert Miles Rd 2 (planted border)** *28-05-00* (40 017 00 N, 2 894 00 E)
- ✓ sandy soils, no colour variation in core, medium brown colour
- ✓ planted flowering plants
- ✓ adjacent to road

Sample 9 - **Incinerator 1** *28-05-00* (39 996 00 N, 2 892 00 E)
- ✓ soil sample in planted border
- ✓ sandy texture, light brown colour
- ✓ natural soils, been in place for more than 10 years
- ✓ c. 20m from road

Sample 11 - **border by lighthouse** *28-05-00* (39 988 00 N, 2 890 00 E)
- ✓ sandy texture, medium brown colour
- ✓ kestrels nesting in area
- ✓ species include geraniums, fig trees, rosettes, bears breech, asparagus, mastic tree
- ✓ close proximity to road

Sample 12 - **battery (by Jumpers)** *30-05-00* (40 011 00 N, 2 884 00 E)
- ✓ very old planted border, more than 50 years old
- ✓ sample by eucalyptus tree, planted daisy species
- ✓ sandy texture, dark brown colour, OM present,
- ✓ no colour variation in core
- ✓ adjacent to road
- ✓ birds and insects

Soils

Sample 1 - **GOG catchment 1.** (40 019 00 N, 2 893 00 E)
- ✓ Steep slope, bare exposed soils, very steep slope c. 17° steep
- ✓ Lots seagulls in area, bones, wood debris
- ✓ 70m above sea level, strong possibility for wind erosion/exposure, effect of gravity!
- ✓ Wind blown sands, moisture at 15-20 cm, sands exposed for 2 years, before covered with corrugated iron sheets for c.100 years, Max sand depth c. 1.30m
- ✓ Close to ashvault plant

Sample 2 - **GOG catchment 2, seeded section.** (40 017 00 N, 2 893 00 E)
- ✓ Steep slope, very steep slope c. 17° steep, covered plastic matting to bind sands
- ✓ Flowering plants, e.g. vulpia alopecuros, nicotina gloca (wind blown not seeded), high vegetation density
- ✓ Spiders, seagulls, butterfly (snow white and snow blue), insects, snakes
- ✓ Some tin/iron sheeting at base of slope, by vegetation
- ✓ No moisture in sand, 78m above sea level, soil depth c.1.30m

Sample 3 - **Private Garden Flat Bastion Rd.** (40 017 00 N, 2 885 00E)
- ✓ sandy texture to soils, slight variation in core, generally medium brown colour
- ✓ vegetation, festuca, rye, palm trees, daisies, tulips roses (planted species)
- ✓ soils - 1 and a half years in place. Bought from Spain, normal quality soils
- ✓ had ammonia and fertilisers added, birds, insects, butterflies
- ✓ in town area, 5m below road but adjacent to it

Sample 4 - **Europort 1.** (40 025 00 N, 2 878 00 E)
- ✓ open grass area, public garden, c.10m from the sea (site at sea level or 1-32 m above)
- ✓ soils in place 8 years, flat area, soils imported from Spain
- ✓ underlying terrain, sand reclaimed off Europa Point, site on reclaimed land
- ✓ grasses, festuca and rye
- ✓ no colour variation in core, sandy texture, medium brown colour

Sample 6 - **roadside border, opposite old Med club.** (40 029 00 N, 2 885 00 E)
- ✓ soils in place long time, c.30 years, eucalyptus, boxus species
- ✓ sandy soils, no colour variation in core, medium brown colour
- ✓ adjacent to road
- ✓ some small insects in soils, planted flowering plants

Sample 7 - **Sir Herbert Miles Rd 1 (cliff to sea)** (40 018 00 N, 2 894 00 E)
- ✓ soils in place long time
- ✓ sandy soils as in catchments, no colour variation in core

christanthenons, greater soft storksbill

QUESTIONAIRE FOR HOUSE DUST SAMPLING IN GIBRALTAR

DATE: TIME: MAP REFERENCE: SAMPLE N°:

1) Sample type (a) house dust (b) garden soils (c) water (d) hair (e) food
1) Family name _____
2) Address _____

_____

4) Is the residence (a) house (b) flat. *which floor* _____
4a) Is the property (a) government (b) Private (c) owner/occupier (d) MoD
5) Number of adults in residence _____
5a) Occupations _____
6) Number of Children _____ Ages: _____
7) Do you have a house maid/cleaner? (a) Yes (b) No
1) How often is the house cleaned? _____
2) Do you own a vacuum cleaner? (a) Yes (b) No
3) Age of property? _____
4) How long have you resided in this property? _____
5) When was the last time you redecorated? _____
11a) Did you remove the old paint? (a) Yes (b) No
11b) If **Yes** how was the paint removed? _____
12) Any smokers in the home? (a) Yes (b) No
12a) *number of smokers and how many per day* _____
13) Any pets? (a) Yes (b) No (c) number___ (d) type/s_____
13a) If **Yes,** how many and what type? _____
14) Form of heating? (a) central (b) electricity (heaters) (c) gas (d) other: please specify: _____
15) Air conditioning? (a) Yes (b) No
15a) Do you have an extractor over the oven/cooker? (a) Yes (b) No
15b) Do you burn incense or use candle scence burners? (a) Yes (b) No
16) Floor type? (a) wood (b) ceramic (c) marble (d) carpets (e) linoleum (f) other: please specify _____
1) Distance of premises from road _____
2) Type of road (a) main road – very busy
(b) secondary road – not that busy
(c) residential road
19) Do you have a garden? (a) Yes (b) No *Size* _____
20) Exposed soils (a) Yes (b) No *amount exposed* _____
1) How much is natural soils and how much is imported soils _____
2) Is the garden near the road (a) Yes (b) No *proximity* _____
3) Any home grown produce (a) Yes (b) No *what* _____
4) Do you use fertilisers on the soils (a) Yes (b) No *which* _____
5) Do you consider this location to bring in a lot of dust (a) Yes (b) No
25a) Why _____
6) Do you think this varies with the weather (a) Yes (b) No
7) How many seafood meals do you have per week? _____
27a) How many of these meals are:
(a) local catch (produce) _____
(b) retail bought (supermarket) _____
Any other comments?

_____

_____

_____

_____

_____

_____

Thank you for your co-operation

Methodology

Total metal digestion metal digestion -Attack 2

Procedure Nitric and Perchloric acid attack

References : Thompson and Walsh (1988)

Description
The acid digestion of soils, stream sediments and rocks for multi-element analysis by ICP-AES.

Method Nitric and Perchloric acid attack

Sample types: Rocks, soils, stream sediments
Sample Weight: 0.250g Final Volume: 10.0 ml
Dilution Factor: 40 ml/g

SAFETY TRAINING:
Schedule: A
B2 (Perchloric Acid)
B5 (Centrifuge)

COSHH Assessment

Hydrochloric Acid A.R. 36% w/w
Nitric Acid A.R. 70% w/w
Perchloric Acid A.R. 60% w/w

SAFETY POINTS:
1. Do not add Perchloric Acid to samples in the absence of Nitric Acid.
2. Samples with high organic content may react vigorously with Nitric and Perchloric Acids. Watch for frothing when adding Nitric Acid. If frothing occurs, increase step 1 dwell time to 12 hours.
3. This method must not be attempted on samples containing oil or bitumen.

BATCH ORGANISATION

Maximum Batch Size: N/A
Block Time: 36 hours
Total Prep Time: 3 days

Solution Storage Limit: Preferably less than 3 months (if capped)

QUALITY CONTROL (QUTE)

Reagent Blanks: 5% (of total number of samples) 2
Duplicated Samples: 10% (of total number of samples)
Reference Materials: 4% (all RM's should be duplicated)

Possible Reference Materials: HRM1, HRM2 + Certified RM's as appropriate

EQUIPMENT

	Location Room	cupboard
Test tubes 18mm o.d. x 180 mm (pyrex)	B110	
Wire test tube racks (plastic coated)	B 110	
Stainless steel test tube racks	B110	
Aluminium heating block (deep, 252 holes)	B110	FC 1
Shallow aluminium heating block (315 holes)	B110	FC 3
Oxford dispensers (calibrated gravimetrically to 0.05ml)	B110	
Centrifuge tubes 18mm x 110mm (polystyrene)	B110	
Vortex tube mixer	B110	
Balance, top pan	B110	
Centrifuge GF8	B110	

REAGENTS

Water - Deionised (D.I.W.)
Nitric Acid A.R. 70% w/w
Perchloric Acid A.R. 60% w/w
Hydrochloric Acid 5M A.R. (to make 5M HCl dilute 430ml concentrated HCl (36% w/w) to 1 litre with D.I.W.

PROCEDURE

- Prepare a weighing list using form A6.
- Number the set of test tubes waterproof marker pen.
- Weigh 0.250g (.001) sample onto a clean piece of weighing paper using top pan balance. Transfer carefully into clean, dry, numbered tubes (in wire test tube racks)
- Add 4.0 ml Nitric Acid into each tube from an Oxford Dispenser.
- Add 1.0 ml Perchloric Acid from and Oxford Dispenser.
- Place tubes in the deep aluminium heating block. Switch programmer to "manual" mode then set up as follows:

Rise rate Sec/deg	Dwell Time Hrs	Dwell Temp °C
001	3.0	50
001	3.0	150
001	18.0	190
001	0.1	195

- Check the fume cupboard is on and switch programmer to "auto".
- On completion of attack cycle check that each tube has been heated to dryness.
- Transfer into stainless steel racks.
- When tubes are cool add 2.0 ml Hydrochloric Acid (5m) to each tube using an Oxford Dispenser calibrated gravimetrically.

- Place tubes into shallow heating block and leave to leach for one hour at 60°C.
- Transfer tubes into wire racks and allow to cool.
- Add 8.0 ml water from an Oxford Dispenser, calibrated gravimetrically, and mix each tube, using a vortex mixer.
- Decant into labelled polystyrene tubes, cap and if necessary, centrifuge at 2000 rpm for 2 minutes.
- Solutions equilibrate at 25°c after 12 hours and are then ready for ICP-AES analysis.

Good stopping points: After steps 8 & 13.

Safety points: refer to the attack 2 and 3T procedures.

