

A  
THESIS  
entitled

SECONDARY DISPERSION OF MERCURY AND  
ASSOCIATED ELEMENTS AT KEEL, EIRE

submitted  
for the  
degree of

DOCTOR OF PHILOSOPHY

in the

FACULTY OF SCIENCE OF THE UNIVERSITY OF LONDON

by

DAVID STUART EVANS

Royal School of Mines  
Imperial College

November, 1971

### ABSTRACT

Applied geochemical investigations have been carried out at the Keel zinc-cadmium-lead prospect in the Irish Republic. Particular emphasis has been placed on the application of mercury as a prospecting aid in the glaciated environment and for interpreting soil anomalies.

A multi-element examination of iron and manganese-rich residues of oxidized and leached carbonate rock near the Keel deposit has confirmed the presence of a large, metal-rich reservoir believed to be a capping. Metal enrichment ratios suggest that zinc, cadmium, lead, silver, and mercury have been derived from disseminated sphalerite-galena-pyrite. Metals have been retained and/or scavenged by hydrous iron and manganese oxides and as insoluble residues. Subcropping exposures of the capping have contributed significant amounts of metals to the formation of soil anomalies.

In soil, lead and mercury anomalies are closely associated with faulting. Zinc and cadmium have dispersed more widely, element movement being facilitated by ground and stream waters. The nature of the soil profile and soil conditions in general are of some importance in the interpretation of metal anomalies in the Keel area. The surficial horizons of mineralized peaty gleysolic soils are highly enriched in lead, silver, and mercury. A small basin peat developed over subcropping sulphide-bearing veins is highly anomalous in zinc and cadmium. Freely-drained soils show comparatively less metal enrichment than do poorly-drained soils.

A literature review on the presence of mercury in the secondary environment indicates that while the element may disperse as simple inorganic ions and complexes, the influence of active and residual biochemical interactions superimposes some controls on migration. The bioconversion of inorganic mercury to methyl and dimethylmercury(ic) compounds and chelating reactions with sulphhydryl (SH) groups are important aspects in the secondary dispersion and retention of the element.

Preliminary experiments to determine the presence of mercury in soil gas at Keel have been moderately successful. The sampling technique is based on the pumping of soil air through a series of 60 mesh silver gauze filters to amalgamate mercury vapour and mercury-bearing compounds. Mercury can be determined down to  $10 \text{ ng/m}^3$ . Initial results indicate that the soil gas component of naturally-occurring mercury is in complex equilibrium with solid and ionic organic and inorganic forms of the element. It is proposed that soil air movement (and outgassing) at Keel is by gaseous diffusion rather than mass flow in response to reduced air pressures.

CONTENTS

|                                                                            | <u>Page</u><br><u>No.</u> |
|----------------------------------------------------------------------------|---------------------------|
| ABSTRACT . . . . .                                                         | i                         |
| CONTENTS . . . . .                                                         | ii                        |
| LIST OF TABLES . . . . .                                                   | viii                      |
| LIST OF FIGURES . . . . .                                                  | xi                        |
| LIST OF PLATES . . . . .                                                   | xiv                       |
| <br>CHAPTER 1 INTRODUCTION . . . . .                                       | <br>1                     |
| 1.1 GENERAL . . . . .                                                      | 1                         |
| 1.2 HISTORY OF THE KEEL DEPOSIT . . . . .                                  | 1                         |
| 1.3 MERCURY GEOCHEMISTRY IN MINERAL EXPLORATION . . . . .                  | 3                         |
| 1.3.1 Background . . . . .                                                 | 3                         |
| 1.3.2 Current Trends . . . . .                                             | 5                         |
| 1.4 SCOPE OF RESEARCH . . . . .                                            | 7                         |
| 1.4.1 Opening Remarks . . . . .                                            | 7                         |
| 1.4.2 Thesis Content . . . . .                                             | 8                         |
| 1.5 STUDY SUPPORT AND ACKNOWLEDGEMENTS . . . . .                           | 9                         |
| <br>CHAPTER 2 GEOLOGY, MINERALOGY AND GENESIS OF THE KEEL DEPOSIT. . . . . | <br>11                    |
| 2.1 PREVIOUS WORK . . . . .                                                | 11                        |
| 2.2 QUATERNARY GEOLOGY . . . . .                                           | 11                        |
| 2.3 STRATIGRAPHY . . . . .                                                 | 11                        |
| 2.4 STRUCTURE . . . . .                                                    | 12                        |
| 2.5 ONEBODIES . . . . .                                                    | 14                        |
| 2.6 MINERALOGY AND METALLOGENESIS OF THE KEEL DEPOSIT . . . . .            | 15                        |
| 2.6.1 Opening Remarks . . . . .                                            | 15                        |
| 2.6.2 Sphalerite . . . . .                                                 | 16                        |
| 2.6.3 Galena . . . . .                                                     | 16                        |
| 2.6.4 Chalcopyrite . . . . .                                               | 16                        |
| 2.6.5 Tetrahedrite . . . . .                                               | 16                        |
| 2.6.6 Silver Sulphosalts . . . . .                                         | 18                        |
| 2.6.7 Pyrite . . . . .                                                     | 18                        |
| 2.6.8 Barytes . . . . .                                                    | 19                        |
| 2.7 ASSOCIATED MINERALOGICAL STUDIES . . . . .                             | 19                        |
| 2.7.1 Fluid Inclusions . . . . .                                           | 19                        |
| 2.7.2 Primary Dispersion . . . . .                                         | 19                        |
| 2.7.3 Cadmium Geochemistry . . . . .                                       | 20                        |

|                                                                                           | Page<br><u>No.</u> |
|-------------------------------------------------------------------------------------------|--------------------|
| 2.7.4 Silver-zinc and Silver-lead Relationships . . .                                     | 20                 |
| 2.7.5 Paragenesis . . . . .                                                               | 20                 |
| 2.7.6 Supergene Minerals . . . . .                                                        | 22                 |
| 2.7.7 Metallogenesis . . . . .                                                            | 23                 |
| <br>CHAPTER 3 THE DECOMPOSED ZONE . . . . .                                               | <br>25             |
| 3.1 GENERAL . . . . .                                                                     | 25                 |
| 3.2 PREVIOUS WORK . . . . .                                                               | 26                 |
| 3.3 LOCATION AND GEOLOGICAL SETTING . . . . .                                             | 29                 |
| 3.4 HISTORY AND DESCRIPTION OF THE DECOMPOSED ZONE . . . .                                | 30                 |
| 3.4.1 Introduction . . . . .                                                              | 30                 |
| 3.4.2 Gossan versus Capping . . . . .                                                     | 31                 |
| 3.4.3 Limonite at Keel . . . . .                                                          | 32                 |
| 3.4.3.1 "Fluffy" limonite . . . . .                                                       | 33                 |
| 3.4.4 Some Textures Observed . . . . .                                                    | 33                 |
| 3.4.5 Mineralogy . . . . .                                                                | 33                 |
| 3.5 A GEOCHEMICAL MODEL FOR GENESIS OF THE DECOMPOSED ZONE                                | 35                 |
| 3.5.1 The Importance of Water-table level . . . . .                                       | 35                 |
| 3.5.2 The Need for Sulphur to Oxidize and Leach . . .                                     | 37                 |
| 3.5.3 A Comparison with Genesis of the Tynagh<br>Residual Deposit . . . . .               | 39                 |
| 3.5.4 Base Metal Retention . . . . .                                                      | 39                 |
| 3.6 METALS IN THE DECOMPOSED ZONE . . . . .                                               | 40                 |
| 3.6.1 Introduction . . . . .                                                              | 40                 |
| 3.6.2 Metal Enrichment Ratios . . . . .                                                   | 42                 |
| 3.6.3 Discussion on Tables 8 and 9 . . . . .                                              | 42                 |
| 3.6.4 Correlation Pairs . . . . .                                                         | 45                 |
| 3.7 METAL DISPERSION THROUGH GLACIAL TILL AT KEEL . . . .                                 | 46                 |
| 3.7.1 Introduction . . . . .                                                              | 46                 |
| 3.7.2 Cold-extractable Metals in Decomposed Zone<br>and Till . . . . .                    | 46                 |
| 3.8 SUMMARY . . . . .                                                                     | 51                 |
| <br>CHAPTER 4 SECONDARY DISPERSION OF SELECTED METALS, KEEL<br>AND ARDAGH AREAS . . . . . | <br>54             |
| 4.1 GENERAL . . . . .                                                                     | 54                 |
| 4.2 PHYSIOGRAPHY . . . . .                                                                | 54                 |
| 4.2.1 Ireland . . . . .                                                                   | 54                 |
| 4.2.2 The Longford District . . . . .                                                     | 55                 |
| 4.3 GLACIAL GEOLOGY AND GEOMORPHOLOGY . . . . .                                           | 55                 |
| 4.4 SOILS . . . . .                                                                       | 56                 |



|                                                                                    | <u>Page</u><br><u>No.</u> |
|------------------------------------------------------------------------------------|---------------------------|
| 4.5 PREVIOUS WORK . . . . .                                                        | 57                        |
| 4.5.1 Use and Examination of previous work. . . . .                                | 59                        |
| 4.6 REGIONAL GEOCHEMICAL PATTERNS . . . . .                                        | 61                        |
| 4.6.1 Introduction . . . . .                                                       | 61                        |
| 4.6.2 Zinc . . . . .                                                               | 61                        |
| 4.6.3 Cadmium . . . . .                                                            | 63                        |
| 4.6.4 Lead . . . . .                                                               | 64                        |
| 4.6.5 Mercury . . . . .                                                            | 65                        |
| 4.7 ADDITIONAL SOIL SAMPLING AND RESULTS . . . . .                                 | 66                        |
| 4.7.1 Keel Area . . . . .                                                          | 66                        |
| 4.7.2 Relationship of Soil Anomalies with the<br>Decomposed Zone . . . . .         | 69                        |
| 4.7.3 Other Areas . . . . .                                                        | 70                        |
| 4.7.3.1 Garrycam . . . . .                                                         | 70                        |
| 4.7.3.2 Drumming Cross Roads . . . . .                                             | 71                        |
| 4.7.3.3 Ardagh Hill . . . . .                                                      | 71                        |
| 4.7.3.4 Kenagh and Moydow . . . . .                                                | 73                        |
| 4.7.4 Lateral Hydromorphic Dispersion of Zinc<br>and Cadmium . . . . .             | 74                        |
| 4.7.4.1 Geochemical considerations of<br>lateral hydromorphic dispersion . . . . . | 75                        |
| 4.8 ENVIRONMENTAL MAGNIFICATION OF SOIL ANOMALIES AT KEEL. . . . .                 | 79                        |
| 4.8.1 Introduction . . . . .                                                       | 79                        |
| 4.8.2 Metal Anomalies in Peaty Gleys and Gleysolic<br>Soils at Keel . . . . .      | 80                        |
| 4.8.3 Metals in Peat at Keel . . . . .                                             | 83                        |
| 4.8.4 Metal Levels in Anomalous Freely-drained Soils. . . . .                      | 94                        |
| 4.9 BIOGEOCHEMISTRY AT KEEL . . . . .                                              | 97                        |
| 4.10 SUMMARY . . . . .                                                             | 101                       |
| CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS - PART A . . . . .                       | 107                       |
| 5.1 GENERAL . . . . .                                                              | 107                       |
| 5.2 CONCLUSIONS . . . . .                                                          | 107                       |
| 5.3 RECOMMENDATIONS . . . . .                                                      | 110                       |
| 5.3.1 Suggestions for Applied Geochemical Usage . . . . .                          | 110                       |
| 5.3.2 Additional Research Requirements . . . . .                                   | 112                       |
| CHAPTER 6 MERCURY AND THE SECONDARY ENVIRONMENT - A REVIEW . . . . .               | 114                       |
| 6.1 GENERAL . . . . .                                                              | 114                       |
| 6.2 GEOCHEMICAL CYCLE OF MERCURY . . . . .                                         | 114                       |
| 6.3 MERCURY REACTION AND DISTRIBUTION IN SOILS . . . . .                           | 116                       |
| 6.4 THE PRESENCE AND MOBILITY OF MERCURY IN THE<br>HYDROSPHERE . . . . .           | 117                       |

|                                                                                                                               | Page<br><u>No.</u> |
|-------------------------------------------------------------------------------------------------------------------------------|--------------------|
| 6.5 MERCURY INTERACTION WITH AND MOVEMENT IN THE BIOSPHERE . . . . .                                                          | 121                |
| 6.6 THE PRESENCE AND DISPERSION OF MERCURY IN THE ATMOSPHERE . . . . .                                                        | 125                |
| 6.7 MERCURY POLLUTION . . . . .                                                                                               | 128                |
| 6.7.1 The Relative Importance of Mercury Pollution on the Use of the Element as a Pathfinder in Mineral Exploration . . . . . | 138                |
| 6.8 ANALYTICAL METHODS AND TECHNIQUES FOR MERCURY ANALYSIS                                                                    | 140                |
| CHAPTER 7 MERCURY IN SOIL GAS AT KEEL . . . . .                                                                               | 146                |
| 7.1 GENERAL . . . . .                                                                                                         | 146                |
| 7.1.1 Introduction . . . . .                                                                                                  | 146                |
| 7.1.2 Gaseous Aspect of Primary Halos of Mercury . . . . .                                                                    | 146                |
| 7.1.3 Gaseous Movement of Mercury from Mineralized Occurrences . . . . .                                                      | 147                |
| 7.2 SOME CASE HISTORY APPLICATIONS OF GASEOUS DISPERSION IN MINERAL EXPLORATION . . . . .                                     | 148                |
| 7.2.1 Mercury . . . . .                                                                                                       | 148                |
| 7.2.2 Radon Gas in Uranium Prospecting . . . . .                                                                              | 149                |
| 7.2.3 Other Gases in Mineral Exploration . . . . .                                                                            | 151                |
| 7.3 EXPERIMENTS TO DETERMINE MERCURY VAPOUR IN LABORATORY AIR . . . . .                                                       | 153                |
| 7.3.1 Introduction . . . . .                                                                                                  | 153                |
| 7.3.2 Collectors for Mercury Vapour and/or Volatile Mercury Compounds . . . . .                                               | 153                |
| 7.3.3 Apparatus and Materials . . . . .                                                                                       | 156                |
| 7.3.4 Results of Laboratory Experiments . . . . .                                                                             | 157                |
| 7.3.5 Transport of Hg-free and Exposed Ag Gauze to and from the Field Area . . . . .                                          | 161                |
| 7.4 SOIL GAS COLLECTION PROCEDURES . . . . .                                                                                  | 162                |
| 7.4.1 Introduction . . . . .                                                                                                  | 162                |
| 7.4.2 Previous Work at Keel . . . . .                                                                                         | 162                |
| 7.4.3 Soil Gas from Depth . . . . .                                                                                           | 163                |
| 7.4.4 Soil Gas in Near-surface Horizons . . . . .                                                                             | 164                |
| 7.5 RESULTS AND DISCUSSION OF FIELD TESTS . . . . .                                                                           | 164                |
| 7.5.1 Introduction . . . . .                                                                                                  | 164                |
| 7.5.2 Presentation of Soil Gas Results . . . . .                                                                              | 165                |
| 7.5.3 Additional Experiments . . . . .                                                                                        | 169                |
| 7.5.3.1 The effect of water vapour on the collecting efficiency of Ag gauze. . . . .                                          | 169                |
| 7.5.3.2 Consecutive pumping tests. . . . .                                                                                    | 169                |
| 7.5.3.3 Bacterial evolution of Hg vapour/ volatile Hg compounds . . . . .                                                     | 171                |
| 7.5.3.4 Pyrolysis of soil gas vapours . . . . .                                                                               | 171                |
| 7.5.3.5 Mercury in atmospheric air at Keel . . . . .                                                                          | 173                |
| 7.5.4 Meteorological Considerations on the Presence of Mercury in Soil Gas at Keel . . . . .                                  | 173                |