- Do not add Perchloric Acid to samples in the absence of Nitric Acid.
- Samples with high organic content may react vigorously with Nitric and Perchloric Acids. Watch for frothing a when adding Nitric Acid. If frothing occurs increase step 1 dwell time to 12 hours.
- This method must not be attempted on samples containing oil or bitumen.

Critical points: Do not reprogram block when in Auto mode

Limitations: Some common minerals are attacked to a negligible extent only, quartz, feldspar, rutile, chromite, cassiterite, zircon, beryl or to a minor degree, barite. Certain element contained in these minerals will give low results.

METHOD: Five Step Sequential Extraction (after Tessier, modified by Li, 1993)

Analytes:	GEN5 suite of elements
Sample types:	rocks, soils, stream sediments
Sample Weight:	1.000g
Final Volume:	10.0ml
Dilution Factor:	20, 80, 13.333, 13.333, 100 ml g^{-1}

SAFETY TRAINING:

Schedule: A
B2 (Perchloric Acid and Hydrofluoric Acid)
B5 (Centrifuge)

COSHH Assessment:

1. Hydrochloric Acid A.R. 36% w/w
2. Nitric Acid A.R. 70% w/w
3. Perchloric Acid A.R. 60% w/w
4. Hydrofluoric Acid A.R. 40% w/w
5. Magnesium Chloride A.R.
6. Sodium Acetate A.R

SAFETY POINTS:

1. Do not add Perchloric Acid to samples in the absence of Nitric Acid.
2. Samples with high organic content may react vigorously with Nitric and perchloric Acids. Watch for frothing when adding Nitric Acid. If frothing occurs, increase step 1 dwell time to 12 hours
3. This method must not be attempted on samples containing oil or bitumen.

BATCH ORGANISATION:

Maximum batch size: 25 samples (38 solutions)
Block time: 36 hours (or 5pm day 1 to 9 am day 3)
Total Prep time: 3 days
Solution storage limit: preferably less than 3 months if capped)

QUALITY CONTROL (QUTE)

Reagent Blanks: 5% (of total number of samples)
Duplicated samples: 10% (of total number of samples)
Reference materials: 4% (all RM's should be duplicated)
Possible reference materials: HRM2 + certified RM's as appropriate

EQUIPMENT

1. 50 ml Polysulphone centrifuge tubes & polyproplene caps
2. PTFE test tubes 140 x 25 mm
3. test tubes 18mm o.d. x 180mm (PYREX)
4. wire test tube racks (plastic coated)
5. stainless steel test tube racks
6. Aluminium heating block (deep, 252 holes)
7. Aluminium heating block (38 holes)
8. Shallow heating block (315 holes)
9. Oxford dispensers (calibrated gravimetrically to not more than 0.05 ml)
10. Centrifuge tubes 18mm x 110mm (polystyrene)
11. Vortex tube mixer
12. Balance, top pan
13. Centrifuge GF*

REAGENTS

1. Water – Deionised (D.I.W)
2. Nitric Acid A.R. 70% w/w
3. Perchloric Acid A.R. 60% w/w
4. Hydrofluoric Acid A.R. 40% w/w
5. Hydrochloric Acid A.R. 5M, dilute 430 ml concentrated HCL (36% w/w) to 1 litre D.I.W
6. Hydrochloric Acid A.R 4M, dilute 344ml concentrated HCL (36% w/w) to 1 litre D.I.W
7. Hydrochloric Acid A.R 0.3M, dilute 36ml concentrated HCL (36% w/w) to 1 litre
8. Magnesium Chloride 0.5M at pH 7.0 (weigh 50.825g $MgCl_2.6H_2O$ A.R. into a 1 litre beaker. Dissolve by the addition of sufficient DIW to bring volume to about 350 ml. Adjust the pH to 7 with 4M HCL and NH_3 (1ml and bring up to 10ml with DIW) dilute further as needed) bring up to 500ml mark with DIW once have correct pH.
9. Sodium Acetate, prepare 1M NaOAc and adjust tp pH 5 with Acetic Acid. Weigh 68.04g NaOAc A.R. and add 350 ml DIW. Bring to pH 5 and then mark up volume to 500ml mark with DIW.
10. Hydroxylammonium Peroxide, **freshly prepare** 3.2M solution in 20% v/v Nitric Acid. Weigh 2.78g $Ho.NH_3$ CL into volumetric flask and add 500ml DIW. Add 250ml conc HOAC (acetic acid) and make up to 1000ml volume with DIW. ***REMEMBER ALWAYS ADD ACID TO WATER NEVER WATER TO ACID***
11. Hydrogen Peroxide **freshly prepare** a 30% H_2O_2 solution and adjust to pH 2.0 with Nitric Acid .
12. Ammonium Acetate, prepare 3.2M solution in 20% v/v Nitric Acid. Weigh 123.33g and add 200ml DIW. Add 100ml v/v HNO_3, and bring up to 500ml mark.
13. Nitric acid A.R. 0.02M. Add 0.322ml of conc Nitric Acid to 240ml DIW, dilute to 250ml with a squeezy bottle. Decant into a beaker, stir and ready to use.

PROCEDURE

1. Prepare a weighing list using form A6
2. Number the set of polysulphone centrifuge tubes using a permanent pen
3. Weigh 1.000g sample onto a clean piece of weighing paper using top pan balance. Transfer carefully into clean, dry, numbered centrifuge tubes in wire test tube racks).

Step 1 (Exchangeable)

Firstly, 8.0ml of 0.5M Magnesium Chloride (pH 7.0) solution was added into each tube. The tubes were placed in a mechanical shaker and agitated for 10 minutes. They were then centrifuged at 2,000 rpm for 15 minutes. 4 ml of the first supernatant was decanted, into a new set of test tubes. The residue was washed with 8 ml D.I.W. The tubes were shaken for 2 minutes, and the second supernatant was subsequently discarded after centrifuging for 10 minutes. The dilution factor of these was 20 ml/g and the final concentration of Mg in the test solutions was about 48600 μg/ml.

Treatment of the extraction solutions

To the supernatants from each step, 1 ml concentrated Nitric Acid was added, from an Oxford dispenser and placed on a heating block. The block was set to 50°C for 3 hours, then to 75°C for 7 hours, 100°C for 10 hours and 140°C until the sample reaches dryness. The tubes were then transferred into stainless steel racks. When cooled 2 ml Hydrochloric Acid (5 M) was added to each tube and placed in a shallow heating block and left to leach for one hour at 70°C. After the tubes were allowed to cool, 8.0 ml D.I.W. was added from and Oxford dispenser (calibrated gravimetrically) and mixed each tube using a vortex mixer. The solutions were then decanted into polystyrene tubes and capped. The solutions were then sent for ICP-AES analysis.

STEP 2 (Bound to Carbonates and Specifically Adsorbed)

8ml of 1 M Sodium Acetate (pH 5.0) was added to the solid residue from the first extraction tubes and capped. The capped tubes were placed in the mechanical shaker and left under continuous shaking for 5 hours. They were then centrifuged at 2, 000 rpm for 15 minutes. 1 ml of the supernatant was removed as described above. The

extraction solution then underwent the method outlined above. The final dilution factor of these solutions was 80 ml/g, with a Na concentration in test solutions of about 23,000 μg/ml.

STEP 3 (Bound to Mn-Fe oxide fraction)

20 ml of 0.04 M Hydroxylammonium Chloride in 25% (v/v) Acetic Acid was added to the residue form the second extraction, and the level of 20 ml on the tubes was marked using a fine marker pen. The tubes were then placed on a heating block and set to 96°C for 6 hours (uncapped). The tubes were agitated hourly. When the attack was completed, the tubes were transferred to racks and allowed to cool. D.I.W. was then added to each tube to the 20 ml mark and capped. The solution was mixed thoroughly on the mechanical shaker for 5 minutes, followed by centrifuge at 2,000 rpm for 15 minutes. 15 ml of the supernatant was removed, and the samples were cleaned using D.I.W as described above. The dilution factor for this step was 13 ml/g.

Step 4 (Bound to organic/sulphide fraction)

3 ml of 0.02 M Nitric Acid and 5 ml 30% Hydrogen Peroxide (pH 2.0) was added to the residue from the third extraction. The uncapped tubes were placed on a heating block and the temperature was raised very slowly from 40°C to 85°C, in increments of 5°C, as the more organic material in the samples, the more violent the reaction that occurred. A bowl of ice water was used to cool any samples as a precaution. Once the temperature reached 85°C the tubes were left for 2 hours with occasional agitation. On completion of the attack, the tubes were transferred to racks and left to cool.

When cool, another 3 ml 30% Hydrogen Peroxide (pH 2.0) was added and the tubes taken back to the heating block, and set to 85°C for 3 hours. During this time, the tubes were shaken intermittently. After this time, the tubes were removed from the heating block and allowed to cool. After cooling, 5 ml of 3.2 M Ammonium Acetate in 20% (v/v) Nitric Acid, was added. The solutions were then diluted to the 20 ml mark with D.I.W. and the caps put on. The tubes were then placed in the mechanical

shaker for 30 minutes, followed by centrifuge at 2, 000 rpm for 15 minutes. In this step, 15 ml of the supernatant was removed and the tubes washed with D.I.W.

Step 5 (Residual fraction)

The residue from step 4, was transferred volumetrically, using D.I.W. to large PTFE test tubes. The residue was mixed with D.I.W. (5 ml) and decanted into the PTFE tubes a maximum of 5 times. 4 ml of concentrated Nitric Acid, 2 ml concentrated Perchloric Acid and 15 ml concentrated Hydrofluoric Acid was added to each PTFE tube. The tubes were placed on the heating block and the temperature was set as follows: 90°C for 9 hours; 140°C for 3 hours; 190 ° C for 10 hours and 195 ° C for 1 minute.

When the attack cycle was complete, the tubes were removed from the heating block and placed in wire racks and left to cool. Once cool, 5 ml of 4 M Hydrochloric Acid was added to each tube, and then placed for 1 hour on heating block at 70°C to leach. Then tubes were again removed and left to cool, after which 8 ml of 0.3 M Hydrochloric Acid was added from an Oxford dispenser and each tube mixed using a vortex mixer.