|                                                                                                                              | <u>Page</u><br><u>No.</u> |
|------------------------------------------------------------------------------------------------------------------------------|---------------------------|
| 7.5.5 Physical, Hydrological, and Chemical Considerations on the Presence of Mercury in Soil Gas at Keel . . . . .           | 176                       |
| 7.6 SUMMARY . . . . .                                                                                                        | 179                       |
| CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS - PART B . . . . .                                                                 | 182                       |
| 8.1 GENERAL . . . . .                                                                                                        | 182                       |
| 8.2 CONCLUSIONS . . . . .                                                                                                    | 182                       |
| 8.3 RECOMMENDATIONS . . . . .                                                                                                | 185                       |
| 8.3.1 Suggestions for Applied Geochemical Usage of Mercury in Soil/Soil Air/Atmospheric Air in Mineral Exploration . . . . . | 185                       |
| 8.3.2 Additional Research Requirements . . . . .                                                                             | 186                       |
| SELECTED REFERENCES . . . . .                                                                                                | 190                       |
| APPENDIX 1 SAMPLE COLLECTION AND PREPARATION . . . . .                                                                       | 202                       |
| A1.1 SOILS . . . . .                                                                                                         | 202                       |
| A1.2 PITS . . . . .                                                                                                          | 202                       |
| A1.3 STREAM SEDIMENTS . . . . .                                                                                              | 202                       |
| A1.4 PLANTS . . . . .                                                                                                        | 203                       |
| A1.5 WATER . . . . .                                                                                                         | 203                       |
| A1.6 DECOMPOSED ZONE AND ROCKS . . . . .                                                                                     | 203                       |
| A1.7 PREPARATION . . . . .                                                                                                   | 204                       |
| APPENDIX 2 MERCURY ANALYSIS . . . . .                                                                                        | 205                       |
| A2.1 GENERAL . . . . .                                                                                                       | 205                       |
| A2.2 INSTRUMENTATION . . . . .                                                                                               | 205                       |
| A2.3 CALIBRATION PROCEDURES . . . . .                                                                                        | 206                       |
| A2.4 MERCURY DETERMINATION . . . . .                                                                                         | 206                       |
| A2.4.1 Soils, Rocks, and Oxidized Material . . . . .                                                                         | 206                       |
| A2.4.2 Grass, Organic-rich Soils, and Peats . . . . .                                                                        | 207                       |
| A2.4.3 Water . . . . .                                                                                                       | 210                       |
| A2.4.4 A Modified Procedure for Organic-rich Samples. . . . .                                                                | 211                       |

|                                                                | Page<br><u>No.</u> |
|----------------------------------------------------------------|--------------------|
| APPENDIX 3 ATOMIC ABSORPTION AND FLAME EMISSION PROCEDURES . . | 212                |
| A3.1 GENERAL . . . . .                                         | 212                |
| A3.2 TOTAL ATTACK PROCEDURE . . . . .                          | 212                |
| A3.2.1 Inorganic Material and Peats . . . . .                  | 212                |
| A3.2.2 Grass . . . . .                                         | 212                |
| A3.2.3 Water . . . . .                                         | 213                |
| A3.3 DETERMINATION . . . . .                                   | 213                |
| A3.4 COLD-EXTRACTABLE PROCEDURE . . . . .                      | 214                |
| A3.5 PRECISION OF ANALYSES . . . . .                           | 215                |
| A3.6 ADDITIONAL NOTES . . . . .                                | 215                |
| APPENDIX 4 SPECTROGRAPHY . . . . .                             | 219                |
| A4.1 GENERAL . . . . .                                         | 219                |
| A4.2 SAMPLE PREPARATION . . . . .                              | 219                |
| A4.3 CONTROL AND PRECISION OF ANALYSES . . . . .               | 219                |
| APPENDIX 5 COLORIMETRIC AND TITRIMETRIC PROCEDURES . . . . .   | 224                |
| A5.1 GENERAL . . . . .                                         | 224                |
| A5.2 COLORIMETRIC PROCEDURES . . . . .                         | 224                |
| A5.2.1 Arsenic . . . . .                                       | 224                |
| A5.2.2 Antimony . . . . .                                      | 224                |
| A5.2.3 Selenium . . . . .                                      | 225                |
| A5.2.4 Phosphorus . . . . .                                    | 225                |
| A5.2.5 Gold . . . . .                                          | 225                |
| A5.3 TITRIMETRIC PROCEDURES . . . . .                          | 226                |
| A5.3.1 Organic Carbon . . . . .                                | 226                |
| A5.3.2 Carbonate . . . . .                                     | 226                |
| APPENDIX 6 DATA RECORDS . . . . .                              | 227                |

LIST OF TABLES

| <u>Table<br/>No.</u> | <u>Title</u>                                                                                            | <u>Page<br/>No.</u> |
|----------------------|---------------------------------------------------------------------------------------------------------|---------------------|
| 1                    | Articles on applied mercury investigations presented at Geochemical Prospecting Symposia . . . . .      | 5                   |
| 2                    | Lithologies at Keel . . . . .                                                                           | 13                  |
| 3                    | Sulphide mineralogy and element assemblage . . . . .                                                    | 17                  |
| 4                    | Zn-Cd ratios of Keel ore . . . . .                                                                      | 21                  |
| 5                    | Some assay values of Decomposed Zone material . . . . .                                                 | 27                  |
| 6                    | Samples and assays cited in consultant's report . . . . .                                               | 28                  |
| 7                    | Binocular microscope and hand lens study of oxidized and leached rock . . . . .                         | 34                  |
| 8                    | Relative enrichment ratios . . . . .                                                                    | 43                  |
| 9                    | Basic statistical data on total element levels in the Decomposed Zone (106 samples) . . . . .           | 44                  |
| 10                   | Correlation pairs for selected elements in Decomposed Zone, rocks, and tills . . . . .                  | 47                  |
| 11                   | Cold extraction buffer mixtures . . . . .                                                               | 49                  |
| 12                   | Comparison of cold extractants on selected samples from the Decomposed Zone . . . . .                   | 50                  |
| 13                   | Secondary dispersion of selected metals through glacial till covering the Decomposed Zone . . . . .     | 52                  |
| 14                   | Contouring data for regional soils . . . . .                                                            | 60                  |
| 15                   | Statistical data to accompany Figure 16 . . . . .                                                       | 68                  |
| 16                   | Selected metals in anomalous, poorly-drained soils near Drumming Cross Roads . . . . .                  | 72                  |
| 17                   | Selected metals in waters, Keel and Ardagh areas . . . . .                                              | 76                  |
| 18                   | Total and EDTA-extractable metals in stream sediments, Ardagh area . . . . .                            | 77                  |
| 19                   | Metal distribution in an anomalous peaty, gleyed, and podzolized profile, Keel . . . . .                | 82                  |
| 20                   | Metal distribution in selected size fractions for an anomalous, peaty gleysolic profile, Keel . . . . . | 84                  |
| 21                   | Results of partial extraction experiments on an anomalous peaty gleysolic profile, Keel . . . . .       | 85                  |

| <u>Table<br/>No.</u> | <u>Title</u>                                                                                                                                         | <u>Page<br/>No.</u> |
|----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|
| 22                   | Metal distribution in a gleyed profile fringing<br>an anomalous basin peat, Keel . . . . .                                                           | 87                  |
| 23                   | Metal distribution in a gleyed profile fringing<br>an anomalous basin peat, Keel . . . . .                                                           | 87                  |
| 24                   | Metal distribution in an anomalous basin peat, Keel. .                                                                                               | 88                  |
| 25                   | Metal distribution in a highly anomalous basin peat,<br>Keel . . . . .                                                                               | 89                  |
| 26                   | A comparison of metal levels in the near-surface<br>horizons of a weakly mineralized basin peat and a<br>highly anomalous basin peat . . . . .       | 93                  |
| 27                   | Metal distribution in a freely-drained modified<br>Grey-Brown Podzolic profile overlying mineralized<br>till and the Decomposed Zone, Keel . . . . . | 95                  |
| 28                   | Metal distribution in a mineralized, Modified Grey-<br>Brown Podzolic profile, Keel . . . . .                                                        | 96                  |
| 29                   | Ranges and means of selected metals in grasses<br>growing on mineral soils, Keel area . . . . .                                                      | 100                 |
| 30                   | Selected metals in mineralized peats and associated<br>grasses, Keel area . . . . .                                                                  | 102                 |
| 31                   | Maximum mercury concentration in air measured at<br>scattered mineralized and non-mineralized areas of<br>the Western United States . . . . .        | 126                 |
| 32                   | Anomalous and background levels of mercury in soils<br>at deposits of selected metals . . . . .                                                      | 127                 |
| 33                   | Mercury compounds known to be used in world<br>agriculture . . . . .                                                                                 | 130                 |
| 34                   | The volatility of some mercurial fungicides . . . . .                                                                                                | 131                 |
| 35                   | Some inorganic mercury chemicals used in industry . .                                                                                                | 134                 |
| 36                   | Estimated trends in consumption of mercury . . . . .                                                                                                 | 135                 |
| 37                   | Quantities of mercury compounds used in or sold to<br>agriculture, 1965 . . . . .                                                                    | 136                 |
| 38                   | Ultra-violet reduction of some organomercurials in<br>solution to mercuric ion . . . . .                                                             | 144                 |
| 39                   | Physical constants of some potentially useful<br>organo-metallic compounds for mineral exploration . .                                               | 152                 |
| 40                   | Apparatus and materials employed in laboratory air<br>experiments and in soil gas investigations . . . . .                                           | 158                 |

| <u>Table<br/>No.</u> | <u>Title</u>                                                                                                                                    | <u>Page<br/>No.</u> |
|----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|
| 41                   | Results of dynamic sampling experiments for the determination of mercury vapour in laboratory air. . .                                          | 160                 |
| 42                   | Summarized results on mercury in soil and soil gas, 1970 investigations . . . . .                                                               | 166                 |
| 43                   | Anomalous soil gas sites and corresponding levels of mercury in soil, 1970 investigations . . . . .                                             | 168                 |
| 44                   | The possible effect of water vapour on the amalgamation of mercury vapour and/or mercury-containing compounds with 60 mesh silver gauze . . . . | 170                 |
| 45                   | Results of consecutive pumping experiments . . . . .                                                                                            | 172                 |
| 46                   | Results of pyrolysis experiments . . . . .                                                                                                      | 174                 |
| A1                   | Precisions of mercury in soil analyses based on replicate determinations . . . . .                                                              | 208                 |
| A2                   | Precisions of atomic absorption analyses (Zn, Cd, Pb, Fe, Mn) . . . . .                                                                         | 216                 |
| A3                   | Precisions of atomic absorption (Ca, Mg) and flame emission (K, Rb) analyses . . . . .                                                          | 217                 |
| A4                   | Spectrograph specifications and operating parameters. .                                                                                         | 221                 |
| A5                   | Spectral wave lengths and useful ranges of elements determined . . . . .                                                                        | 222                 |
| A6                   | Precisions of semi-quantitative spectrographic analyses by replicate determinations . . . . .                                                   | 223                 |
| A7                   | Elemental data on Decomposed Zone material used to calculate relative enrichment ratios . . . . .                                               | 227                 |
| A8                   | Elemental data on mineralized tills used to calculate relative enrichment ratios . . . . .                                                      | 228                 |
| A9                   | Elemental data on rocks used to calculate relative enrichment ratios . . . . .                                                                  | 229                 |

LIST OF FIGURES

| <u>Figure<br/>No.</u> | <u>Title</u>                                                                                                                                                                                               | <u>Following<br/>Page No.</u> |
|-----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|
| 1                     | Location Reference . . . . .                                                                                                                                                                               | 2                             |
| 2                     | Zn and Pb in stream sediments, Keel area . . . . .                                                                                                                                                         | 2                             |
| 3                     | Stratigraphy at Keel . . . . .                                                                                                                                                                             | 12                            |
| 4                     | Sub-drift geology of the Keel inlier . . . . .                                                                                                                                                             | 12                            |
| 5                     | Cross section of the Keel deposit . . . . .                                                                                                                                                                | 14                            |
| 6                     | Drillholes intersecting the Decomposed Zone . . . . .                                                                                                                                                      | 29                            |
| 7                     | Isopach contours showing thickness of the Decomposed<br>Zone . . . . .                                                                                                                                     | 29                            |
| 8                     | Cross sections of the Decomposed Zone . . . . .                                                                                                                                                            | rear<br>pocket                |
| 9                     | Selected elements in two drillholes intersecting<br>the Decomposed Zone . . . . .                                                                                                                          | "                             |
| 10                    | Sample location reference map . . . . .                                                                                                                                                                    | "                             |
| 11                    | Distribution of Zn in soils, Keel inlier . . . . .                                                                                                                                                         | "                             |
| 12                    | Distribution of Cd in soils, Keel inlier . . . . .                                                                                                                                                         | "                             |
| 13                    | Distribution of Pb in soils, Keel inlier . . . . .                                                                                                                                                         | "                             |
| 14                    | Distribution of Hg in soils around Keel . . . . .                                                                                                                                                          | "                             |
| 15                    | Soils and Location Reference . . . . .                                                                                                                                                                     | 67                            |
| 16                    | Selected elements in soil over the Keel deposit . . . . .                                                                                                                                                  | 67                            |
| 17                    | Selected elements in soil overlying the Decomposed<br>Zone and mineralized faults at Keel . . . . .                                                                                                        | 69                            |
| 18                    | Selected metals in soils, Garrycom, Keel . . . . .                                                                                                                                                         | 70                            |
| 19                    | Selected metals in soil, Drumming Cross Roads, Ardagh<br>area . . . . .                                                                                                                                    | 71                            |
| 20                    | Selected metals in soil, Ardagh Hill, Ardagh . . . . .                                                                                                                                                     | 72                            |
| 21                    | Lateral hydromorphic dispersion of zinc and cadmium<br>from a mineralized stream to adjacent soils, Keel . . . . .                                                                                         | 74                            |
| 22                    | Lateral hydromorphic dispersion of Zn and Cd in soils<br>adjacent to an anomalous stream, Ardagh area. Pattern<br>modified by surficial accumulation of metals in<br>peaty, poorly-drained soils . . . . . | 74                            |