25 ml of supernatant was decanted into a volumetric flask. The PTFE tubes were washed with 0.3 M Hydrochloric Acid and decanted into the flask. The final volume was made up to 25 ml with 0.03 M Hydrochloric Acid. The solutions from the flask were poured into polystyrene tubes, capped and delivered to the ICP Laboratory. The dilution factor in this step was 25 ml/g.

Instrumental Detection Limits of ICP-AES (mg/kg) for elements for all chemical analysis (concentration in mg/kg)

Digestion Method		***Dilution Factor of Method***	***Cr***	***Co***	***Ni***	***Cu***	***Zn***	***Cd***	***Pb***	***As***
Total		40	0.4	0.2	0.4	0.04	0.04	0.2	1.2	0.4
Sequential Extraction	Step 1	20	0.2	0.1	0.2	0.02	0.02	0.1	0.6	0.2
	Step 2	80	0.8	0.4	0.8	0.08	0.08	0.4	2.4	0.8
	Step 3	13.333	0.133	0.067	0.133	0.013	0.013	0.067	0.4	0.133
	Step 4	13.333	0.133	0.067	0.133	0.013	0.013	0.067	0.4	0.133
	Step 5	100	1	0.5	1	0.1	0.1	0.5	3	1

Table D1 Bias for reference material HRM 1

HRM 1		R2239	R2239	R2239	n	mean	St Dev	bias	bias%	t-stat calculated	t-stat tabulated	range of duplicates	precision (mean duplicates-absolute difference)
	AV	HRM1	HRM1	HRM1				(mean-AV)	100*bias/AV	5%	5%		
Li	3.9	3.51	3.92	3.29	3	3.57	0.32	-0.33	-8.40	1.77	4.30	0.63	17.66
Na	35	14.21	25.93	11.10	3	17.08	7.82	-17.92	-51.19	3.96	4.30	14.83	86.80
K	650	629.65	626.93	566.56	3	607.71	35.67	-42.29	-6.51	2.05	4.30	63.09	10.38
Be	0.23	0.22	0.25	0.23	3	0.23	0.02	0.00	1.51	-0.37	4.30	0.03	12.80
Mg	420	384.54	391.58	382.21	3	386.11	4.88	-33.89	-8.07	12.01	4.30	9.37	2.43
Ca	450	473.50	519.33	451.49	3	481.44	34.61	31.44	6.99	-1.57	4.30	67.84	14.09
Sr	6	5.96	5.74	5.96	3	5.89	0.13	-0.11	-1.88	1.56	4.30	0.22	3.71
Ba	18	18.21	19.54	19.01	3	18.92	0.67	0.92	5.09	-2.37	4.30	1.33	7.03
Al	4500	4230.03	4393.45	4303.97	3	4309.15	81.83	-190.85	-4.24	4.03	4.30	163.42	3.79
La	8	10.22	8.17	9.58	3	9.32	1.05	1.32	16.51	-2.18	4.30	2.05	21.99
Ti	280	372.84	354.91	337.42	3	355.06	17.71	75.06	26.81	-7.33	4.30	35.42	9.98
V	14	13.50	13.67	13.54	3	13.57	0.09	-0.43	-3.06	8.26	4.30	0.13	0.95
Cr	13	12.87	9.96	13.92	3	12.25	2.05	-0.75	-5.78	0.63	4.30	3.96	32.32
Mn	100	137.26	77.33	135.21	3	116.60	34.03	16.60	16.60	-0.84	4.30	59.93	51.40
Fe	8200	8468.31	8246.21	8173.24	3	8295.92	153.69	95.92	1.17	-1.08	4.30	295.07	3.56
Co	2	1.49	2.17	2.06	3	1.91	0.36	-0.09	-4.72	0.45	4.30	0.68	35.62
Ni	5	5.25	5.39	5.22	3	5.29	0.09	0.29	5.81	-5.51	4.30	0.17	3.23
Cu	3	2.83	3.36	2.86	3	3.01	0.30	0.01	0.47	-0.08	4.30	0.53	17.57
Ag	...	-0.13	0.27	0.04	3	0.06	0.20	0.06	...	-0.55	4.30	0.40	628.12
Zn	22	20.73	21.29	20.58	3	20.87	0.37	-1.13	-5.14	5.22	4.30	0.71	3.41
Cd	...	0.12	0.84	0.11	3	0.36	0.42	0.36	...	-1.48	4.30	0.72	202.20
Pb	13	10.85	13.28	11.05	3	11.73	1.35	-1.27	-9.77	1.63	4.30	2.43	20.72
P	420	393.42	413.53	375.67	3	394.21	18.94	-25.79	-6.14	2.36	4.30	37.86	9.61
S	180	139.62	152.93	144.64	3	145.73	6.72	-34.27	-19.04	8.82	4.30	13.31	9.13
As	...	4.70	6.71	4.36	3	5.26	1.27	5.26	...	-7.17	4.30	2.35	44.65

Table D2 Bias for reference material HRM 2

	HRM2	R2239	R2239	R2239	n	mean	St Dev	bias	bias%	t-stat	t-stat	range of	precision (mean duplicates- absolute
	AV	HRM2	HRM2	HRM2				(mean-AV)	100*bias/AV	calculated	tabulated 5%	duplicates	difference)
Li	155	180.10	186.68	170.83	3	179.21	7.96	24.21	15.62	-5.26	4.30	15.85	8.84
Na	1000	807.74	785.85	775.75	3	789.78	16.36	-210.22	-21.02	22.24	4.30	32.00	4.05
K	7500	7514.18	7722.55	7421.59	3	7552.77	154.15	52.77	0.70	-0.59	4.30	300.96	3.98
Be	2.5	2.92	2.75	2.83	3	2.83	0.09	0.33	13.29	-6.76	4.30	0.17	6.00
Mg	13000	13029.10	13144.10	12977.40	3	13050.20	85.33	50.20	0.39	-1.02	4.30	166.70	1.28
Ca	5900	6146.22	6121.50	5822.24	3	6029.99	180.34	129.99	2.20	-1.25	4.30	323.98	5.37
Sr	1250	1378.71	1431.94	1242.18	3	1350.94	97.88	100.94	8.08	-1.78	4.30	189.76	14.05
Ba	600	605.32	651.68	594.50	3	617.17	30.38	17.17	2.86	-0.98	4.30	57.18	9.26
Al	35000	35947.00	36212.30	35471.70	3	35877.00	375.23	877.00	2.51	-4.04	4.30	740.60	2.06
La	24	23.75	24.82	22.91	3	23.83	0.96	-0.17	-0.72	0.31	4.30	1.92	8.05
Ti	680	887.15	872.23	884.25	3	881.21	7.91	201.21	29.59	-43.99	4.30	14.92	1.69
V	58	62.70	63.12	53.19	3	59.67	5.62	1.67	2.88	-0.51	4.30	9.94	16.65
Cr	420	565.20	540.65	486.82	3	530.89	40.09	110.89	26.40	-4.79	4.30	78.38	14.76
Mn	1400	1655.02	1624.97	1456.62	3	1578.87	106.93	178.87	12.78	-2.89	4.30	198.40	12.57
Fe	47000	51605.80	52059.20	49086.20	3	50917.07	1601.70	3917.07	8.33	-4.23	4.30	2973.00	5.84
Co	48	52.52	52.49	43.97	3	49.66	4.93	1.66	3.46	-0.58	4.30	8.55	17.21
Ni	250	289.51	296.79	250.35	3	278.88	24.98	28.88	11.55	-2.00	4.30	46.44	16.65
Cu	590	589.21	603.80	563.37	3	585.46	20.48	-4.54	-0.77	0.38	4.30	40.43	6.91
Ag	2	2.10	1.41	1.43	3	1.65	0.40	-0.35	-17.60	1.54	4.30	0.70	42.30
Zn	400	435.85	447.68	361.03	3	414.85	46.99	14.85	3.71	-0.55	4.30	86.65	20.89
Cd	2.5	4.21	3.60	1.55	3	3.12	1.40	0.62	24.87	-0.77	4.30	2.66	85.36
Pb	510	543.94	558.54	457.44	3	519.97	54.64	9.97	1.95	-0.32	4.30	101.10	19.44
P	670	655.92	672.40	618.87	3	649.06	27.42	-20.94	-3.12	1.32	4.30	53.54	8.25
S	2200	1983.11	2006.55	1982.91	3	1990.86	13.59	-209.14	-9.51	26.62	4.30	23.64	1.19
As	170	160.48	166.36	162.79	3	163.21	2.96	-6.79	-3.99	3.97	4.30	5.87	3.60

Table D3 Bias for reference material NIST SRM 2709

	NIST SRM 2709	R2239	R2239	R2239	n	Mean	St Dev	bias	bias%	t-stat calculated	t-stat tabulated	range of duplicates	precision (mean duplicates-absolute difference)
	AV	NIST SRM2709	NIST SRM2709	NIST SRM2709									
Li	...	49.28	46.38	45.10	3	46.92	2.14	46.92	...	-37.90	4.30	4.18	8.91
Na	11600	802.86	780.14	711.46	3	764.82	47.59	-10835.18	-93.41	393.88	4.30	91.41	11.95
K	20300	9861.06	9670.98	9328.48	3	9620.17	269.90	-10679.83	-52.61	68.46	4.30	532.58	5.54
Be	...	1.17	1.19	1.08	3	1.15	0.06	1.15	...	-34.52	4.30	0.11	9.43
Mg	15100	13087.70	12279.10	12212.90	3	12526.57	487.08	-2573.43	-17.04	9.14	4.30	874.80	6.98
Ca	18900	16818.00	15412.70	15329.90	3	15853.53	836.28	-3046.47	-16.12	6.30	4.30	1488.10	9.39
Sr	231	192.97	199.85	196.80	3	196.54	3.45	-34.46	-14.92	17.28	4.30	-3.83	-1.95
Ba	968	872.12	845.87	838.33	3	852.11	17.73	-115.89	-11.97	11.31	4.30	33.78	3.96
Al	75000	44262.70	42170.90	40785.40	3	42406.33	1750.56	-32593.67	-43.46	32.21	4.30	3477.30	8.20
La	...	19.07	8.92	7.54	3	11.84	6.30	11.84	...	-3.25	4.30	11.53	97.39
Ti	3420	1995.58	1959.79	1894.31	3	1949.90	51.36	-1470.11	-42.99	49.52	4.30	101.27	5.19
V	112	88.11	80.68	83.91	3	84.23	3.72	-27.77	-24.79	12.91	4.30	7.42	8.81
Cr	130	35.88	28.15	31.80	3	31.94	3.87	-98.06	-75.43	43.85	4.30	7.73	24.21
Mn	538	540.87	490.84	498.63	3	510.11	26.92	-27.89	-5.18	1.79	4.30	42.24	8.28
Fe	35000	35625.90	31399.30	31577.50	3	32867.57	2390.45	-2132.43	-6.09	1.54	4.30	4226.60	12.86
Co	13.4	12.11	10.48	10.81	3	11.14	0.86	-2.26	-16.88	4.54	4.30	1.63	14.64
Ni	88	79.67	72.82	72.80	3	75.10	3.96	-12.90	-14.66	5.64	4.30	6.87	9.14
Cu	34.6	34.30	31.60	30.75	3	32.22	1.85	-2.38	-6.89	2.22	4.30	3.55	11.03
Ag	0.41	0.46	0.45	0.39	3	0.43	0.04	0.02	5.99	-1.12	4.30	0.07	16.07
Zn	106	99.74	99.55	90.25	3	96.51	5.43	-9.49	-8.95	3.02	4.30	9.49	9.84
Cd	0.38	0.76	0.02	-0.08	3	0.23	0.46	-0.15	-38.90	0.56	4.30	0.84	360.27
Pb	18.9	15.05	17.48	16.47	3	16.33	1.22	-2.57	-13.58	3.65	4.30	1.41	8.65
P	620	549.04	574.84	578.99	3	567.62	16.22	-52.38	-8.45	5.59	4.30	-25.79	-4.54
S	890	816.34	847.49	868.27	3	844.03	26.14	-45.97	-5.16	3.04	4.30	-31.15	-3.69
As	17.7	16.54	14.31	15.09	3	15.31	1.13	-2.39	-13.48	3.64	4.30	2.23	14.59

Table D4 Bias for reference material NIST SRM 2711

	NIST SRM 2711	R2239	R2239	R2239	n	mean	St Dev	bias (mean-AV)	bias% (bias/AV%)	t-stat calculated	t-stat tabulated	range of duplicates	precision (mean duplicates-absolute difference)
	AV	NIST SRM2711	NIST SRM2711	NIST SRM2711									
Li	...	21.95	21.40	19.14	3	20.83	1.49	20.83	...	-24.21	4.30	2.81	13.49
Na	11400	495.91	499.40	473.99	3	489.77	13.78	-10910.23	-95.70	1369.90	4.30	25.42	5.19
K	24500	7757.35	7546.75	7011.55	3	7438.55	384.49	-17061.45	-69.64	76.77	4.30	745.80	10.03
Be	...	1.25	1.22	1.14	3	1.20	0.05	1.20	...	-38.31	4.30	0.10	8.66
Mg	10500	8291.81	8004.03	7576.11	3	7957.32	360.13	-2542.68	-24.22	12.21	4.30	715.70	8.99
Ca	28800	21750.40	21164.00	20125.80	3	21013.40	822.70	-7786.60	-27.04	16.37	4.30	1624.60	7.73
Sr	245.3	58.64	57.20	55.15	3	56.99	1.75	-188.31	-76.77	185.75	4.30	3.49	6.12
Ba	726	269.67	262.75	249.37	3	260.60	10.32	-465.40	-64.10	78.03	4.30	20.30	7.79
Al	65300	31997.00	31111.40	29782.70	3	30963.70	1114.51	-34336.30	-52.58	53.30	4.30	2214.30	7.15
La	...	31.81	31.21	20.32	3	27.78	6.47	27.78	...	-7.43	4.30	11.49	41.38
Ti	3060	1040.95	1020.29	976.39	3	1012.54	32.97	-2047.46	-66.91	107.44	4.30	64.56	6.38
V	81.6	51.42	49.88	47.56	3	49.62	1.94	-31.98	-39.19	28.46	4.30	3.86	7.79
Cr	...	9.41	8.63	7.15	3	8.40	1.15	8.40	...	-12.68	4.30	2.25	26.84
Mn	638	583.81	561.96	404.32	3	516.70	97.93	-121.30	-19.01	2.14	4.30	179.49	34.74
Fe	28900	26810.50	25735.30	24696.10	3	25747.30	1057.25	-3152.70	-10.91	5.16	4.30	2114.40	8.21
Co	...	8.33	8.01	7.44	3	7.92	0.45	7.92	...	-30.25	4.30	0.89	11.28
Ni	20.6	17.71	17.63	16.36	3	17.23	0.75	-3.37	-16.34	7.71	4.30	1.35	7.81
Cu	114	118.76	113.53	104.87	3	112.38	7.02	-1.62	-1.42	0.40	4.30	13.89	12.36
Ag	4.63	1.97	2.19	2.40	3	2.18	0.21	-2.45	-52.84	19.76	4.30	0.43	19.62
Zn	350.4	332.89	318.05	301.97	3	317.64	15.47	-32.76	-9.35	3.66	4.30	30.92	9.74
Cd	41.7	39.96	38.10	35.82	3	37.96	2.07	-3.74	-8.96	3.12	4.30	4.14	10.91
Pb	1162	1118.35	1076.91	1028.41	3	1074.56	45.02	-87.44	-7.53	3.36	4.30	89.94	8.37
P	860	739.09	718.64	642.58	3	700.10	50.85	-159.90	-18.59	5.44	4.30	96.50	13.78
S	420	411.70	380.96	370.32	3	387.66	21.49	-32.34	-7.70	2.60	4.30	41.38	10.67
As	105	98.12	92.19	88.81	3	93.04	4.71	-11.96	-11.39	4.39	4.30	5.94	6.38

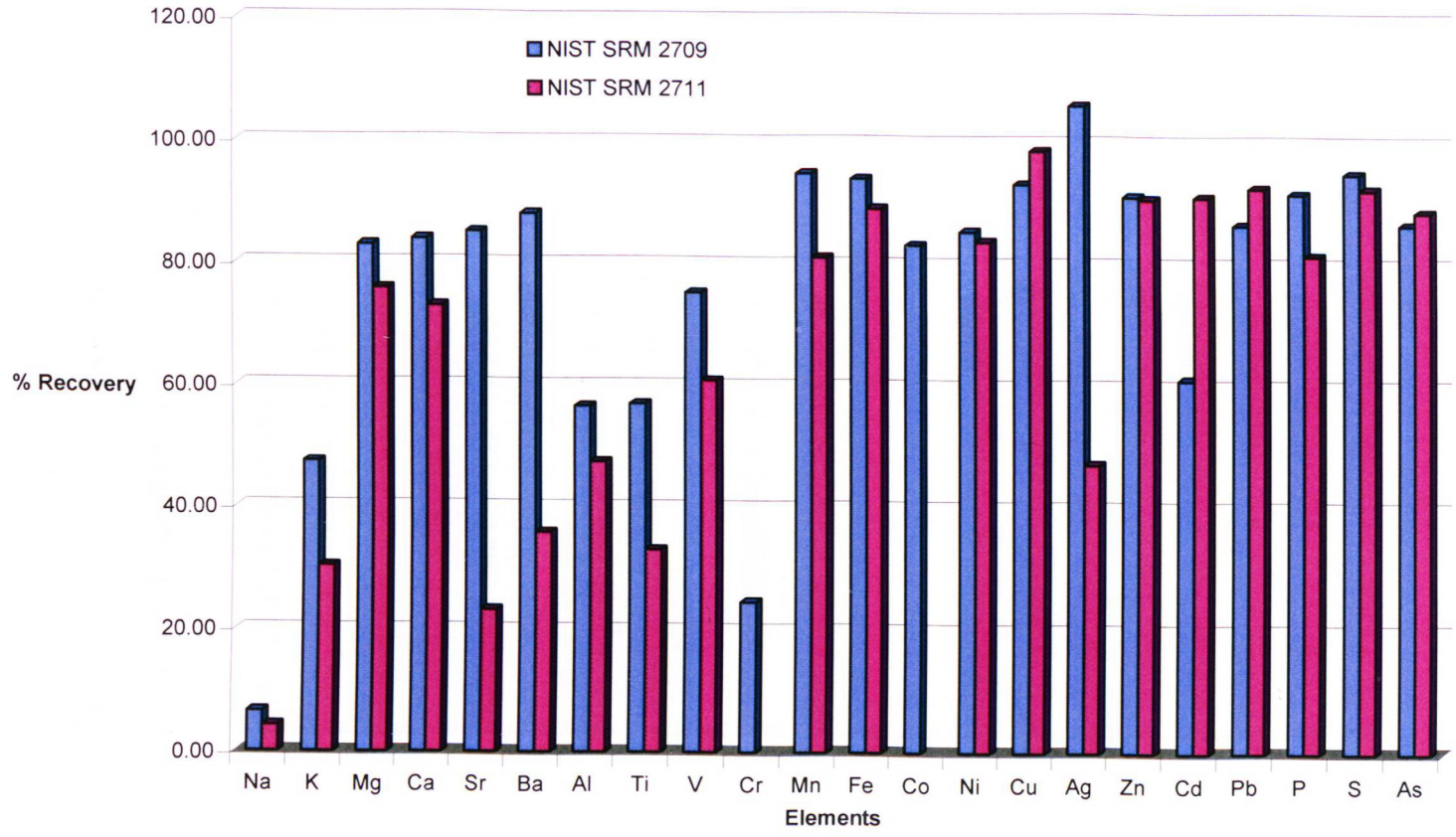


Figure D1 Percentage recovery for standard reference material for the sum of elements from nitric/percholric acid digestion