| <u>Figure<br/>No.</u> | <u>Title</u>                                                                                              | <u>Following<br/>Page No.</u> |
|-----------------------|-----------------------------------------------------------------------------------------------------------|-------------------------------|
| 23                    | Lateral hydromorphic dispersion of zinc and cadmium in soils about mineralized streams, Ardagh area . . . | 75                            |
| 24                    | Thickness of glacial drift, Keel . . . . .                                                                | 79                            |
| 25                    | Pb, Hg, and Ag in mineralized, peaty gleysolic soils, Keel . . . . .                                      | 80                            |
| 26                    | Selected metals in a mineralized basin peat, Keel . .                                                     | 88                            |
| 27                    | Relationship between Zn in hawthorn and Zn in soil, Keel . . . . .                                        | 97                            |
| 28                    | Relationship between Pb in gorse and Pb in soil, Keel                                                     | 97                            |
| 29                    | Relationship between Zn in soil and Zn in hawthorn, Ardagh . . . . .                                      | 97                            |
| 30                    | Selected metals in grass, Keel . . . . .                                                                  | 98                            |
| 31                    | Generalized geochemical cycle of Hg . . . . .                                                             | 115                           |
| 32                    | Mercury interconversions in nature . . . . .                                                              | 115                           |
| 33                    | Fields of stability for aqueous species of Hg . . . .                                                     | 117                           |
| 34                    | Known transformation pathways of Hg and its compounds in nature . . . . .                                 | 115                           |
| 35                    | Concentration of methylmercury in bottom sediment . .                                                     | 122                           |
| 36                    | Hg in soil air and atmospheric air over an unnamed deposit in the USSR . . . . .                          | 148                           |
| 37                    | Hg in air at 200 ft. altitude, Bruce Peninsula, Ont., Canada . . . . .                                    | 148                           |
| 38                    | Mercury content in soil gas at Cortez, Nevada, USA . .                                                    | 149                           |
| 39                    | High sensitivity calibration graph for the mercury vapour spectrophotometer . . . . .                     | 156                           |
| 40                    | The effect of air flow rate on the amalgamation of Hg vapour with 60 mesh Ag gauze . . . . .              | 157                           |
| 41                    | Efficiency of a series of 60 mesh Ag gauze for collecting Hg vapour . . . . .                             | 159                           |
| 42                    | Sampling hood and field arrangement to obtain from depth soil gas . . . . .                               | 163                           |
| 43                    | Sampling hood and field arrangement to obtain near-surface soil gas . . . . .                             | 164                           |
| 44                    | Mercury in soil gas at Keel, March, 1970 . . . . .                                                        | 165                           |

| <u>Figure<br/>No.</u> | <u>Title</u>                                                                                             | <u>Following<br/>Page No.</u> |
|-----------------------|----------------------------------------------------------------------------------------------------------|-------------------------------|
| 45                    | Mercury in soil, Keel . . . . .                                                                          | 165                           |
| 46                    | Mercury in soil gas at Keel, all results, 1970 . . . . .                                                 | 165                           |
| 47                    | Relationship between mercury in soil air and mercury<br>in soil at Keel . . . . .                        | 165                           |
| 48                    | Mean monthly rainfall at Newtown Forbes, Co. Longford<br>for the period 1916-1950 . . . . .              | 173                           |
| 49                    | Mean monthly temperature ranges at Newtown Forbes, Co.<br>Longford for the period 1916-1950 . . . . .    | 173                           |
| 50                    | Measured values for diffusion of gases through dry<br>granular materials . . . . .                       | 176                           |
| A1                    | Calibration curve of mercury vapour spectrophotometer.                                                   | 206                           |
| A2                    | Calibration graph, $\text{SnCl}_2$ release technique for<br>determining Hg . . . . .                     | 209                           |
| A3                    | A comparison of analytical techniques for determining<br>Hg in organic-rich, mineralized soils . . . . . | 211                           |

LIST OF PLATES

| <u>Plate<br/>No.</u> | <u>Title</u>                                                                                           | <u>Following<br/>Page</u> |
|----------------------|--------------------------------------------------------------------------------------------------------|---------------------------|
| 1                    | Drillhole K117 (59-71 ft.) . . . . .                                                                   | 28                        |
| 2                    | Drillhole K86 (81-102 ft.) . . . . .                                                                   | 28                        |
| 3                    | Drillhole K100 (47-69 ft.) . . . . .                                                                   | 28                        |
| 4                    | Drillhole K100 (69-87 ft.) . . . . .                                                                   | 28                        |
| 5                    | Drillhole K120 (144-156 ft.) . . . . .                                                                 | 28                        |
| 6                    | Drillhole K120 (156-171 ft.) . . . . .                                                                 | 28                        |
| 7                    | Anomalous peaty, gleyed, and podzolized soil<br>profile, Keel . . . . .                                | 81                        |
| 8                    | Highly anomalous basin peat overlying<br>gleyed till, Keel . . . . .                                   | 88                        |
| 9                    | Dynamic sampling apparatus in position to obtain<br>"near-surface" (L) and "from depth" (R) soil gas . | 164                       |

## CHAPTER 1

### INTRODUCTION

#### 1.1 GENERAL

Geochemical exploration in areas of transported overburden has often been hampered by the disruption of anomalies through obscuring, rafting, or covering of the secondary expressions of the metals sought. The use and application of the so-called "pathfinding" elements has been somewhat successful in aiding interpretation in such circumstances.

Mercury is a strongly chalcophilic element and is found in trace amounts in most hydrothermal ore deposits (James, 1962). Russian investigators, notably Saukov (1946) and Ozerova (1962), established the presence of primary and secondary halos of mercury associated with mercury and polymetallic deposits. Subsequent work by Western geochemists, notably Hawkes (with Friedrich 1966a, 1966b, and with Williston, 1962) and James (1962, 1964, and with Webb, 1964), has confirmed Soviet findings.

With the development of flameless atomic absorption instruments, mercury geochemistry has become a relatively important part of mineral exploration.

Research here examines the secondary dispersion of mercury applied to the study of metal halos over a glaciated Zn-Cd-Pb deposit in the Irish Republic.

#### 1.2 HISTORY OF THE KEEL DEPOSIT

Discovery of the Keel deposit represents an almost classic example of a successfully applied geochemical survey.

In 1962, Anglo-Austral Mines Ltd., a wholly-owned subsidiary exploration company of the Rio Tinto Zinc Corporation Ltd., acquired a group of mineral exploration licences in the Longford District, Eire.

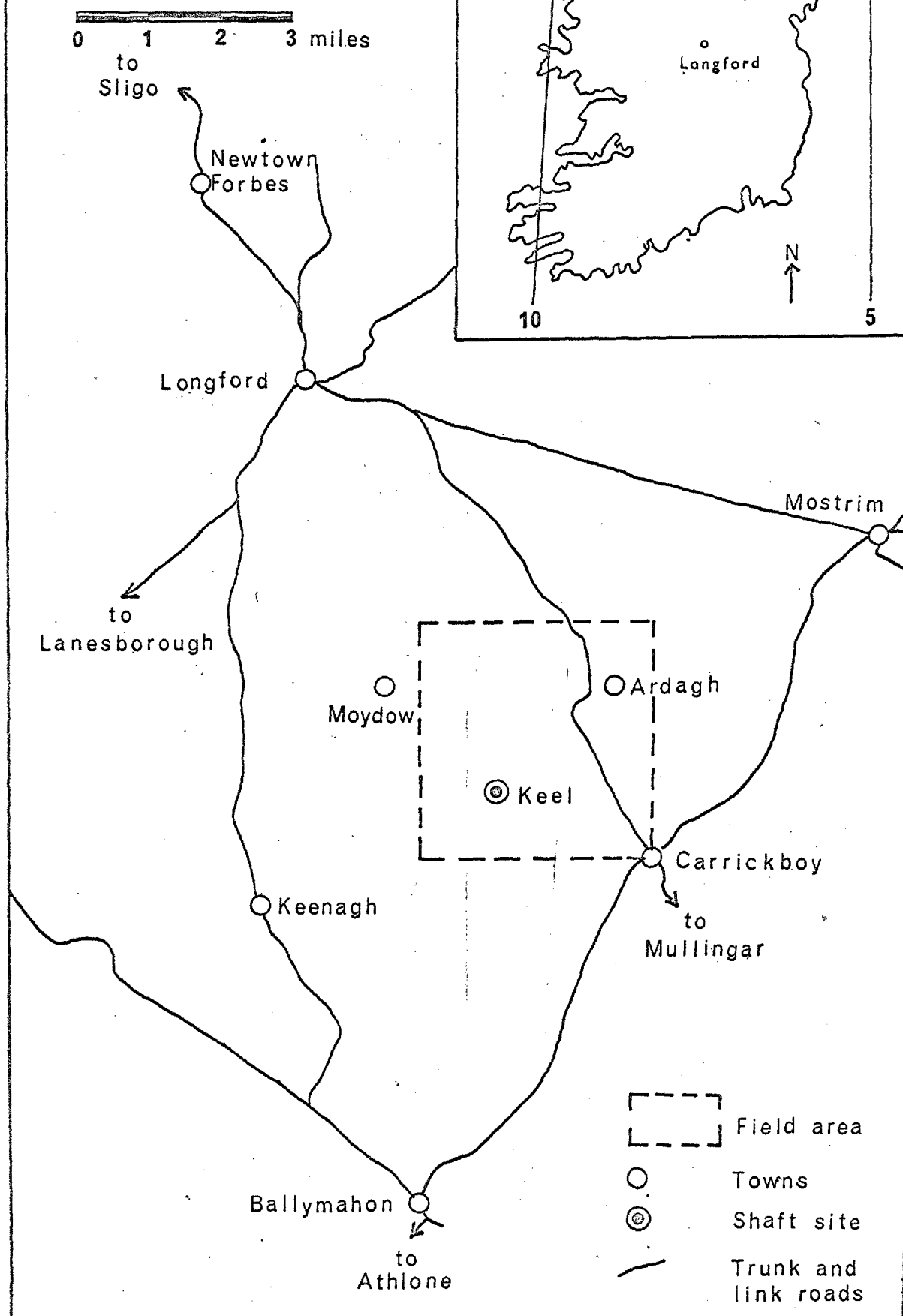
These licences surrounded two Silurian inliers within the Lower Carboniferous succession immediately south of the County Town of Longford (see Fig. 1 for location reference). Presumably, this setting was selected on the basis of prior mineral discoveries in similar geological environments elsewhere in Ireland (i.e. Tynagh, Gortdrum, and Silvermines).

Stream sediment samples were collected at one-half mile intervals over the licences and into County Roscommon in the west. Analysis for Cu, Pb, and Zn presented an easily discernible zinc anomaly and an accompanying, more subtle lead anomaly associated with the southernmost inlier (Fig. 2). The peak values were centered near and around the Townland of Keel on the south flank of the inlier. Subsequent orientation and reconnaissance soil surveys uncovered a broad zinc anomaly. Lead analysis confirmed the presence of an intense, but much more narrowly defined soil anomaly while copper values remained much the same in anomalous areas as in background regions. The results and maps of this survey are presented, interpreted, and discussed in Chapter Four.

An extensive drilling programme was initiated and quickly revealed encouraging sections of disseminated and massive sphalerite with lesser, but economically important amounts of galena. Assay values of the "ore-lengths" confirmed dominant zinc mineralization and also the presence of above average cadmium values associated with the sphalerite. Silver values (1 to 3 Troy ozs./ton) are typical of the Irish deposits. The geology, mineralogy, and genesis of the Keel deposit are discussed in Chapter Two.

Drilling was followed by the sinking of a shaft at Keel with over one mile of exploratory drifting at 200, 400, and 500 ft. levels. In 1968, the operation was put under care and maintenance and all exploration and development temporarily ceased. In 1970, American Smelting and Refining Co. Ltd. ("ASARCO") acquired an option to do

Fig. 1  
Location  
Reference



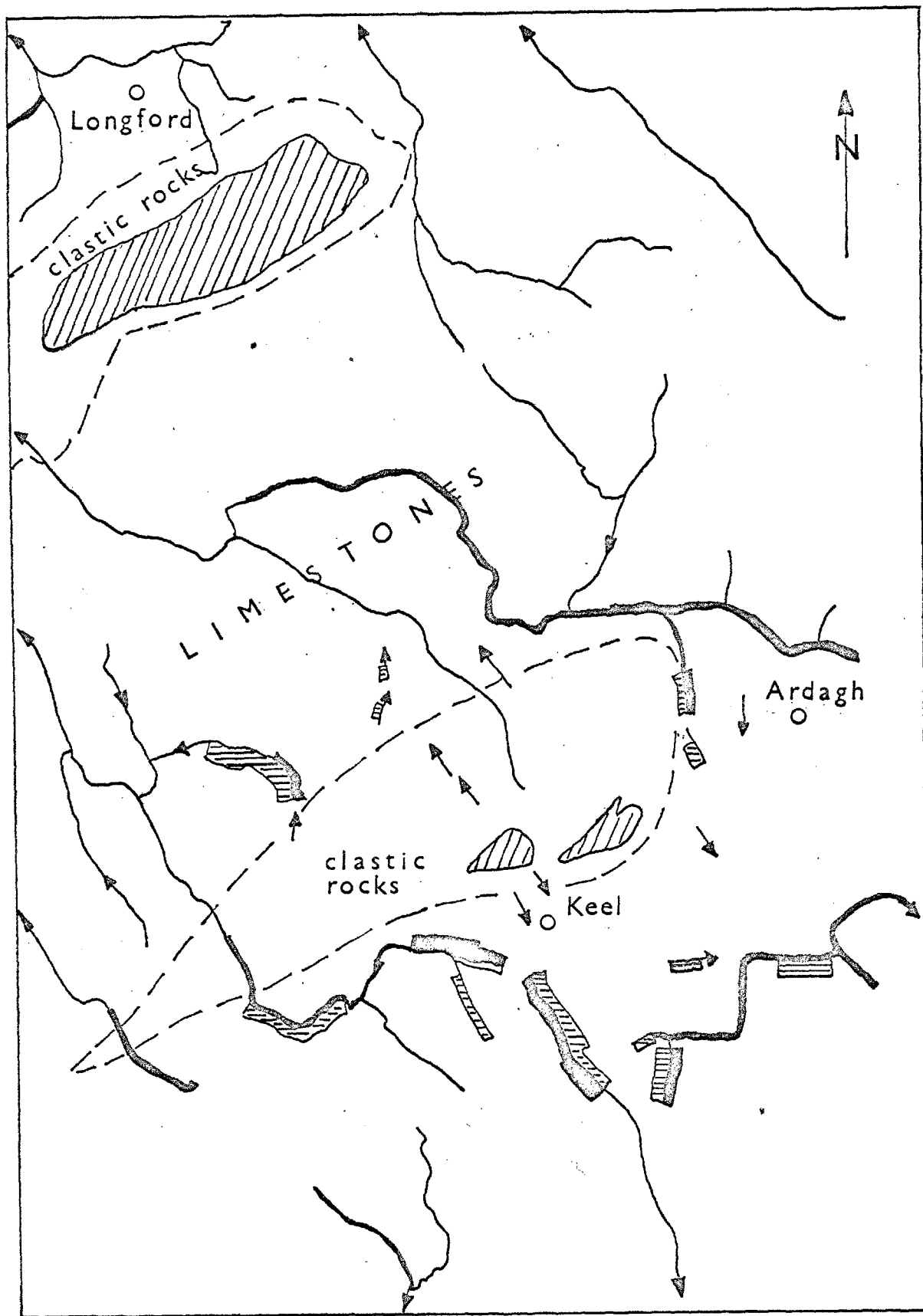
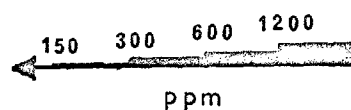
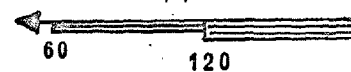


Fig. 2

Zn & Pb in  
stream sediments,  
Keel area



Zn in stream  
sediments



Pb in stream  
sediments



Silurian

after Riofinex unpub.



miles

further exploration on the licences and at the time of writing were actively engaged in an additional surface assessment of the Keel area and Longford District at large.

### 1.3 MERCURY GEOCHEMISTRY IN MINERAL EXPLORATION

#### 1.3.1 Background

James (1962) states "Broad patterns of primary dispersion are frequently formed by mercury around both mercury and polymetallic deposits. These halos are believed to reflect predominantly gaseous dispersion, and may be expected to be most marked where the rocks are most porous, or where fracturing has occurred prior to, or simultaneously with mineralization."

The above hypothesis essentially forms the basis for the application of Hg as a prospecting guide. It follows from initially emplaced primary halos that similarly broad halos could form in the secondary environment and provide easily accessible sampling material (i.e. soils, tills, plants) in areas of transported or deep residual overburden.

James (op. cit.) has admirably researched and reviewed the primary and secondary geochemistry of Hg and application to mineral exploration through March 1961. He concludes that most hydrothermal orebodies have associated mercury halos with somewhat variable abundance levels, usually higher with lower temperature deposits. Further, mercury can disperse via mechanical, saline, and gaseous forms and appears highly influenced by certain secondary environmental processes. Research to the above date appears confined primarily to bedrock and soil samples.

Donovan (1965) has updated James' (1962) study as regards prospecting application and provided additional information from his own



studies on mercury and base metal dispersion at the then newly-found Tynagh deposit, Co. Galway, Ireland. Shorter studies on other mineral occurrences in West-Central Ireland are also included in this work.

In general, the 1960's saw the application of mercury pathfinding to mineral exploration progress through several stages of waxing and waning interest. The writer views this inconsistency as initial hopes of a potentially useful exploration tool frustrated through inadequate analytical methods, and perhaps a lack of understanding and appreciation of the complex geochemical nature of mercury dispersion.

The analytical aspect has advanced to meet the increasing requirements of modern prospecting. Colorimetric methods (Ward et al., 1963) and early Hg vapour meters (such as those originally manufactured by Lemaire Instruments, Reno, Nevada, U.S.A.) have been replaced by sophisticated flameless atomic absorption instruments. James and Webb (1964), Vaughn (1967), and Barringer (1966) all describe specialized equipment for the low level (nanogram) detection of mercury in geological samples.

In contrast, the understanding of the supergene movement of mercury has advanced comparatively little beyond Saukov's (1946) original data and concepts. True, elemental associations and environmental controls on dispersion have been more firmly established, but the aspect of "mode of dispersion", particularly gaseous phase and forms, has received little attention.

Perhaps the best indication of continued interest in mercury dispersion is reflected by the number of articles presented at Geochemical Prospecting Symposia. Table 1 discloses a small, but steady contribution of published work during the latter half of the last decade.

Table 1. Articles on applied mercury investigations presented at Geochemical Prospecting Symposia

| Conference and Year | Case History Studies | Analytical Methods and Techniques | Complementary Investigations |
|---------------------|----------------------|-----------------------------------|------------------------------|
| Ottawa, 1966        | 3                    | 1                                 | 2                            |
| Golden, 1968        | 3                    | -                                 | 3                            |
| Toronto, 1970       | 1                    | 2                                 | 3                            |

From time to time additional articles on mercury dispersion in mineral exploration and ore genesis appear in the geochemical, geological and mining literature, but the main contributor in recent years has been the extensive application of mercury pathfinding by the United States Geological Survey (U.S.G.S.). U.S.G.S. results are usually published as Circulars, Bulletins, Open-File Reports and sometimes as Professional Paper Research Chapters.

### 1.3.2 Current Trends

At the time of writing, two recent developments have brought about renewed interest in mercury dispersion systems in the secondary environment. The first was the discovery of a Hg in air anomaly over a gold deposit at Cortez, Nevada, U.S.A. by geochemists of the U.S.G.S. (McCarthy et al., 1969). The importance of this investigation centres on the Hg in air anomaly defining the surface expression of the orebody more closely than does the Hg in soil anomaly. Also, there is the more obvious use of airborne geochemistry in regional assessment studies in mineral exploration.

The above research has, in turn, stimulated additional development for the direct reading of airborne geochemical anomalies. Barringer Research Ltd., Toronto, Canada is presently investigating atmospheric mercury vapour anomalies in a variety of climates and environments with

the use of helicopter-mounted and vehicle-mounted portable mercury spectrometers (A. R. Barringer, pers. comm.).

The second development is of more indirect value to geochemical prospecting. Jensen and Jernelov (1969) in Sweden have been able to identify dimethylmercury which has been generated in river and lake bottom muds by microorganisms. These findings parallel earlier Japanese discoveries of mercury-resistant bacteria with the ability to release substantial amounts of mercury vapour (Suzuki et al., 1968). The apparent ease of the biotransformation of inorganic mercury into the highly volatile and dangerous dimethyl compound has touched off an unprecedented amount of research into mercury pollution sources and associated problems. The geochemist is now confronted with new environmental factors to interpret mercury dispersion, those of Hg pollution and bacterium-induced volatilization of organomercurials and Hg vapour.

Review articles on mercury in the secondary environment have recently been published by Jonasson (1970), the U.S.G.S. (Professional Paper 713, 1970), and Wotjalik (1971). Also, numerous papers on Hg abundance and analysis (mainly in tissue and water) have appeared in trade and academic journals.

The writer has reviewed the use and application of mercury as a geochemical guide to mineralization in an unpublished internal report (Evans, 1969). Some important conclusions stemming from this study are:

- i) Mercury in soil gas and air promises to be a useful tool in mineral exploration although environmental controls may be restricting.
- ii) Mercury hydrochemistry and biogeochemistry are poorly documented and their importance is a relatively unknown factor in the secondary accumulation and dispersion of the element.
- iii) The mercury-organic matter relationship is by association only.

The actual mechanism(s) of Hg concentration are unknown.

- iv) Mercury association and correlation in geological material has been

exhibited with a host of chalcophilic elements, Ca, Ba, Fe, Mn, and number of sulphur complexes and compounds.

- v) The influence of Hg pollution on the use of the element as a pathfinder in mineral exploration has received little, if any attention.

#### 1.4 SCOPE OF RESEARCH

##### 1.4.1 Opening Remarks

The present study forms part of a combined research effort in the Department of Geology, Royal School of Mines to integrate several disciplines within geological science around a mineral exploration problem. The ultimate aim of the project is to correlate the important findings of each study towards the advancement of mineral exploration science and technology.

Four concurrent programmes are presently under study at the Royal School of Mines with some or all field data derived from the Keel prospect. An additional associated project investigating mercury in biochemical systems is being undertaken by the Department of Botany, Imperial College.

Monitoring of magneto-telluric currents may prove a useful geophysical tool in probing deep-seated primary environments. Measuring equipment has been developed in the Department of Geophysics, Royal School of Mines with thought for use in ore genesis (structural aspect) and regional geological studies (C. Hewlitt, pers. comm.).

Photogeology has had previous success identifying overburden-covered rock-types and structures. Multi-spectral photography (visible, ultra-violet and infra-red regions) may be helpful in the examination of in-situ plant-soil-metal relationships through the establishment of "geochemical reflectivities" (N. Press, pers. comm.). Such studies are in progress in the Photogeology Section, Department of Geology, Royal School of Mines.

Primary dispersion is being actively investigated by the Department of Mining Geology, Royal School of Mines, at the Keel prospect through analysis of major, minor, and trace constituents of wallrock and sulphides. Although distinctive halos have not as yet been recognized, there is some indication that certain element levels and ratios may be useful guides in searching for "Keel-type" ore (J. Watling, pers. comm.).

Secondary dispersion of selected elements in the Keel area has been studied by the writer through an examination of the respective supergene metal halos as a contribution by the Applied Geochemistry Research Group, Royal School of Mines.

#### 1.4.2 Thesis Content

Emphasis has been placed on the examination of the secondary dispersion of mercury with particular reference to soil air as a mode of element migration. Equipment and apparatus have been implemented or developed to collect soil air and atmospheric air samples.

Other elements investigated include Zn, Pb, Cd, Ag, Ba, Fe, Mn, As, and Sb with overall importance attached to the Zn, Pb, and Cd results and their respective secondary dispersion characteristics. The cadmium investigation is regarded with some significance. The pronounced levels in soil and associated material at Keel have made it possible to assess this element's mobility and distribution as compared to zinc.

Secondary environmental controls, particularly organic matter sequestering and iron-manganese retention of base metals have received study, comment, and conclusion on their influence in the Keel area.

Discussion, conclusions, and recommendations are divided into two separate sections. The first describes and concludes on soil anomaly formation while the second summarizes on the soil air experiments and their inferred prospecting value.

Sampling techniques, statistical control of analyses, computer

data records, and analytical methods are included in a series of appendices at the rear of the volume.

#### 1.5 STUDY SUPPORT AND ACKNOWLEDGEMENTS

Materials, equipment, and travelling expenses have been provided through a generous grant made available by Barringer Research Ltd., Toronto, Canada. The Company president, Dr. A. R. Barringer (also Visiting Professor at Imperial College), initiated the research and the writer wishes to thank Dr. Barringer for his active participation and enthusiastic interest throughout the entire course of study.

Student support was in the form of a three year Research Assistantship in the Applied Geochemistry Research Group, Imperial College.

As previously mentioned, the field area is presently under mineral exploration licence to Rio Tinto Finance and Exploration Ltd. ("Riofinex"). The writer has been indeed fortunate to have had access to the Keel property for sampling and observations as well as being permitted to view much confidential information. Mr. R. Rice, Dr. A. W. Smith, and Dr. G. Richards (now of Royal Dutch Shell Oil Company) were extremely cooperative in the London offices of the Rio Tinto Zinc Corporation Ltd., while Dr. C. Morley, Mr. V. Byrne, Mr. F. Casey, and Mr. J. Dowler provided cheerful and able assistance in Ireland.

The writer also wishes to acknowledge the continued cooperation of the American Smelting and Refining Co. Ltd. geologists and staff at the Keel site during the present option agreement.

The study forms part of the continuing research on mercury dispersion and geochemical exploration methods and techniques in the Applied Geochemistry Research Group under the direction of Professor J. S. Webb. Professor Webb has maintained a high degree of interest in the research project which the writer gratefully acknowledges.

Discussions with Dr. J. M. Patterson (Baryanin Explorations Ltd.,

Athlone, Ireland), Dr. J. S. Tooms and research staff and students of the Applied Geochemistry Research Group have all proved beneficial and are gratefully appreciated.

Mr. W. T. Meyer ably supervised the research and has been extremely helpful throughout the individual stages of the study programme.

Finally, the writer wishes to acknowledge the unending support and help of his wife, Frances, during all aspects of the research and thesis preparation.

## CHAPTER 2

### GEOLOGY, MINERALOGY AND GENESIS OF THE KEEL DEPOSIT

#### 2.1 PREVIOUS WORK

The material discussed in this chapter has been subject of a recent research degree: "Geology and Mineralization of the Keel Area Co. Longford, Republic of Ireland" by J.M. Patterson (1970). The writer here has borrowed freely from this work throughout this chapter and again in later chapters. Patterson mentions an almost total lack of geological references near and around the Longford District; hence, his work is regarded as the sole reference.

#### 2.2 QUATERNARY GEOLOGY

Description and discussion of physiography, geomorphology, drainage, glacial till, soils, and vegetation of the Keel area are included in Chapter Four under secondary environmental influences affecting the supergene dispersion of the trace and associated elements under study.

#### 2.3 STRATIGRAPHY

The Geological Map of Ireland (1962) places the area of interest within a region underlain by clastic rocks and limestones of Lower Carboniferous age. The presence of two small inliers (Silurian-? Devonian) appear to be the only outcropping non-Lower Carboniferous rocks.

Patterson states: "The Longford area is situated on the shelf area between the Lower Paleozoic Longford-Down Massif to the north and the deep water basin facies to the south. This places it in the zone of optimum sedimentary variation, an aspect which is readily apparent from both drill cores and underground exposures." Further, he interprets



the Lower Carboniferous sediments as derived from a northerly transgressing sea across the Pre-Devonian land mass. Locally, deposition has been affected by the then existing topography and also by regression sequences. Early deposition of the Lower Carboniferous is characteristic of a shallow water environment of local provenance. The presence of cross-bedding and ripple marks supports near shore sedimentation. Later deposition indicates a gradually regressing shoreline (some minor transgressions) and a deeper water environment of fine-grained clastic rocks and fossiliferous chemical sediments. A stratigraphic section depicting the Keel lithologies is shown in Figure 3 and a sub-drift geological map of the Keel inlier is represented in Figure 4.

Table 2 summarizes Patterson's research on the recognized lithologies found at Keel by surface and subsurface mapping and diamond drilling.

## 2.4 STRUCTURE

The pear-like shape (plan) of the Keel inlier appears to have been initially formed through a Caledonian folding of the Lower Paleozoic (Silurian) rocks at the time Lower Carboniferous clastics and sandy limestones were being actively deposited.

Further Hercynian (Variscan) movements modified the Caledonian strike to a more E-W trend through compression from the south, causing further folding of the Lower Carboniferous beds. Thus, the Silurian rocks were uplifted to form the core of the inlier with the overlying Lower Carboniferous beds dipping north and south.

As stress developed in the Lower Carboniferous sediments a weakness developed in the  $\sigma_3$  plane (i.e. zone of compression) which ended with faulting and faulting systems. Three fault systems in the Keel area have been recognized by Patterson.