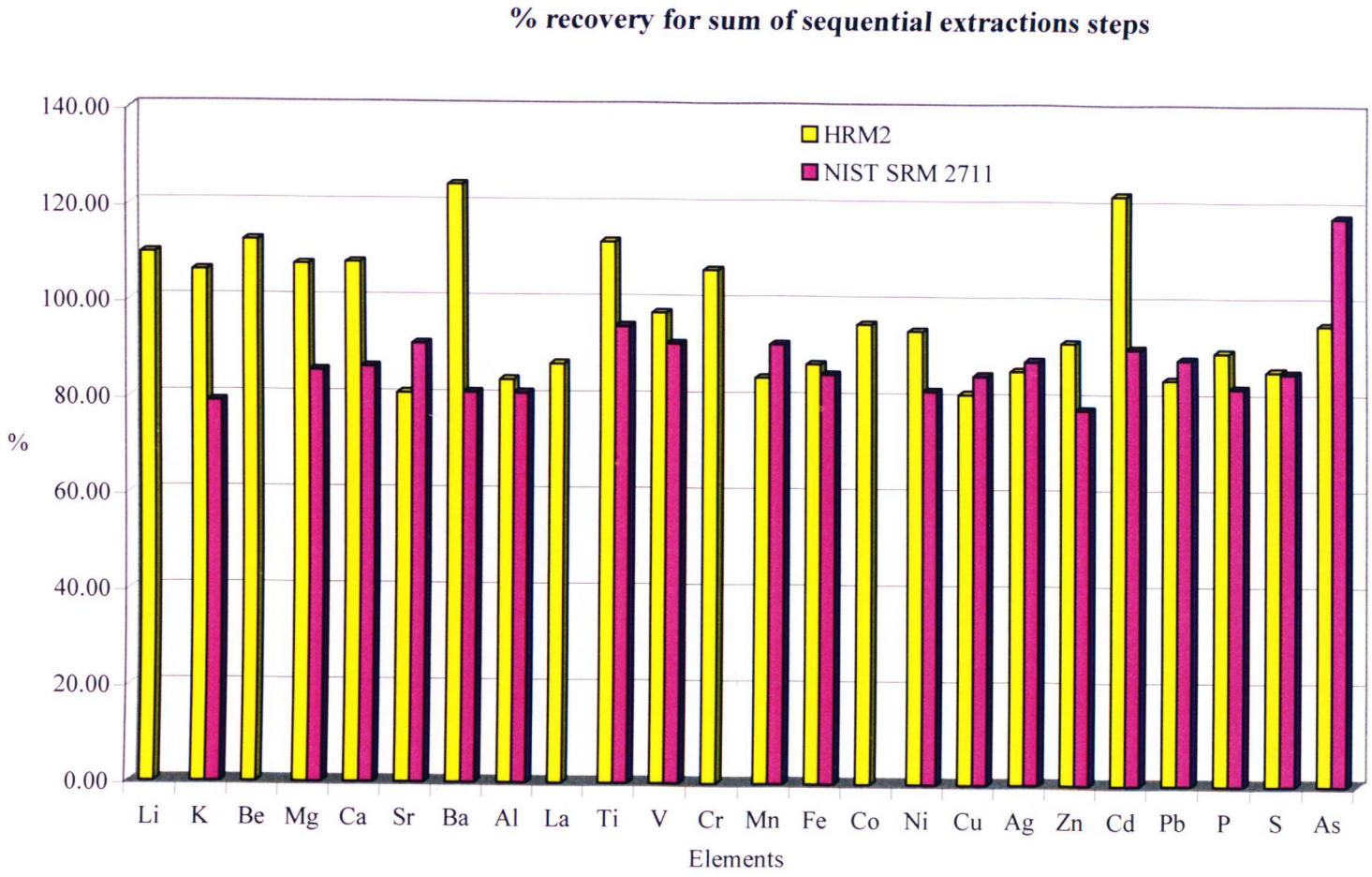


Figure D2 Percentage recovery for standard reference materials for the sum of elements from sequential extraction steps in soils

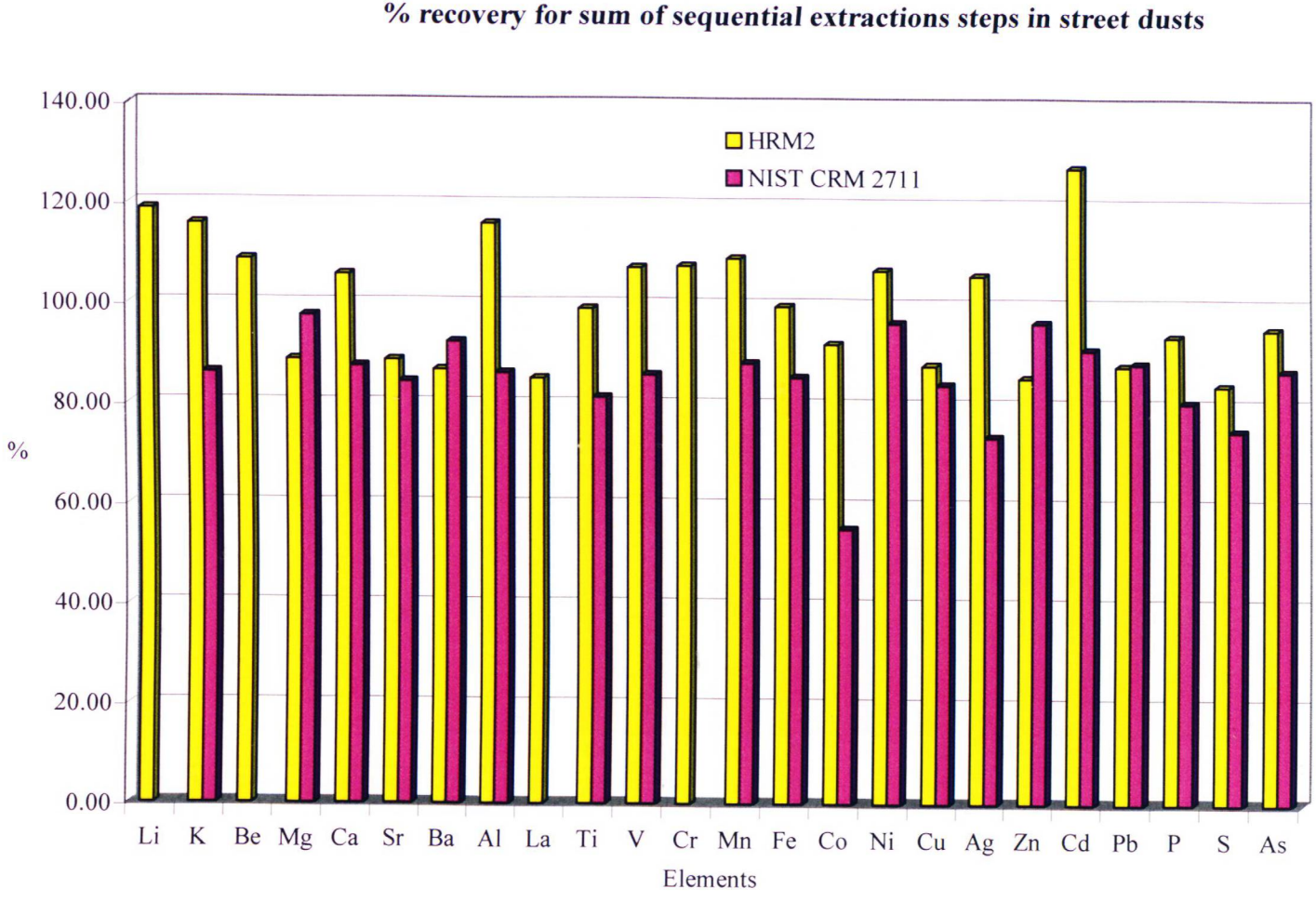
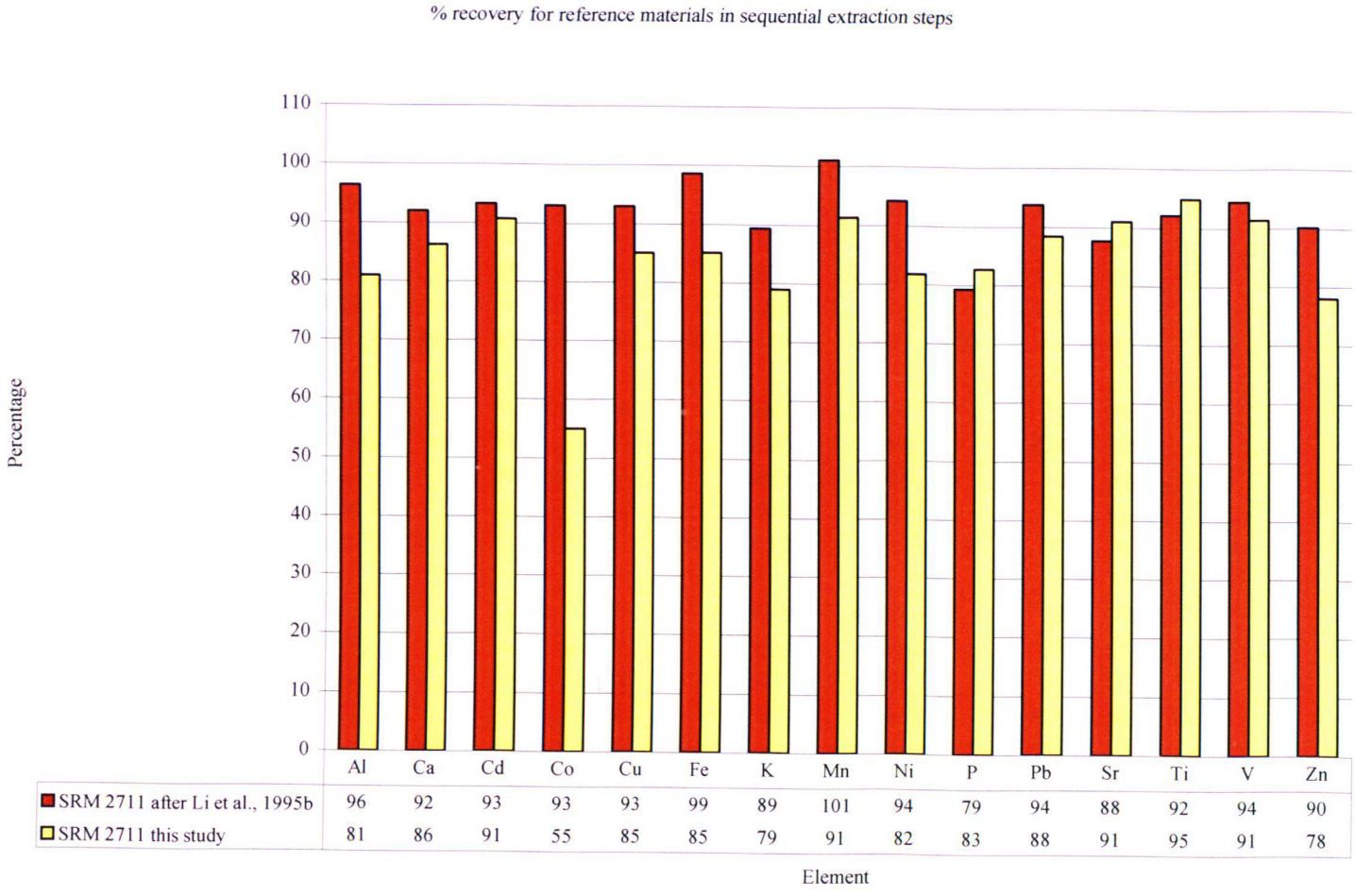