Fig. 3

Stratigraphy at Keel

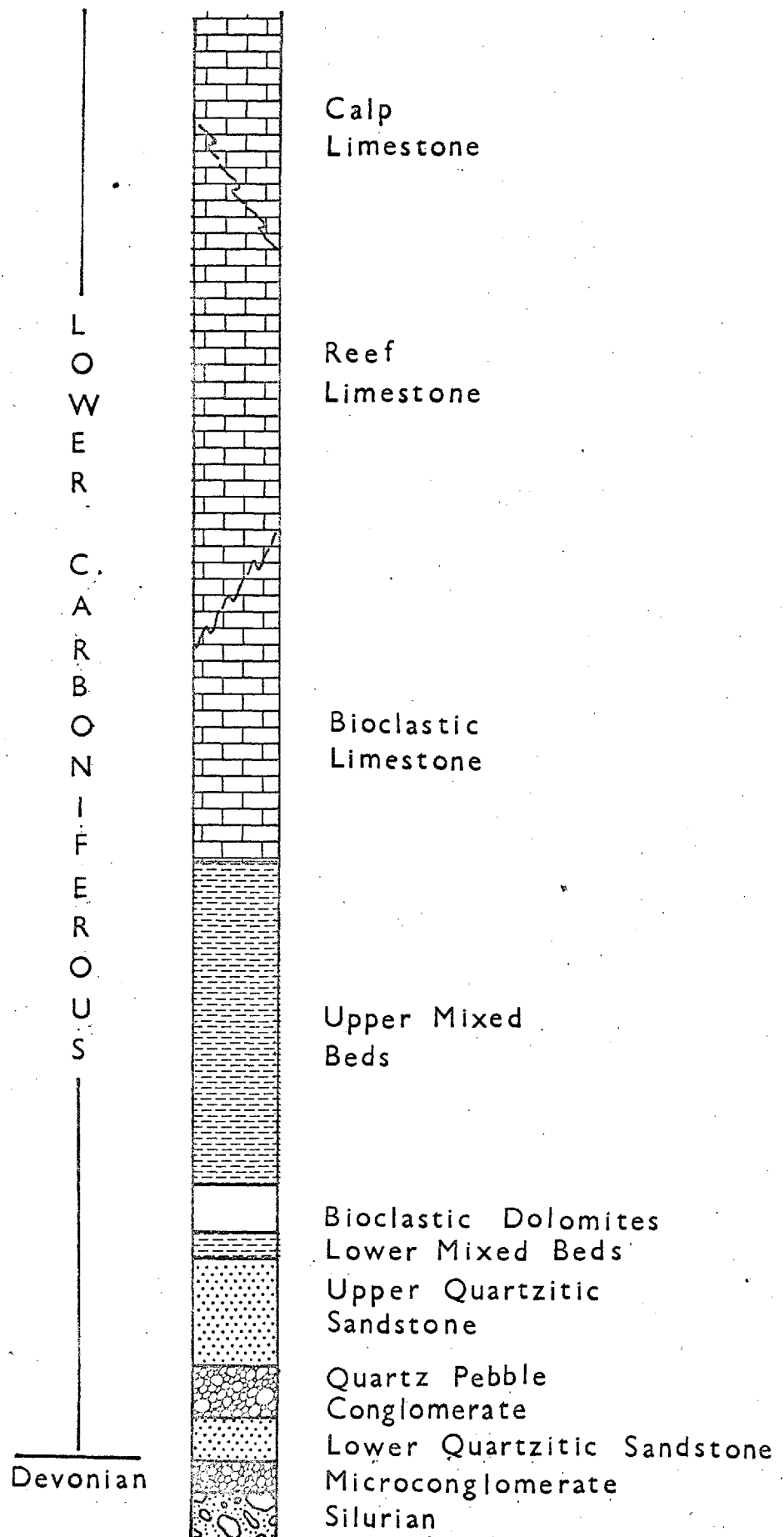


Fig. 4

Sub-drift geology of  
the Keel inlier

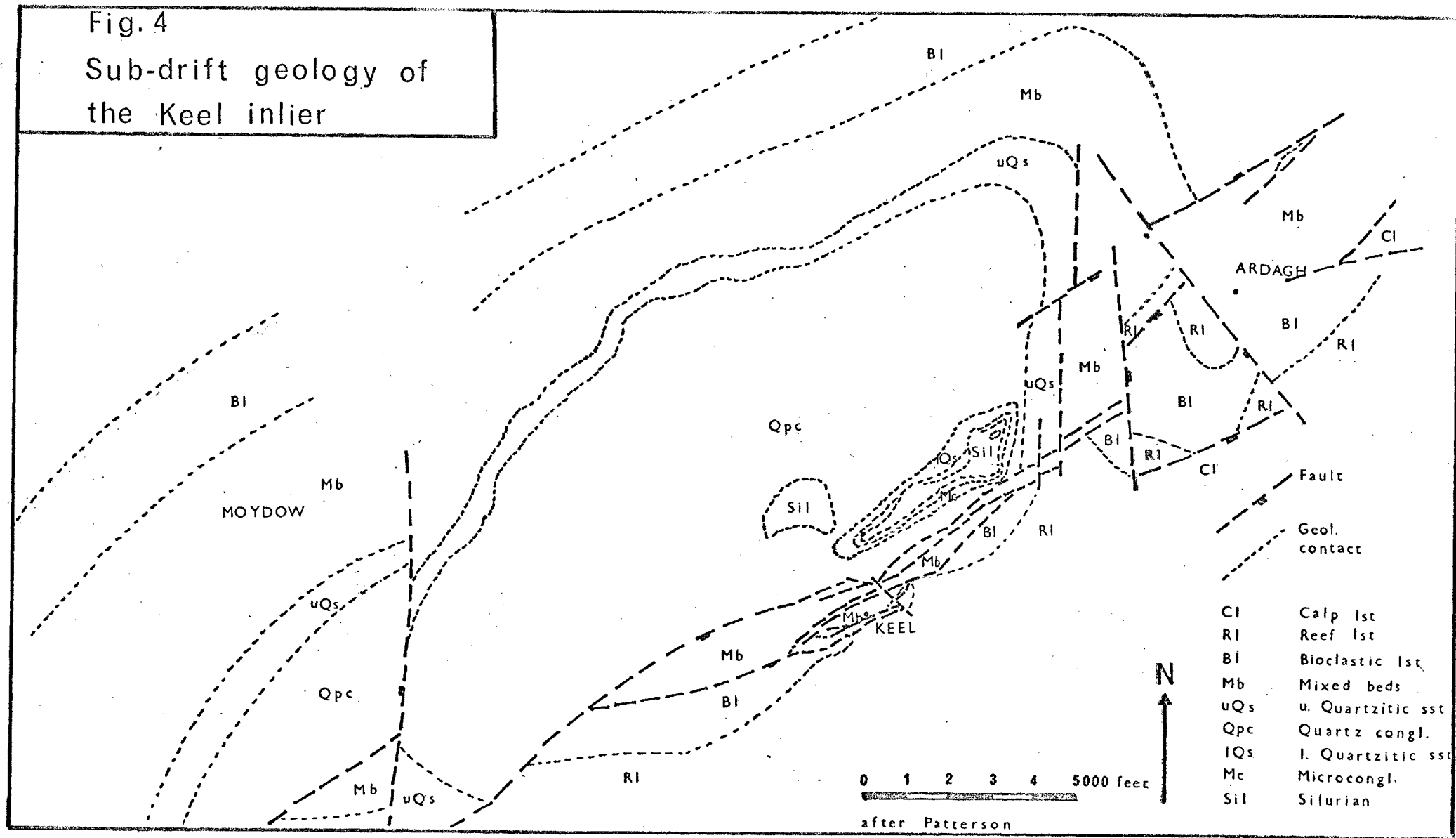


Table 2. Lithologies at Keel

| Lithology                |            | Description                                                                            | Some Associated Features                                                            |
|--------------------------|------------|----------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| Calp Limestone           |            | Well-bedded and jointed dense black limestone and shale                                | Fossiliferous, vuggy, abundant slumping and folding                                 |
| Massive (Roof) Limestone |            | Pale grey fine-grained calcite mudstone                                                | Fossiliferous, vuggy, calcite-filled fractures, pyritiferous                        |
| Bioclastic Limestone     |            | Interbedded black fine-grained mudstone and dark grey fine-grained limestone           | Fossiliferous, pyrite in shaley horizons, slumping, slickensides on shaley surfaces |
| Upper Mixed Beds         | Mixed Beds | Interbedded sandstones and mudstones (dolomitized), some oolitic limestone horizons    | Fossiliferous, easily weathered, transitional to Bioclastic Limestone               |
| Bioclastic Dolomites     |            | Porous, well-bedded, vuggy, dolomites                                                  | Fossiliferous, easily weathered, development of "Decomposed Zone"                   |
| Lower Mixed Beds         |            | Dark grey fine-grained mudstones and muddy sandstones and sandy dolomitized limestones | Secondary carbonate in fractures                                                    |
| Basal Clastic Group      |            | Upper Quartzitic Sandstone, Quartz Pebble Conglomerate, Lower Quartzitic Sandstone     | Important host units for sulphide mineralization                                    |
| Microconglomerate        |            | Re-worked Silurian and chert fragments                                                 | Red and green shades may indicate varying redox conditions during deposition        |
| Silurian                 |            | Dark grey, green and red shaley mudstones and coarse grits                             | Shaley cleavage, tight minor folds, low grade metamorphism                          |

- i) Low angle normal faults striking approximately E-W and dipping north. These faults are very tight and contain little or no sulphide mineralization.
- ii) High angle normal faults striking approximately E-W and dipping SE with associated minor faults dipping north. The massive sulphide mineralization in the Keel deposit is directly associated with some of these faults.
- iii) N-S faults with an associated joint system. Post-ore faults.

The age of the E-W fault systems is difficult to assess. Patterson suggests faulting may have begun at the end of the Hercynian orogeny (i.e. Permo-Carboniferous to Permian times). The N-S faults have been ascribed to Tertiary movements.

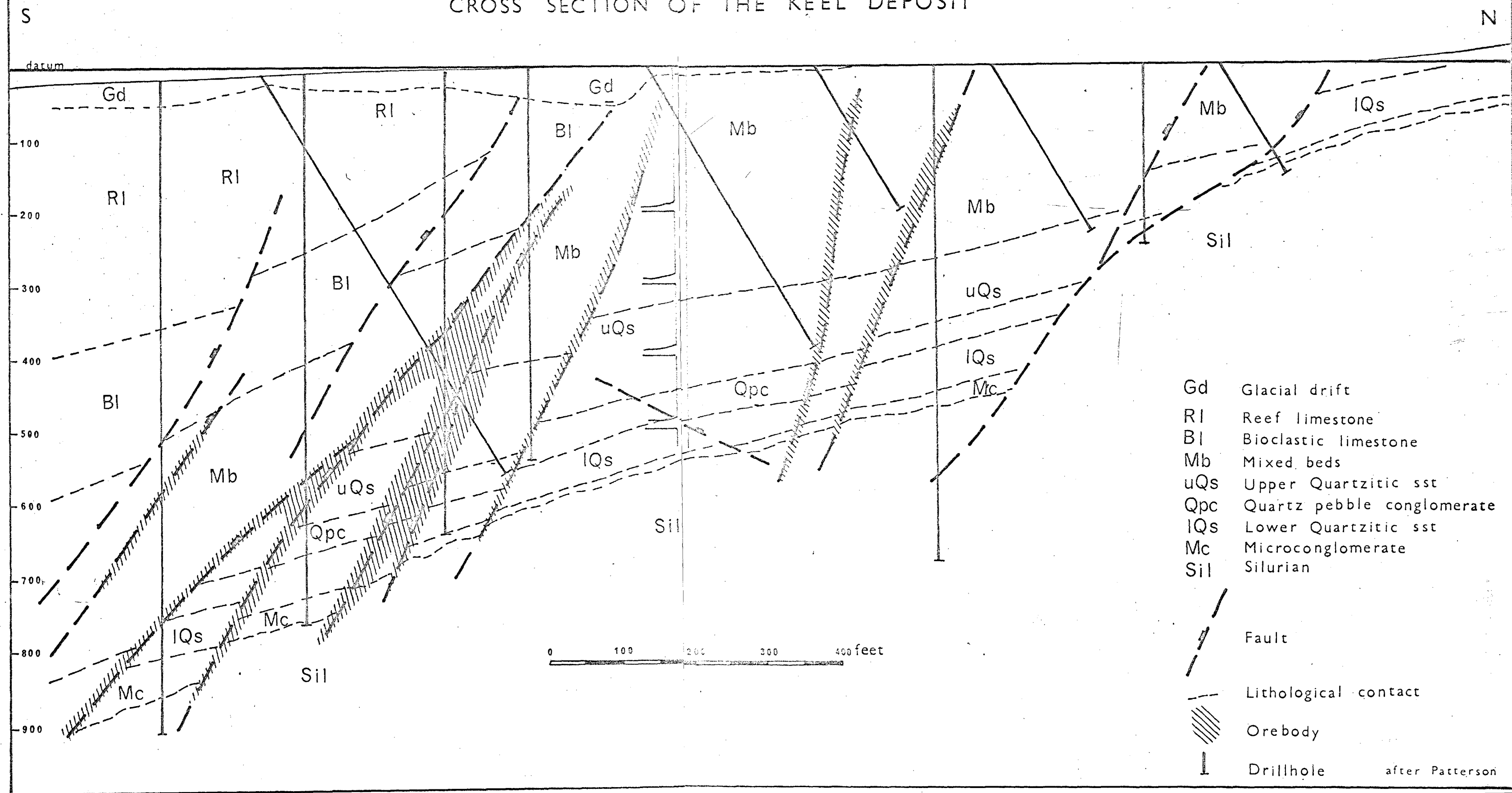
## 2.5 OREBODIES

An interpretation of the initial drilling programme conducted by Rio Tinto Zinc Finance and Exploration Ltd. indicated four stratiformally controlled orebodies associated with high angle E-W faulting. These orebodies were within the Quartzitic Sandstone, the Quartz Pebble Conglomerate and two deposits in the Upper Mixed Beds and possibly related to the top of the Bioclastic Dolomites. As potential appeared favourable and there existed a certain complexity of geology and structure, underground exploration was carried out to establish controls on the occurrence. Figure 5 is a composite cross section of the deposit compiled from drilling data, subsurface mapping, and subsequent study and interpretation by Patterson.

The Keel deposit is, more or less, a stratabound deposit with almost all mineralization confined to the Basal Clastic Group and Mixed Beds sequences. Patterson indicates some chemical and/or physical incompatibility of Keel ore with the overlying Bioclastic Limestones but no similar situation arising with the underlying Silurian. The

Fig. 5

## CROSS SECTION OF THE KEEL DEPOSIT



mineralization within the different orebodies (now established as veins) is primarily of massive sulphide and/or breccia ore (mostly sphalerite) in the Mixed Beds with disseminated sulphides (again, mostly sphalerite) in the Quartz Pebble Conglomerate, Quartzitic Sandstone, and Sandstone units within the Mixed Beds. It should be noted some shaley horizons within the Basal Clastic Group and Mixed Beds have successfully restricted migration of ore solutions.