Figure D3 Percentage recovery for standard reference material for the sum of elements from sequential extraction steps in street dusts



	Al	Ca	Cd	Co	Cu	Fe	K	Mn	Ni	P	Pb	Sr	Ti	V	Zn
SRM 2711 after Li et al., 1995b	96	92	93	93	93	99	89	101	94	79	94	88	92	94	90
SRM 2711 this study	81	86	91	55	85	85	79	91	82	83	88	91	95	91	78

Figure D4 A comparison of the recovery of elements analysed by sequential extraction in soils, between this study and results reports by Li et al. (1995)

Table D5 The precision of elements analysed from five sequential solutions in street dusts

STEP 1			Median			Median			Median			Median			Median
	Li			*K*			*Be*			*Ca*			*Sr*		
	0.06	0.27		68	349		0.01	0.01		2710	2260		3.90	8.03	
	0.12	0.27		23	350		0.01	0.01		1653	2231		2.55	8.23	
mean	0.09	0.27		45	350		0.01	0.01		2182	2245		3.22	8.13	
[X1-X2]	0.06	0.01		45	0.23		0.00	0.00		1057	29		1.35	0.20	
[X1-X2]%	67	2.39	35	98	0.07	49	0.00	0.00	0.00	49	1.30	25	42	2.50	22
STEP 2	0.12	0.62		58	392		0.01	0.04		61600	26776		29	52	
	0.16	0.58		28	409		0.01	0.03		71530	27030		9.88	53	
mean	0.14	0.60		0.20	0.20		0.01	0.03		66565	26903		19	52	
[X1-X2]	0.14	0.04		0.08	0.08		0.00	0.01		9930	254		19	0.56	
[X1-X2]%	100	6.84	53	40	40	40	0.00	37	18	15	0.94	8	97	1.06	49
STEP 3	1.16	2.20		64	942		11700	0.56		55900	4997		29	29	
	0.55	2.39		23	1020		973	0.59		36800	5194		20	32	
mean	0.85	2.29		44	981		6337	0.58		46350	5095		24	31	
[X1-X2]	0.61	0.20		40	78		10727	0.03		19100	196		8.57	3.21	
[X1-X2]%	71	8.54	40	93	8	50	169	4.45	87	41	3.85	23	35	10	102
STEP 4	0.19	0.09		13	136		323	0.03		1070	1165		0.95	3.55	
	0.12	0.14		5	211		129	0.05		1093	1472		0.11	5.22	
mean	0.15	0.12		9	173		226	0.04		1082	1318		0.53	4.38	
[X1-X2]	0.07	0.05		8	75		194	0.02		23	307		0.84	1.68	
[X1-X2]%	44	40	42	89	43	66	86	52	69	2.13	23	13	159	38	99
STEP 5	18.60	21		7310	8804		2620	0.88		1700	12505		27	81	
	5.60	10.78		1200	4722		5610	0.73		1460	13861		12.20	116	
mean	12.10	16.03		4255	6763		4115	0.81		1580	13183		19.75	99	
[X1-X2]	13.00	10.48		6110	4082		2990	0.15		240	1356		15.10	35	
[X1-X2]%	107	65	86	144	60	101	73	19	46	15	10	13	76	36	56

Table D5 The precision of elements analysed from five sequential solutions in street dusts (continued)

STEP 1			Median			Median		Median			Median			Median			Median		Median
		Ba			*Al*			*La*			*Ti*			*V*			*Cr*		
		4.25	5.72		43	37		0.10	0.47		0.72	0.71		0.25	0.03		0.20	0.25	
		3.63	5.01		30	43		0.30	0.11		0.40	0.51		0.30	0.05		0.60	0.03	
	mean	3.94	5.36		37	40		0.20	0.29		0.56	0.61		0.28	0.04		0.40	0.14	
	[X1-X2]	0.62	0.71		13	6.13		0.20	0.37		0.32	0.20		0.05	0.01		0.40	0.21	
	[X1-X2]%	16	13.21	14	36	15.18	25	100	126	113	57	32	45	18.18	36	27	100	153	127
STEP 2		12.40	42		98	483		0.80	1.24		0.32	3.32		0.30	0.54		0.60	3.01	
		13.06	45		100	455		0.60	0.64		0.12	2.99		0.30	0.35		0.60	2.87	
	mean	12.73	43		99	469		0.70	0.94		0.22	3.15		0.30	0.45		0.60	2.94	
	[X1-X2]	0.66	2.08		2	27		0.20	0.60		0.20	0.33		0.00	0.19		0.00	0.13	
	[X1-X2]%	5.18	4.77	4.98	2.02	5.80	3.91	29	63	46	91	10	51	0.00	43	21	0.00	4.56	2.28
STEP 3		10.40	109		660	2706		0.60	2.27		1.85	23		5.07	6.31		0.60	17.67	
		11.04	112		514	2494		0.07	2.62		1.24	21		4.73	6.16		3.00	16.63	
	mean	10.72	111		587	2600		0.33	2.44		1.55	22		4.90	6.23		1.80	17.15	
	[X1-X2]	0.64	3.02		146	213		0.53	0.34		0.61	2.23		0.34	0.15		2.40	1.04	
	[X1-X2]%	5.97	2.73	4.35	24.87	8.17	17	160	14.11	87	40	10	25	6.88	2.40	4.64	133	6.08	70
STEP 4		1.49	27		242	205		0.27	0.31		9.61	1.52		2.47	0.25		1.93	1.47	
		1.38	29		186	289		0.30	0.46		7.96	2.11		1.17	0.34		0.98	2.40	
	mean	1.44	28		214	247		0.28	0.39		8.79	1.81		1.82	0.30		1.46	1.93	
	[X1-X2]	0.11	1.95		56	84		0.03	0.15		1.65	0.60		1.30	0.09		0.95	0.92	
	[X1-X2]%	7.87	6.87	7.37	26	34	30	11.75	39	25	19	33	26	72	31	51	65	48	57
STEP 5		174.00	1996		17600	20053		6.	11.31		1000.00	2258		21	25		165	223	
		138.70	2008		18190	20429		4	10.09		805	2301		20	25		133	230	
	mean	156.35	2002		17895	20241		5.	10.70		903	2220		20	25		149	226	
	[X1-X2]	35.30	12.48		590	375		2	1.23		195	43		1	0.29		32	7.46	
	[X1-X2]%	22.58	0.62	11.60	3.30	1.85	2.58	40	11.46	26	22	1.88	12	5	1.16	3.08	21	3.30	12

Table D5 The precision of elements analysed from five sequential solutions in street dusts (continued)

				Median			Median			Median			Median			Median			Median
		Mn			*Fe*			*Co*			*Ni*			*Cu*			*Zn*		
STEP 1																			
		4.85	1.68		41	33		0.30	0.07		0.60	0.09		0.34	5.82		6.06	2.03	
		3.90	1.27		32	21		0.30	0.06		0.60	0.07		0.06	3.91		5.00	1.17	
	mean	4.38	1.47		37	27		0.30	0.06		0.60	0.08		0.20	4.87		5.53	1.60	
	[X1-X2]	0.95	0.41		9	13		0.00	0.01		0.00	0.02		0.28	1.91		1.06	0.86	
	[X1-X2]%	22	28	25	25	47	36	0.00	16.75	8.38	0.00	27	13.73	140	39	90	19.17	54	36
		50	66		70	428		1.20	1.01		2.40	4.72		0.32	241		189	421	
STEP 2		35	66		74	429		1.20	0.33		1.60	4.98		0.24	221		181	429	
	mean	42	66		72	428		1.20	0.67		2.00	4.85		0.28	231		182	425	
	[X1-X2]	14.80	0.04		4	0.35		0.00	0.69		0.80	0.26		0.08	20.11		8.48	7.77	
	[X1-X2]%	35	0.06	17.48	5.56	0.08	2.82	0.00	103	51	40	5.36	23	29	8.72	18.65	4.59	1.83	3.21
		115	148		1070	56528		0.90	38		9.80	9.75		0.77	33		439	4628	
STEP 3		118	156		908	63975		0.60	42		11.30	9.65		0.23	22		422	5076	
	mean	116	152		989.	60252		0.75	40		10.55	9.70		0.50	28		430	4852	
	[X1-X2]	2.90	8.49		162	7447		0.30	3.57		1.50	0.10		0.55	10.90		17.39	448	
	[X1-X2]%	2.49	5.59	4.04	16.38	12.36	14.37	40	8.98	24	14.23	1.02	7.62	109	39	74	4.04	9.23	6.63
		3.87	15		103	100		0.23	4.73		1.20	1.83		10.10	1225		12.10	228	
STEP 4		1.27	11.97		96	346		0.07	5.92		1.53	3.70		9.10	1484		10.19	297	
	mean	2.57	13.49		99	223		0.15	5.32		1.37	2.77		9.60	1354		11.15	263	
	[X1-X2]	2.60	3.03		7.30	245		0.17	1.20		0.33	1.87		1.00	259		1.91	69	
	[X1-X2]%	101	22	62	7.35	110	59	111	22	67	24	68	46	10.42	19.12	14.77	17.11	26	22
		114	406		12100	226500		3	129		22	38		17.50	4267		80	7011	
STEP 5		130	352		14930	222242		2.50	121		27	42		15.60	3900		69	6500	
	mean	122	379		13515	224371		2.75	125		24	40		16.55	4083		75	6756	
	[X1-X2]	16	54		2830	4258		0.50	7.25		5.00	4.81		1.90	367		10.65	512	
	[X1-X2]%	13.11	14.36	13.74	21	1.90	11.42	18.18	5.80	12	21	12.02	16.43	11.48	8.99	10.24	14.26	7.57	10.92