There appears to be little or no visible wall rock alteration in the Keel deposit. The writer has observed ore/wall rock contacts which have been unusually sharp with no visible indication of chemical addition or subtraction to sediments in direct association with the massive and breccia-type ores.

Massive pyrite of unknown dimensions has been intersected at the base of the Massive (Reef) Limestone to the east of the shaft site. The significance of this mineralization is not fully understood or appreciated.

Clearly, the Keel deposit is epigenetic with relation to the Lower Carboniferous sediments. Whether the source of metal is from a local syngenetic accumulation which has been remobilized into the present structure or is from a distant or, perhaps, a juvenile source still remains to be solved. Ore-genesis at Keel is briefly discussed under "Metallogenesis" in this chapter.

## 2.6 MINERALOGY AND METALLOGENESIS OF THE KEEL DEPOSIT

### 2.6.1 Opening Remarks

The dominant ore mineral in the Keel deposit is sphalerite containing economically significant quantities of cadmium in solid solution. Galena is present in minor amounts throughout the ore-bodies and attains some local importance. Accessory sulphide minerals found include tetrahedrite, chalcopyrite, pyrargyrite, jalpaite, pyrite,

and marcasite. Patterson has analyzed the sulphide minerals from Keel and established the presence of some additional chalcophile traces. Table 3 summarizes his findings.

#### 2.6.2 Sphalerite

The sphalerite in the Keel deposit occurs as fine-grained granular crystals in disseminated occurrences and massive ores through to coarse terminated crystals found in open vugs. Colour ranges from pale yellow to dark brown with darker varieties generally tending to be more iron-rich (up to 2.0 per cent). The cadmium content of Keel sphalerite consistently approximates one per cent. Silver, Mn, Sb, and Cu are commonly detected traces. Limited analytical data from the writer's findings suggests Hg values in sphalerite to be in the 100-500 ppm range.

#### 2.6.3 Galena

Galena usually occurs as well-formed cubes scattered around the sphalerite in the various orebodies. Although usually present in quantities much less than sphalerite, the mineral is of a recoverable grade and does attain some significance in the orebody associated with the K fault. Silver (up to 1100 ppm) and Sb (up to 870 ppm) have been recorded by Patterson in Keel galena. A single Hg determination on a sample of Keel galena by the writer gave a value of 0.5 ppm.

#### 2.6.4 Chalcopyrite

Chalcopyrite is of metallogenic importance only, occurring as minute blebs in sphalerite.

#### 2.6.5 Tetrahedrite (Freibergite)

Tetrahedrite is found with and in both sphalerite and galena and is of considerable economic importance. Silver appears to be held in solid solution in the mineral and there is some indication it varies



Table 3. Sulphide mineralogy and element assemblage

| Ore Mineral  | Elements Present <sup>1</sup> |
|--------------|-------------------------------|
| Sphalerite   | Zn, Cd, Ag, Fe, Mn, Sb (S)    |
| Galena       | Pb, Ag, Sb (S)                |
| Chalcopyrite | Cu, Fe (S)                    |
| Tetrahedrite | Cu, Sb, Ag, Fe (S)            |
| Pyrargyrite  | Ag, Sb (S)                    |
| Jalpaite     | Cu, Ag (S)                    |
| Bourmonite   | Pb, Ag, Sb (S)                |

<sup>1</sup> Identified by Patterson (1970), emission spectrography and electron microprobe analysis

antipathetically with Cu and Sb values (Patterson).

#### 2.6.6 Silver Sulphosalts

Pyrargyrite, jalpaite, and bourmonite have all been observed in relatively trace amounts during polished section studies by Patterson.

#### 2.6.7 Pyrite

Pyrite is ubiquitous throughout the Lower Carboniferous lithologies in the Longford District. The host rock appears to be of little importance and as yet little or no genetic relationship has been shown with the sphalerite mineralization. Pyrite nodules two to three inches thick have been found in shaley horizons in the Mixed Beds. Some marcasite is also present in association with pyrite.

Spectrographic analysis of three selected pyrite samples gave the following results:<sup>1</sup>

| <u>Sample No.</u> | <u>Mn ppm</u> | <u>Cu ppm</u> | <u>Ag ppm</u> | <u>Co ppm</u> | <u>Ni ppm</u> | <u>Pb ppm</u> | <u>Fe %</u> |
|-------------------|---------------|---------------|---------------|---------------|---------------|---------------|-------------|
| 1764              | 2100          | 60            | 29            | 10            | 115           | 640           | M           |
| 1765              | nd            | 220           | 10            | tr            | 15            | 920           | M           |
| 1766              | 180           | 1             | 10            | nd            | 460           | 720           | M           |

(M = Major)

<sup>1</sup> Patterson (1970)

An additional bulk pyrite sample was collected by the writer from new drill core intersecting the massive zone in the Massive (Reef) Limestone and analyzed for a number of metallic elements.

| <u>Sample No.</u> | <u>Mn ppm</u> | <u>Ag ppm</u> | <u>Pb ppm</u> | <u>Zn ppm</u> | <u>Cd ppm</u> | <u>As ppm</u> | <u>Sb ppm</u> | <u>Hg ppm</u> | <u>Fe %</u> | <u>Se ppm</u> | <u>Au ppb</u> |
|-------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|-------------|---------------|---------------|
| KA 54/444         | 1300          | 26            | 4500          | 5100          | 60            | 620           | 9.5           | 3             | 40          | <1            | <50           |

Together, the results suggest that Keel pyrite may be a potential source of some metallic trace elements for the secondary environment.

The importance of trace elements in Keel sulphides, particularly sphalerite, galena, and pyrite is discussed in Chapter Three.

#### 2.6.8 Barytes

Barytes is of minor importance with little or no indicated economic potential, but is of some paragenetic interest. Spectrographic and atomic absorption analysis has indicated that the mineral is of high purity with one to two per cent strontium, presumably in solid solution. Near Garrycam Townland, 60 feet of massive barytes in association with disseminated sphalerite and weathered, iron-stained materials has been intersected. The shape and extent of this occurrence is not known.

### 2.7 ASSOCIATED MINERALOGICAL STUDIES

Patterson has attempted to assess the genesis of the Keel deposit through a study of paragenesis and metallogenesis. His work is very briefly reviewed here with a summary of the most important aspects of his findings.

#### 2.7.1 Fluid Inclusions

An independent study on one sample of crystalline sphalerite on the freezing and filling temperatures of fluid inclusions yielded information indicating Keel mineralization precipitating from solutions with approximately 12 per cent salt content.

#### 2.7.2 Primary Dispersion

A preliminary study of primary dispersion halos indicated very rapid to virtually non-existent metal decay patterns from mineralized faults. As the deposit exhibits little or no wall rock alteration, this is not surprising. Plotting of Zn-Pb ratios indicates decreasing ratios with increasing depth with metal values dropping to near normal geochemical abundance ranges in the upper limestone units.

### 2.7.3 Cadmium Geochemistry

Regression analysis of Zn-Cd assays from the different orebodies has confirmed the very close geochemical relationship between cadmium and zinc in Keel ore. A summary of the Zn-Cd data is shown in Table 4.

The very high degree of correlation between zinc and cadmium has been shown to be due to cadmium in solid solution with zinc in sphalerite. This important feature has made it possible to assess the use of cadmium as a pathfinding element in geochemical prospecting for zinc as well as providing new information on the relative mobilities of these elements in the secondary environment. This aspect is treated in Chapter Four.

### 2.7.4 Silver-zinc and Silver-lead Relationships

Silver values appear dependent on sphalerite mineralization in three of the five orebodies. This relationship has been established by Patterson to be inclusions of tetrahedrite in sphalerite. A Ag for Pb diadochy is suggested from limited analysis of galena samples but Patterson attributes this again to included tetrahedrite.

### 2.7.5 Paragenesis

Patterson concludes from a study of thin and polished sections that Zn and Pb travelled together in solution and were deposited as sulphides almost simultaneously. It follows that associated minor and trace sulphides, such as tetrahedrite, have behaved similarly.

Barytes mineralization has a more interesting paragenetic history with at least three periods of mineralization and/or remobilization and further migration (Patterson, op. cit.).

- i) Widespread barytes flowers (disseminated in many drillhole intersections), weakly to strongly correlated with sulphide mineralization.
- ii) Massive barytes, infillings of fractures and faults.

Table 4. Zn-Cd ratios of Keel ore

| Orebody and Fault | Zn-Cd Ratio | Correlation Coefficient at 95 Per Cent Confidence Level |
|-------------------|-------------|---------------------------------------------------------|
| C                 | 64          | 0.96                                                    |
| D                 | 56          | 0.95                                                    |
| G                 | 74          | 1.02                                                    |
| H                 | 44          | 0.97                                                    |
| K                 | 68          | 0.94                                                    |

After Patterson (1970)

- iii) Very late barytes in vugs, possibly remobilized from earlier massive and/or disseminated sources.

Quartz and calcite-dolomite mineralization are in evidence throughout the Lower Carboniferous succession at Keel. Fracture infilling, coatings on joints, crystal clusters in vugs and stringers of many shapes and forms are found. Although this sort of mineralization is found throughout the succession, quartz remobilization and mineralization are dominant within the siliceous Basal Clastic Group and sandy horizons of the Mixed Beds while secondary and remobilized calcite and dolomite are more prevalent in the upper limestone units and dolomitic and limey horizons of the Mixed Beds.

#### 2.7.6 Supergene Minerals

Patterson has recognized some secondary minerals. Supergene sphalerite is found in association with terminated quartz and calcite crystals as is some secondary pyrite. Cerussite has been observed in near-surface areas along fractures and on galena surfaces apparently exposed to oxidation. Smithsonite? and/or hemimorphite? have been seen at one locality. Secondary greenockite ("cadmium bloom") has been recorded in some drill cores.

Exposed faults and fractures on the three underground levels has disclosed some weathering of mineralized and associated sediments to limonite and iron-stained insoluble residues. By far the most important weathering process has been the formation of the "Decomposed Zone". This term was coined by Company geologists to describe a body developed within and around the Bioclastic Dolomites which appears, on initial observation, to be mixed clays with iron and manganese-rich oxides. As the Decomposed Zone has been the subject of an extensive trace element examination in Chapter Three, description and genesis are left to that chapter.

### 2.7.7 Metallogenesis

Of metallogenic interest, the high cadmium and generally low iron content of Keel sphalerite appear to be of diagnostic and characteristic importance. Patterson has discussed primary cadmium geochemistry and concludes that the unusually constant Zn-Cd ratio is the outstanding feature of the Keel mineralogy.

The use of the iron in sphalerite geothermometer is dismissed on a critical evaluation of pertinent literature sources and chemical and mineralogical findings.

Further, Patterson describes a situation (with supporting evidence) for the movement of hydrothermal fluids (brines) and subsequent sulphide precipitation of the Keel occurrence. The pre-existing structural form appears to be of utmost importance. As earlier noted, the E-W Caledonian folds were modified and accentuated by Hercynian pressures to produce a multiplicity of faults in the NE-SW direction. This preparation provided channels for brine migration. Patterson concludes that a low temperature brine (at least 200°C but certainly less than 450°C) of weakly acidic to moderately alkaline nature, rich in halides (principally chloride), alkali and alkaline metals, base metal halide and/or bisulphide complexes was transported to the Keel site where dilution at reduced temperatures and pressures caused precipitation of sulphide and associated gangue minerals.

The source of the brines is conjectural, but local sources within the Lower Carboniferous must be considered as suitable reservoirs. Sulphur-containing evaporites have been recorded and observed in many localities of the Lower Carboniferous (Patterson) and shaley (metal-rich) horizons are in evidence in much of the stratigraphic succession near and around Keel. Hence, potential sources are available and may provide the necessary elemental constituents required for mineralization. Water may have been derived from either meteoric or juvenile sources,

stocked with halides, alkalis, alkalines, sulphur, and base metals, and transported through faults and the porous lithologies in the Mixed Beds to meet the diluting waters near and around the present Keel deposit.

Other hypotheses on the genesis of Keel mineralization would appear to fall under long distance (telethermal) migration of hydrothermal ore fluids from an igneous emplacement or "sulphide exhalation" from juvenile sources.

Patterson estimates mineralization as during the latter part of the Hercynian orogeny (i.e. Permian time).

A comparison of the Keel occurrence with other Irish base metal deposits associated with Lower Carboniferous lithologies indicates some striking similarities:

- i) Structural association with ENE-WSW primary Caledonian trend and, in particular, with faults and fault systems.
- ii) Occurrence within Mixed Beds (or equivalent) and/or Limestone.
- iii) Stratiform (lateral) and vein-like shapes of orebodies.
- iv) Simple ore-mineralogy with sphalerite generally dominant over galena and low precious metal content.



## CHAPTER 3

### THE DECOMPOSED ZONE

#### 3.1 GENERAL

During the initial stage of drilling the Keel prospect, an iron-rich weathering product of questionable origin was intersected in the near-surface extensions of the Mixed Beds. It was soon apparent that the lateral and vertical extent of the product was of major dimensions and the term "Decomposed Zone" was introduced to describe all highly weathered material associated with the Mixed Beds.

When taken from the core barrel, the material (in a totally weathered state) occurred as damp or wet, dark brown muds of varying consistency (C. Morley, pers. comm.). Riofinex geologists have used numerous terms to describe degrees of weathering. These include "decomposed muds", "limonites", "weathered Mixed Beds", "leached", "oxidized", "slightly, partially, and totally decomposed", "altered", "brecciated and leached", "dedolomitized", "decalcified", "staining (iron and manganese)", "boxwork textures", etc. (Keel drill logs, Riofinex, unpublished information). Clearly, a supergene process of major proportions has been operating within the Mixed Beds (including the Bioclastic Dolomites).

The weathering does not outcrop and no subsurface exposures were found during exploratory drifting. Only narrow intersections are available from drilling, hence limiting a geochemical study of the oxidized and leached material relative to geology, sulphide mineralization, and glacial till. Also, the soft and friable nature of the product led to poor recovery during drilling, further limiting material for observation and analysis.

Company geologists refrained from using the term "gossan" to

describe the weathered and oxidized material and preferred to use the term "Decomposed Zone". The writer believes this fortuitous and the term is retained here as possibly the best descriptive name. Continued use of the term is made as a Proper Name.

As the Decomposed Zone is sometimes found in association with disseminated mineralization, with faults, and exhibits a strike parallel to the trend of the massive sulphide mineralization, a genetic association linked with Keel ore seems probable.

The material was assayed and revealed a distinctly metalliferous nature, containing up to six per cent combined Pb and Zn (Riofinex, unpublished information). Table 5 shows typical assays and accompanying log notations. The possibility that the Decomposed Zone represents a potential source of metal for the soil anomalies has been investigated by both total analysis and cold-extractable studies of elements concerned.

### 3.2 PREVIOUS WORK

Some previous effort has been made by Riofinex to understand the origin and <sup>to</sup> assess the extent of the Decomposed Zone. In addition, underground de-watering problems were encountered during the exploratory mining work, apparently related to the porous Bioclastic Dolomites and associated leached products (M. Mackarel, pers. comm.).

Patterson (op. cit.) has quoted a consultant's report on a mineralogical study of selected samples of the Decomposed Zone and the writer presents some statements from this study. Table 6 shows assay values on the samples investigated.

The report states: "Examination in reflected and transmitted light of the heavy concentrates <sup>1</sup> showed that the only sulphide present

---

<sup>1</sup> separated with bromoform and methylene iodide

Table 5. Some assay values <sup>1</sup> of Decomposed Zone material

| Drill-hole <sup>2</sup> | Footage | Zn<br>% | Pb<br>% | Cd<br>ppm | Log description <sup>1</sup>                                                                                                   |
|-------------------------|---------|---------|---------|-----------|--------------------------------------------------------------------------------------------------------------------------------|
| K79<br>(60°<br>incl.)   | 147-152 | 1.25    | 2.40    | 190       | Brown and black totally decomposed sandy rock. Very little variation in colour.                                                |
|                         | 152-159 | 1.14    | 0.12    | 180       |                                                                                                                                |
|                         | 159-161 | 1.44    | 0.17    | 190       |                                                                                                                                |
|                         | 183-188 | 1.78    | 0.08    | 240       | Maybe Zn and Pb rich.                                                                                                          |
|                         | 188-193 | 4.55    | 0.23    | 820       |                                                                                                                                |
| K83<br>(60°<br>incl.)   | 54- 64  | 0.84    | 0.08    | 170       | Totally decomposed zone. Varying shades of black, brown, chocolate, and yellow, decomposed sandy rock. Trace disseminated ZnS. |
|                         | 64- 71  | 0.96    | 0.05    | 230       |                                                                                                                                |
|                         | 71- 75  | 0.98    | 0.05    | 220       |                                                                                                                                |
|                         | 75- 76  | 0.90    | 0.03    | 170       |                                                                                                                                |
|                         | 76- 80  | 1.76    | 0.10    | 220       |                                                                                                                                |
| K86<br>(vert.<br>hole)  | 70- 75  | 0.52    | 0.03    | 60        | Brown, dark brown, reddish brown, and yellow grey decomposed sandy rock.                                                       |
|                         | 75- 80  | 0.66    | 0.03    | 110       |                                                                                                                                |
|                         | 80- 85  | 0.56    | 0.04    | 80        |                                                                                                                                |
|                         | 111-116 | 0.38    | 0.16    | 30        | Weathered and leached sandstone. Not totally decomposed.                                                                       |
|                         | 116-123 | 0.37    | 0.84    | 20        |                                                                                                                                |
| K117<br>(60°<br>incl.)  | 57- 62  | 0.50    | 0.20    | 100       | Brown and black totally decomposed sandstone and siltstone. Like shoe polish.                                                  |
|                         | 62- 67  | 1.20    | 0.10    | 400       |                                                                                                                                |
|                         | 67- 76  | 1.00    | 0.40    | 300       |                                                                                                                                |
|                         | 177-181 | 3.70    | 0.10    | 800       | Red brown decomposed sandstone. well leached.                                                                                  |
|                         | 181-190 | 2.50    | 0.10    | 1100      |                                                                                                                                |

<sup>1</sup> after Riofinex, unpublished data<sup>2</sup> at 343° orientation

Table 6. Samples and assays cited in consultant's report <sup>1</sup>

| Sample Reference | Drillhole and Footage    | Zn % | Pb % | Cd ppm |
|------------------|--------------------------|------|------|--------|
| R1056            | K43, 206.8-<br>214.0 ft. | 2.62 | 3.36 | -      |
| R1556            | K79, 193.7-<br>198.7 ft. | 5.00 | 0.82 | 820    |
| R1557            | K79, 198.7-<br>206.4 ft. | 4.20 | 1.05 | 620    |

<sup>1</sup> A. Millman, Riofinex, unpublished information



Plate 1 Drillhole K117 (59-71 ft.). Totally decomposed, Fe-rich material. Scale 1:6



Plate 2 Drillhole K86 (81-102 ft.). Partially oxidized and leached rock. Note the unweathered fragment. Scale 1:6





Plate 3 Drillhole K100 (47-69 ft.). Moderately decomposed rock. Scale 1:6



Plate 4 Drillhole K100 (69-87 ft.). Highly leached rock. Note remnant bedding planes. Scale 1:6





Plate 5 Drillhole K120 (144-156 ft.). Partially to moderately oxidized and leached rock. Baryte veins. Scale 1:6



Plate 6 Drillhole K120 (156-171 ft.). Contact between unweathered rock and highly oxidized, leached material. Baryte fragments. Scale 1:6

was pyrite, occurring only as rare traces in K79. The pyrite is in the form of minute residual bodies in collomorphic limonite and goethite/hematite boxworks. Some of these boxworks clearly indicate that they are pseudomorphous after pre-existing micro-granular pyrite. No surviving galena or sphalerite could be recognized -- this is not surprising in view of the degree of oxidation of the pyrite. In K43, collomorphic iron oxides are again very common; also present are minor quantities of colloidal manganese oxides. No sulphides were detectable in this sample. The chief characteristic of all three samples is the dominant presence of iron oxide material.....

Electron probe microanalysis of K79, R1556 confirms the dominant presence of grains showing coincident iron-zinc-manganese with the absence of sulphur and silicon..... It is concluded that the zinc values are present in the form of oxides and hydroxides of iron and manganese."

Further, Patterson regards development of the Decomposed Zone as an "in situ" leaching from actively circulating waters along fault zones in the presence of the porous and chemically reactive Bioclastic Dolomites.

### 3.3 LOCATION AND GEOLOGICAL SETTING

Figure 6 outlines the drillholes intersecting leached and oxidized material. For the sake of continuity, all degrees of decomposition from partially to totally leached rock are included.

Figure 7 is a subsurface plan map showing isopach contours representing continuous zones of leached product. Pinching and swelling are evident, possibly reflecting some fault control and/or a changing chemical susceptibility of the Mixed Beds to advancing decomposition.

Section lines have been constructed and the relationship of



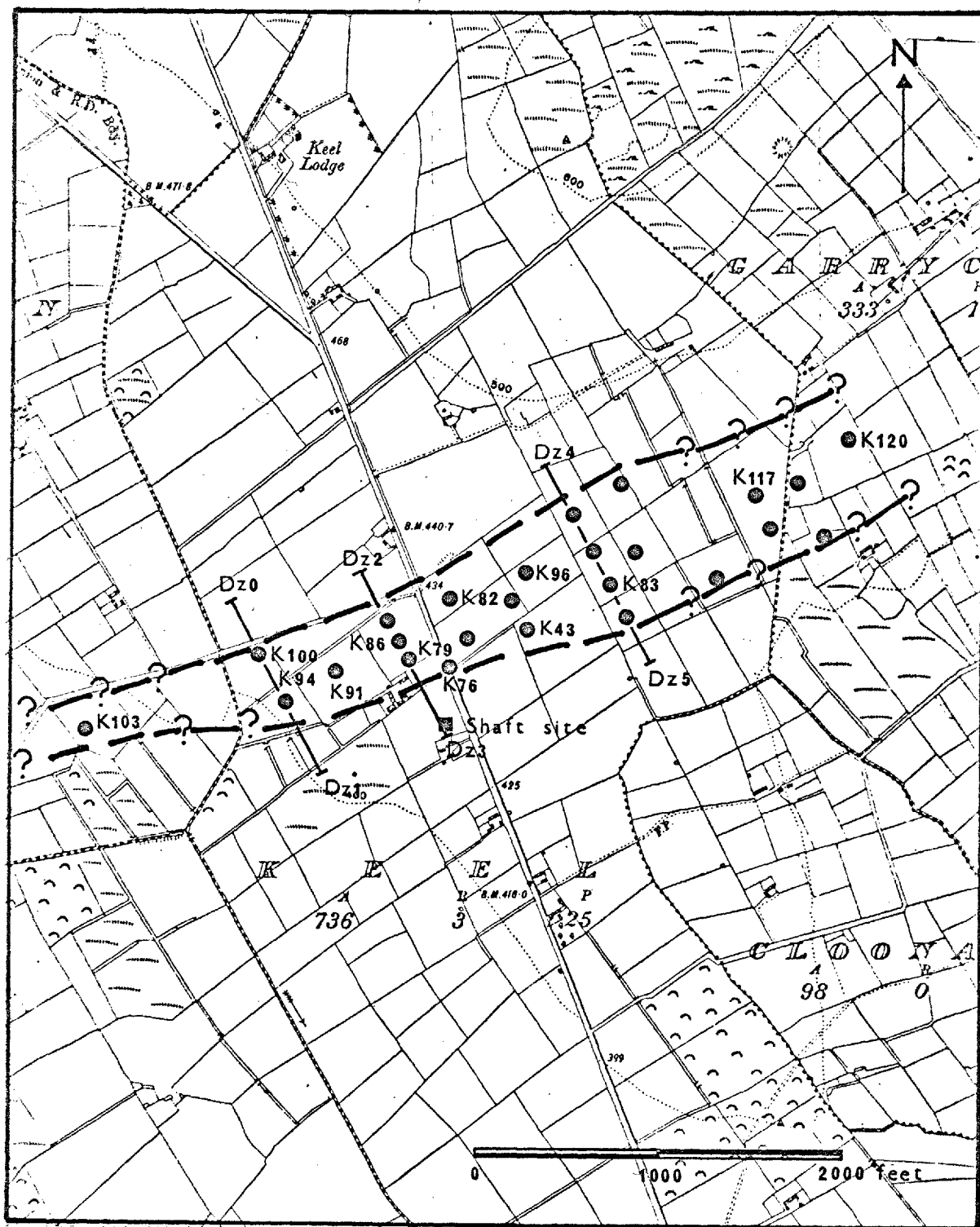


Fig. 6  
Drillholes intersecting  
the Decomposed Zone

● K96 Drillhole & No.  
Dz0 — ● — Dz1 Section line

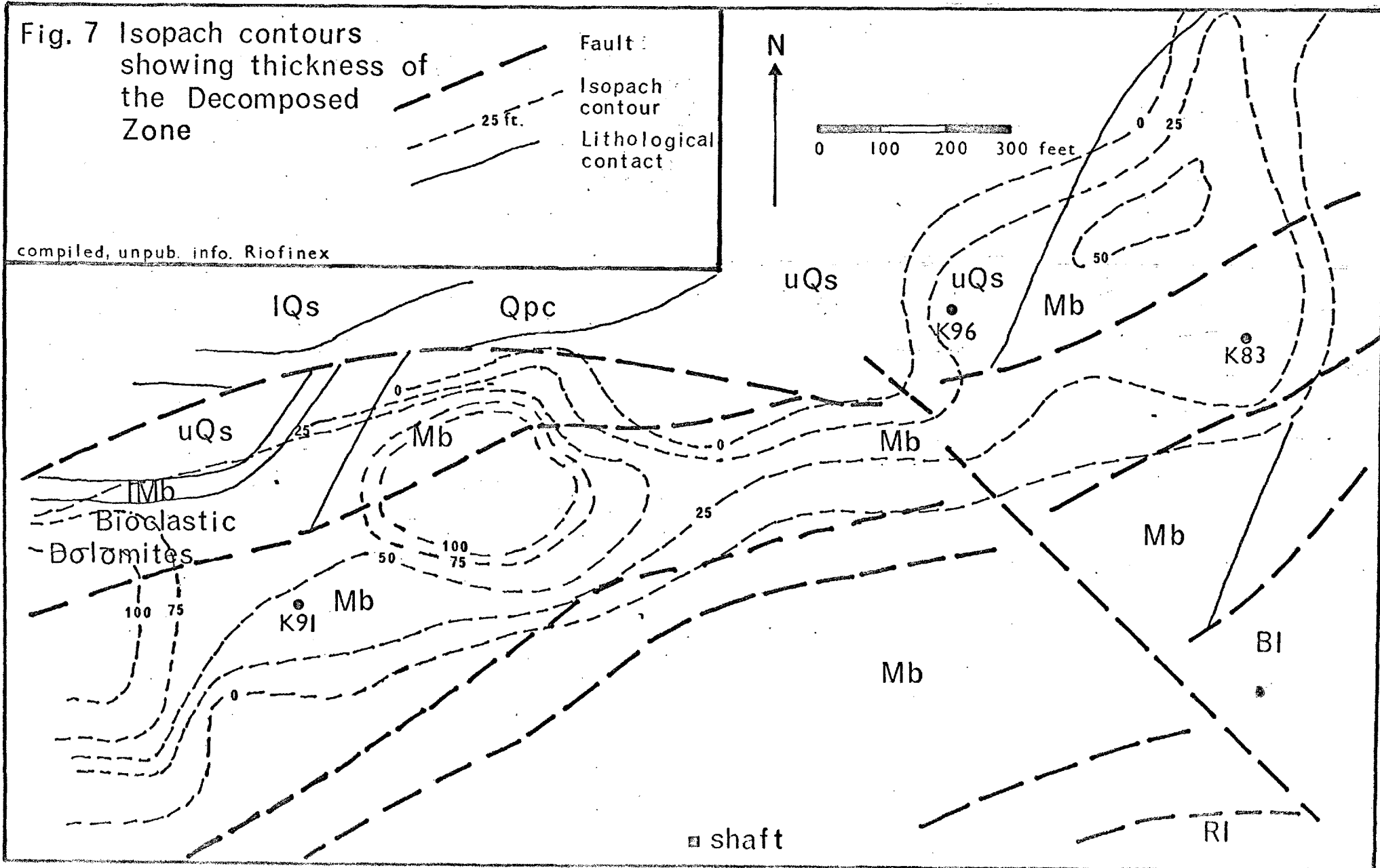
Fig. 7 Isopach contours showing thickness of the Decomposed Zone

Fault  
Isopach contour  
Lithological contact

N

0 100 200 300 feet

compiled, unpub. info. Riofinex



the Decomposed Zone with stratigraphy and structure and the overlying glacial till can be seen in Figure 8.

### 3.4 HISTORY AND DESCRIPTION OF THE DECOMPOSED ZONE

#### 3.4.1 Introduction

It is not within the scope of this research to completely discuss all aspects of the origin of the Decomposed Zone. However, some background information on genesis (particularly geochemical considerations) is required for an understanding of metal accumulation. Of real interest here is the influence of the subcropping metal reserves of the Decomposed Zone on the formation of soil anomalies.

Of prime consequence to a study of the origin of the Decomposed Zone is to ascertain the state of leaching prior to glaciation. That the Decomposed Zone did exist before the Pleistocene epoch (in some form) is known to a limited extent. A leached, iron-stained sandstone clast has been recovered from glacial till during drilling operations some 500 ft. east of the Keel shaft site. Analysis of the sample revealed little Pb, Zn, etc., but the appearance and texture of the sample much resembles some parts of "in-place" Decomposed Zone. Additional fragments of stained and leached material have been found in soil during pitting.