Table D5 The precision of elements analysed from five sequential solutions in street dusts (continued)

				Median			Median		Median			Median
		Pb			*P*			*S*			*As*	
STEP 1												
		1.80	1.55		4.20	5.21		19.30	1369		0.60	0.60	
		1.80	1.01		3.60	5.16		17.50	1372		0.60	0.60	
	mean	1.80	1.28		3.90	5.19		18.40	1371		0.60	0.60	
	[X1-X2]	0.00	0.54		0.60	0.05		1.80	2.70		0.00	0.00	
	[X1-X2]%	0.00	42	21	15.38	0.96	8.17	9.78	0.20	5	0.00	0.00	0.00
		16.80	328		18.80	70		25	430		2.40	1.11	
STEP 2		12.40	363		21	75		28	442		2.40	1.01	
	mean	14.60	346		19.80	73		26	436		2.40	1.06	
	[X1-X2]	4.40	35		2.00	4.57		2.40	12.32		0.00	0.10	
	[X1-X2]%	30	10.07	20	10.10	6.29	8.19	9.09	2.82	5.96	0.00	9.38	4.69
		42	271		48	106		53	55		0.20	20	
STEP 3		39	248		57	128		63	58		0.40	25	
	mean	40	260		52	117		58	57		0.30	22	
	[X1-X2]	3.30	23		9.30	23		9.77	3.08		0.20	5.50	
	[X1-X2]%	8.22	9.11	8.66	17.83	19.23	18.53	17	5.45	11.12	67	25	46
		1.40	97		56	34					0.60	0.50	
STEP 4		1.20	116		49	36		339	475		1.50	0.32	
	mean	1.30	107		52	35		328	452		1.05	0.41	
	[X1-X2]	0.20	18		6.70	2.67		20	45		0.90	0.18	
	[X1-X2]%	15.38	17	16.29	12.80	7.65	10.23	6.33	9.99	8.16	86	43	65
		21	1161		535	1147		244	1821		36	259	
STEP 5		18	1112		546	1120		213	1865		4.50	192	
	mean	20	1137		541	1134		229	1843		20	226	
	[X1-X2]	3.00	49		11	26		31	44		31	66	
	[X1-X2]%	15.38	4.30	9.84	2.04	2.33	2.18	13.57	2.38	7.97	155	29	92

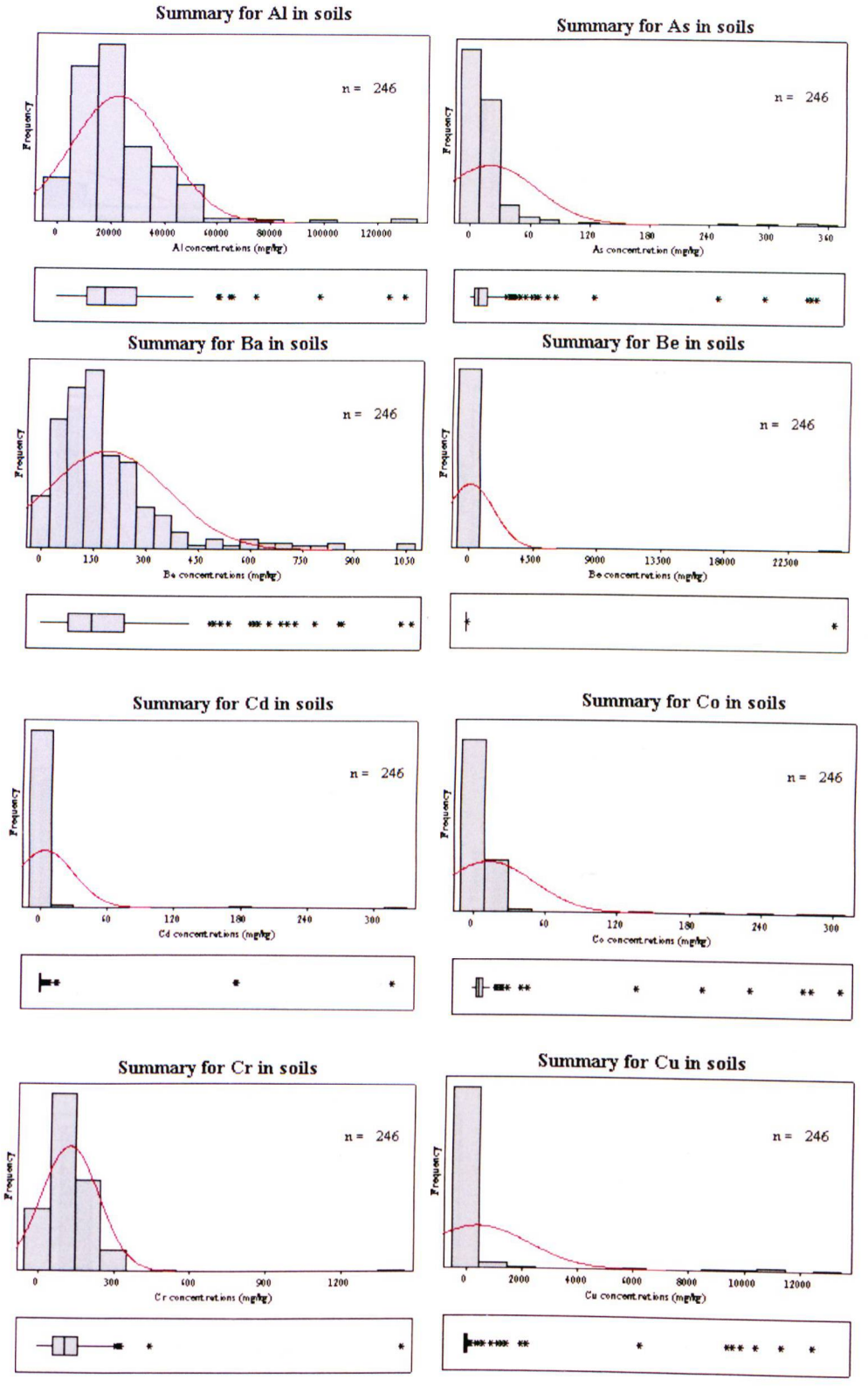


Figure D5 Histograms of selected elements for the entire soil data set

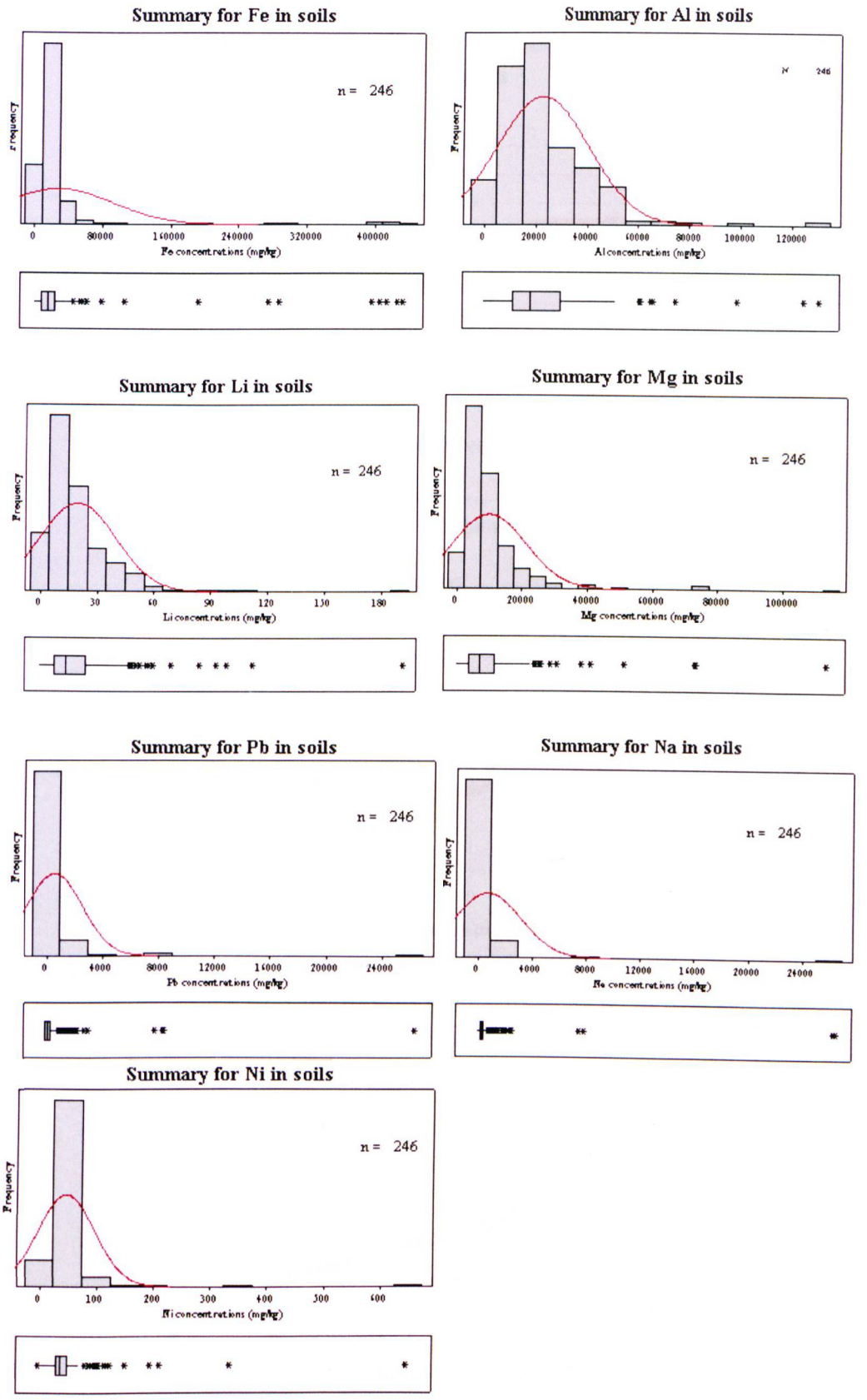
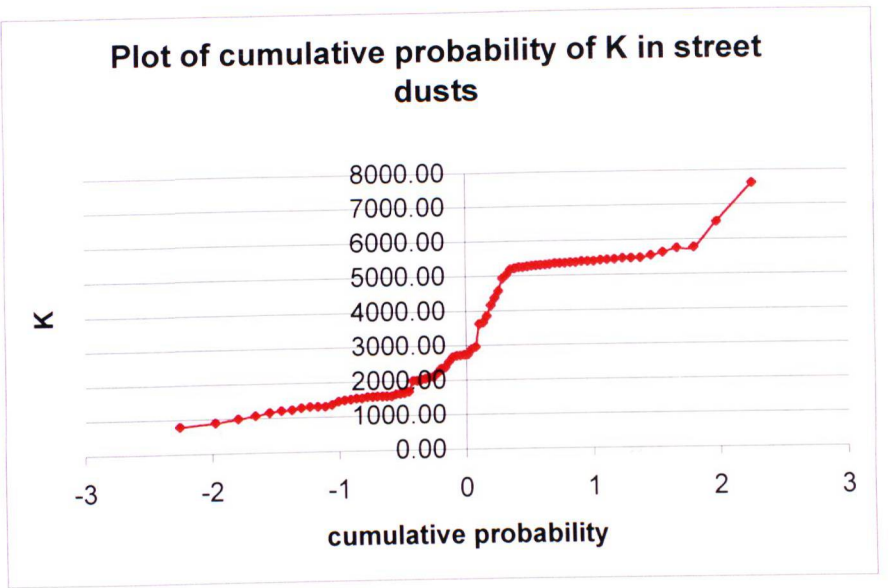
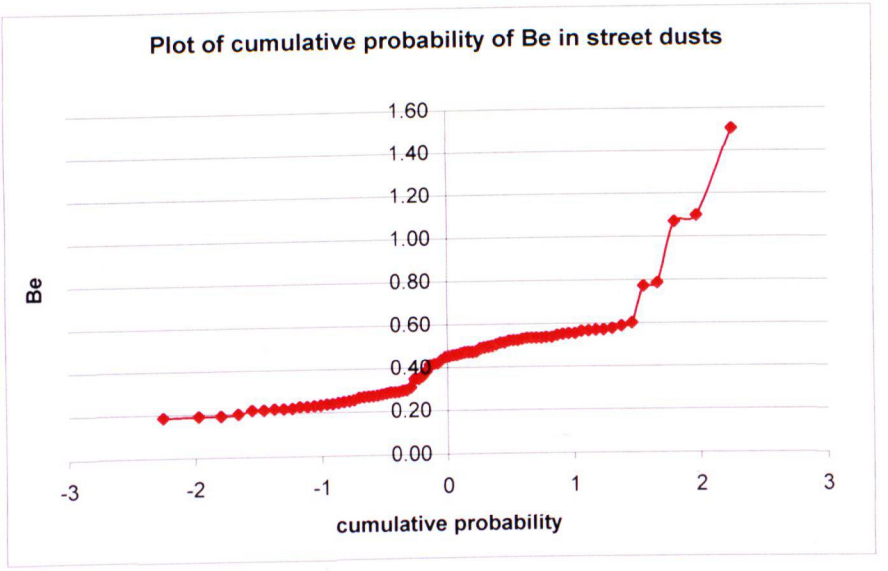


Figure D6 Histograms of selected elements for the entire soil data set





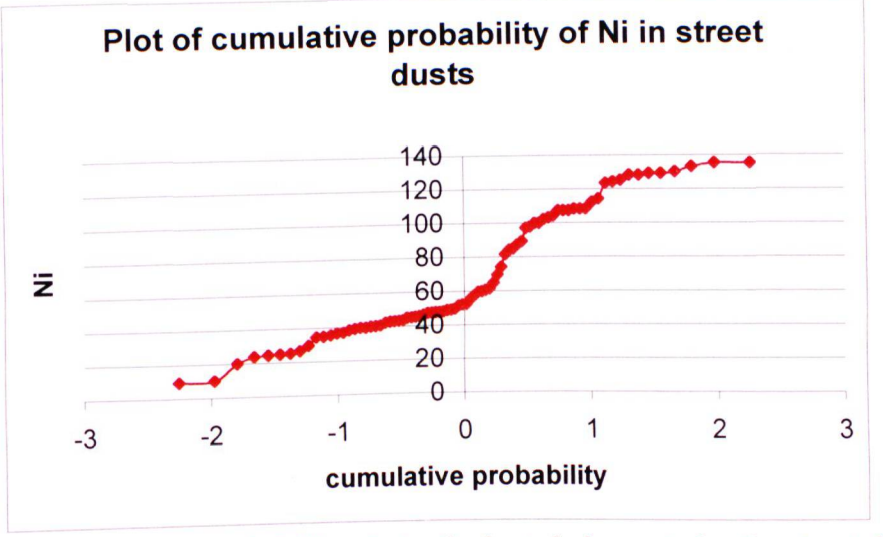


Figure D7 Cumulative probability plots of selected elements for the street dusts

Table D6 ANOVA results for soils in varying land use categories.

		df	Mean Square	F	Sig.
Ln Li	Between Groups	3	.176	.187	.905
Ln Na	Between Groups	3	.373	.555	.645
Ln K	Between Groups	3	.315	.313	.816
Ln Be	Between Groups	3	.426	.344	.793
Ln Mg	Between Groups	3	.340	.315	.814
Ln Ca	Between Groups	3	2.643	1.257	.290
Ln Sr	Between Groups	3	1.060	1.208	.308
Ln Ba	Between Groups	3	3.803	2.965	.033
Ln Al	Between Groups	3	.774	.680	.565
Ln La	Between Groups	3	.301	.364	.779
Ln Ti	Between Groups	3	.942	1.232	.299
Ln V	Between Groups	3	.645	.672	.570
Ln Cr	Between Groups	3	1.849	1.564	.199
Ln M6	Between Groups	3	.919	.406	.749
Ln Mn	Between Groups	3	1.135	1.717	.164
Ln Fe	Between Groups	3	.516	.413	.744
Ln C6	Between Groups	3	.170	.184	.907
Ln N5	Between Groups	3	.555	1.046	.373
Ln C4	Between Groups	3	3.640	1.046	.373
Ln Ag	Between Groups	3	1.023	.677	.567
Ln Zn	Between Groups	3	3.944	1.638	.181
Ln Cd	Between Groups	3	3.822	2.470	.063
Ln Pb	Between Groups	3	10.763	2.612	.052
Ln P	Between Groups	3	3.435	2.253	.083
Ln S	Between Groups	3	1.363	.693	.557
Ln As	Between Groups	3	.665	.503	.680

Low significance values (<.05) indicate that the contrast is significant.

Table D7 ANOVA results for soils in varying sample types categories.

		df	Mean Square	F	Sig.
Ln Li	Between Groups	6	6.190	7.772	.000
Ln Na	Between Groups	6	6.128	11.545	.000
Ln K	Between Groups	6	5.504	6.213	.000
Ln Be	Between Groups	6	3.570	3.049	.007
Ln Mg	Between Groups	6	6.537	7.021	.000
Ln Ca	Between Groups	6	13.037	7.101	.000
Ln Sr	Between Groups	6	5.541	7.255	.000
Ln Ba	Between Groups	6	9.053	8.081	.000
Ln Al	Between Groups	6	6.750	6.794	.000
Ln La	Between Groups	6	6.015	8.760	.000
Ln Ti	Between Groups	6	2.253	3.081	.006
Ln V	Between Groups	6	5.388	6.372	.000
Ln Cr	Between Groups	6	3.197	2.798	.012
Ln Mn	Between Groups	6	3.663	6.188	.000
Ln Fe	Between Groups	6	6.787	6.153	.000
Ln Co	Between Groups	6	7.508	10.053	.000
Ln Ni	Between Groups	6	1.242	2.415	.028
Ln Cu	Between Groups	6	38.724	14.954	.000
Ln Ag	Between Groups	6	4.837	3.465	.003
Ln Zn	Between Groups	6	21.053	10.780	.000
Ln Cd	Between Groups	6	7.530	5.277	.000
Ln Pb	Between Groups	6	44.373	13.924	.000
Ln P	Between Groups	6	16.745	14.564	.000
Ln S	Between Groups	6	29.017	22.994	.000
Ln As	Between Groups	6	6.625	5.599	.000

Table D8 Anova for soils in varying geological categories.

		df	Mean Square	F	Sig.
Ln Li	Between Groups	11	3.315	4.076	.000
Ln Na	Between Groups	11	2.052	3.408	.000
Ln K	Between Groups	11	3.078	3.427	.000
Ln Be	Between Groups	11	1.634	1.354	.196
Ln Mg	Between Groups	11	2.824	2.871	.001
Ln Ca	Between Groups	11	4.629	2.329	.010
Ln Sr	Between Groups	11	1.251	1.451	.151
Ln Ba	Between Groups	11	2.789	2.244	.013
Ln Al	Between Groups	11	3.299	3.204	.000
Ln La	Between Groups	11	3.555	5.169	.000
Ln Ti	Between Groups	11	.574	.740	.700
Ln V	Between Groups	11	2.414	2.726	.003
Ln Cr	Between Groups	11	2.188	1.915	.038
Ln Mn	Between Groups	11	1.086	1.678	.079
Ln Fe	Between Groups	11	1.556	1.270	.243
Ln Co	Between Groups	11	1.377	1.546	.116
Ln Ni	Between Groups	11	.359	.667	.769
Ln Cu	Between Groups	11	8.542	2.636	.003
Ln Ag	Between Groups	11	2.370	1.618	.095
Ln Zn	Between Groups	11	3.255	1.364	.191
Ln Cd	Between Groups	11	6.051	4.453	.000
Ln Pb	Between Groups	11	13.610	3.628	.000
Ln P	Between Groups	11	4.719	3.380	.000
Ln S	Between Groups	11	8.231	4.962	.000
Ln As	Between Groups	11	2.729	2.190	.016

Plate E1 Scrap yard at Devil's Tower Road

Plate E2 Incinerator stack rising to the right of Windmill Hill Flats

Plate E3 Town area 1

Plate E4 Town area 2