The climate of Ireland in pre-Quaternary times is thought to have been somewhat warmer than present day conditions. A humid environment is **thought** to have been prevalent during Tertiary times (Charlesworth, 1957). In such conditions, outcropping sulphides (or equivalent exposure to oxidation) would readily leach a chemically reactive gangue (limey-dolomitic sandstones and shales at Keel) and, perhaps, form an iron-rich gossan or capping.

At no one place has the Decomposed Zone been found to grade into

massive sulphide ore; hence, disseminated mineralization occurrences should be considered for sources of sulphuric acid required for leaching. Patterson (op. cit.) quotes Morley (a pers. comm.) that stratabound disseminated sphalerite is present in two discrete horizons in the Mixed Beds.

### 3.4.2 Gossan versus Capping

It is of some importance to distinguish between gossan and capping. Blanchard's treatise "Interpretation of Leached Outcrops" (1968) describes gossan as a "moderately heavy accumulation of limonitic material, derived in the main from massive sulphide ore minerals or from their iron-yielding gangue associates, which have been leached more or less in place, and which normally overlie an ore zone beneath." In general, the term gossan is not applicable unless cellular pseudomorphs or other porous limonitic material has been developed over an appreciable area.

On the other hand, "capping is a leached upper part of a body of rock that contains disseminated sulphide minerals. Limonite in capping is the result of leaching of small sulphide grains in unweathered rock, and the reproduction of part of all of the iron in situ or as a fringing product."

At Keel, the term "capping" is favoured to describe the Decomposed Zone on three accounts:

- i) The leached product is displaced laterally from the zone of faulting associated with the existing massive sulphide mineralization.
- ii) The dimensions of the Decomposed Zone are such that it is many times wider than the subcropping veins (i.e. a true gossan would subcrop an area approximating the narrow, near-vertical veins as found at Keel).

iii) The Decomposed Zone is developed laterally within the Mixed Beds.

A gossan would tend to transect Mixed Bed lithologies by the virtue of the nature of the veins.

### 3.4.3 Limonite at Keel

The term limonite is used to describe iron-rich weathered and oxidized material in the Keel Decomposed Zone. Blanchard (op. cit.) has quite rightly pointed out that no mineral corresponding to the old formula given for limonite --  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  -- has ever been identified. Hydrous ferric oxides are identified as goethite and lepidocrocite -- both  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . Nevertheless, the term limonite appears entrenched in the geological literature and the writer will continue its use to describe hydrous iron oxides. As manganese is also an important constituent of Decomposed Zone material (up to 13.2 per cent), it is also included under limonite (unless specifically noted). Supergene manganese minerals such as manganite ( $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), pyrolusite, braunite, and psilomelane are usually present in capping or gossan according to Blanchard (op. cit.).

Blanchard has divided the origin of limonites into three classifications: indigenous, fringing and exotic varieties.

Indigenous limonite is that precipitated from iron-bearing solutions within the cavity or space formerly occupied by a sulphide or other iron mineral. Fringing and exotic limonites are derived from iron-bearing solutions transported from local and distant sources.

The writer believes indigenous, fringing, and exotic limonites are present in the Decomposed Zone. Cellular pseudomorphs have been identified, while the environment (porous and chemically reactive lithologies, some iron sulphides, faults) would seem appropriate for the solution of Fe and precipitation of fringing and exotic limonites.

#### 3.4.3.1 "Fluffy" limonite

Limonite produced during neutralization tends to "fluff" up during formation, particularly in the zone of aeration (Blanchard, op. cit.). Totally decomposed, iron-rich material at Keel is of a very light and powdery nature and, in addition, partially corresponds to the environmental controls needed for "fluffy" limonite formation (Blanchard, op. cit.).

- i) Free though not necessarily rapid oxidation (not known at Keel).
- ii) Porosity sufficient during oxidation to permit "fluffing up" of limonites (Mixed Beds very porous).
- iii) Low content, or at least small precipitation of silica from ground water (Keel water has not been monitored for dissolved or colloidal silica but no silica precipitates have been observed.)
- iv) Limonite may be fringing, exotic or an indigenous product (indigenous and fringing limonites found at Keel).

#### 3.4.4 Some Textures Observed

Table 7 shows results of a hand lens and binocular microscope study of selected partially decomposed specimens from drillcore. Of particular interest is the presence of some delicately reticulated voids suggestive of a previous occupation by sphalerite. Cellular pseudomorphs after pyrite have not been positively identified, although poorly preserved voids (squarish appearance) are plentiful. An important feature is the selective decalcification and dedolomitization seen in some samples. Colour ranges from almost white "bleached" samples (originally carbonate-rich shale-mudstones-?) through bright ochrous shades to dark brown, almost black.

#### 3.4.5 Mineralogy

Pulped (>-295 mesh) samples have been analyzed by X-ray diffraction (XRD) using both powder and smear mountings to identify

Table 7. Binocular microscope and hand lens study of oxidized and leached rock

| D.D.H. | Ftge. | Field Description             | Staining                                     | Voids                                                   | Matrix                                                             | Probable Original Rock                  | Notes                                                  | Pertinent Drill Log Information                                 |
|--------|-------|-------------------------------|----------------------------------------------|---------------------------------------------------------|--------------------------------------------------------------------|-----------------------------------------|--------------------------------------------------------|-----------------------------------------------------------------|
| K82    | 46    | Partially decomposed          | Fe (ochrous) coating and Mn (black) paint    | Some circular poorly developed. V. f. resid. box-works. | Sugary to f. g. qtz.                                               | Impure calc. sst., possibly altered     | Remnant, narrow qtz. stringers                         | Massive white veins (qtz.). Broken and stained fault. Weak ZnS. |
| K82    | 58    | -                             | Little Fe and Mn staining, bleached product  | -                                                       | Clays (hydrous micas)                                              | V. f. g. clastic (shale-?) prob. calc.  | Some remnant bedding planes                            | Banded, grey and black siltstone. Soapy texture                 |
| K83    | 31    | Partially decomposed          | Ochrous Fe coatings. Some Mn.                | Many. Squarish appearance                               | Massive barytes, some stringers, qtz.                              | Baryte in sst. with low CO <sub>3</sub> | Orig. rock prob. brecciated and fractured              | Brecciated and leached mid grey sst. Weak ZnS                   |
| K83    | 37    | Partially decomposed          | Dk. br., Light br., reds, ochre, blk.        | None                                                    | Resids. and qtz. coated with limonite                              | Impure sst.                             | Metallic specks-graphite-? Micas, banding              | Decomposed yellow and brown rock                                |
| K83    | 125   | Contact, Decomposed Zone/rock | Rock - dk. grey, Decomposed Zone - dk. brown | Poorly developed                                        | Qtz., some micas, feldspars. Selective leaching of CO <sub>3</sub> | Impure sst.                             | Fronts of advancing decomposition, contact 2 mm wide   | Mixed Beds, dolom. sst.                                         |
| K83    | 142   | Contact, Decomposed Zone/rock | Rock - light grey, D. Z.-red, ochrous Mn     | Poorly developed, selective leaching                    | Qtz., amorph. Fe, Mn                                               | Impure, calc. sst.                      | Baryte flowers in D. Z.                                | Dolom. sst., tr. ZnS                                            |
| K120   | 146   | Partly decomposed             | Ochrous, br., dk. br.                        | Small circular, selective leaching                      | Residuals coated with limonite                                     | Calc. f. g. sst.                        | Advancing 'waves' of leaching. Some baryte             | 143'-148' baryte                                                |
| K120   | 155   | Baryte                        | Ochrous Fe, purple Mn                        | Small, delicate reticul. voids-sphal.?                  | Mixed baryte, qtz.                                                 | Massive baryte, qtz. vein               | Vugs, lined Fe, Mn staining                            | Massive BaSO <sub>4</sub> , sst. rich in ZnS                    |
| K120   | 206   | Baryte and voids              | Little Fe stain                              | Voids in qtz. square and reticulated                    | Qtz., baryte                                                       | Massive baryte, qtz.-rich sst.          | Tr. ZnS in baryte                                      | Tr. ZnS in sst. lengths                                         |
| K76    | 90    | Partly decomposed             | Dk. red, br., ochrous                        | Few real voids                                          | M. g. qtz. coated with limonite                                    | Qtz.-rich sst., some calc/dolom.        | Microtopo. devel. selective leaching                   | Mixed Beds, weathered 97'-100'-leached, brown, sandy rock       |
| K76    | 98    | Partly decomposed             | Br., some ochrous and blk. staining          | Well preserved reticul. voids-sphal.?                   | Qtz., coated with limonite                                         | Calc. sst.                              | Voids in a fracture                                    |                                                                 |
| K100   | 59    | Partially decomposed          | Br., dk. red, and purple                     | Voids of unknown origin                                 | Residual qtz. and clays                                            | Calc. sst.                              | Mn staining transported. Microtopo. selective leaching | Brown decomposed f. g. sst.                                     |

mineral species. The nature and form of the hydrous manganese oxides has not been positively identified, supplementing Millman's evidence of collomorphic varieties. Goethite has been established as the iron mineral. Quartz was identifiable in all samples and in most instances appeared to be the major mineral present. Ten angstrom hydrous micas were identified in most samples and potassium feldspar in a few. Calcite and dolomite peaks were not distinguishable in any totally leached samples

Illites ( $10 \text{ \AA}$  hydrous micas) were found to be present in large quantities in the bleached, almost white samples thought to have originally been calcareous shales and mudstones.

Overall, the mineralogical findings are consistent with analytical data and observations that the Decomposed Zone was originally composed of calcareous-dolomitic sandstones and shales. Decalcified and dedolomitized analogues would contain quartz, clays, and other acid insoluble minerals such as goethite and hydrous Mn oxides.

### 3.5 A GEOCHEMICAL MODEL FOR GENESIS OF THE DECOMPOSED ZONE

#### 3.5.1 The Importance of Water-Table Level

A study of the genesis of the Decomposed Zone is hindered by lack of any real information on water-table levels in pre-Pleistocene time. According to Blanchard (op. cit.), the best examples of preserved leached outcrop and subcrop are those with a history of a gradually decreasing water-table. At Keel, it would seem that a relatively warmer climate (and possibly deep water-table) has been followed by a cool, damp climate and shallow water-table. A climatic reversal in the natural development of the ideal leached outcrop/subcrop would probably change some secondary chemical processes. In addition, delicately formed textural features and soluble secondary



minerals would be lost, further obscuring any remnant history.

Kelly (1958) states that areas of heavy rainfall are unfavourable for the formation of gossan. Hence, a discussion on the genesis of the Decomposed Zone can really only be conjectural and/or comparative with known oxidized and leached outcrops/subcrops.

In the zone of aeration, mixing of atmospheric air and unweathered rock along fractures and joints is aided by rain water and if accompanied by warm temperatures, oxidation can proceed rapidly. At each influx of rain, the solubles are washed away, new surfaces exposed and "new" oxidation begins again.

Conditions are markedly different below the water-table than above it. There is no circulation of air, no intrushes of water and the temperature is much the same year round. Chemical activity in the zone of saturation takes place in a "bath" of solute, and according to Blanchard (op. cit.) reactions are weaker than those in the zone of aeration. Fractures, faulting and porosity are important here in that they provide contact to unreacted areas and channels for circulation.

Although sulphides are vulnerable to attack wherever exposed within the zone of oxidation, the most persistent and widespread attack upon them normally takes place directly above the water-table. Presumably, the presence of both water and air hastens oxidation. As the attack upon this horizon progresses, the rock becomes increasingly porous, the water-table may drop and the process of oxidation "eats" its way deeper.

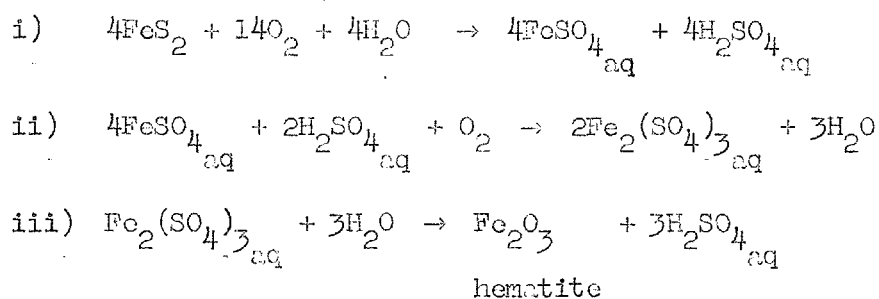
At Keel, the fracturing and faulting of a chemically reactive and porous lithology known to be the host of some disseminated sulphide mineralization provides an ideal environment for the development of the "leached outcrop/subcrop". However, oxidation and leaching processes have been complicated by reactions both above and below the

water-table. The relative importance of pre-glacial weathering opposed to glacial and post-glacial oxidation/leaching is difficult to assess.

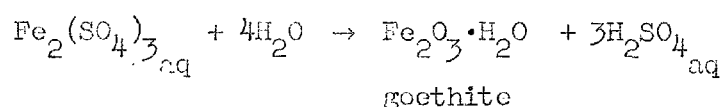
### 3.5.2 The Need for Sulphur to Oxidize and Leach

As sulphides are oxidized most often by reaction with sulphuric acid and/or ferric sulphate solutions, a source (internal or external) of sulphur is required to initiate oxidation and subsequent leaching.

Certain sulphides are deficient in sulphur (i.e.  $\text{Cu}_2\text{S}$ ) while others contain just enough sulphur for their complete solution (i.e.  $\text{PbS}$  and  $\text{ZnS}$ ). A few sulphides contain more than enough sulphur for solution and yield free sulphuric acid on complete oxidation (i.e.  $\text{FeS}_2$ ,  $\text{CuFeS}_2$ ). Keel massive ore is mainly composed of relatively iron-free sphalerite (Chapter One) and little free sulphuric acid and ferrous sulphate could be generated. However, as disseminated pyrite is ubiquitous throughout the Lower Carboniferous elastic rocks and carbonates in the Longford District, additional sulphuric acid and ferrous sulphate potential exists. The presence of pyrite in Keel rocks and ore is well known, but quantitative information is spotty. The occurrence of massive pyrite in the Reef Limestone certainly points to the possibility of additional pyrite sources being present. From Blanchard (op. cit.) the following equations seem appropriate.

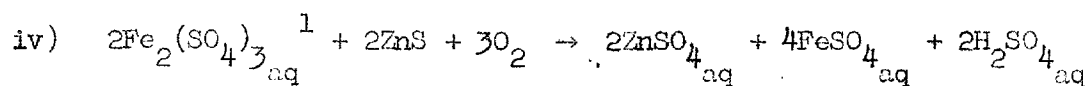


or

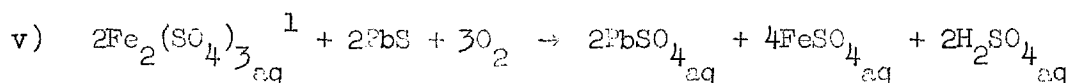


Hydrolysis is not the only process to bring about precipitation of limonite. Any neutralization of sulphuric acid will accomplish the same end. At Keel, this reaction may easily occur with acid, Fe-bearing solution contact with calcite-dolomite. In addition, Blanchard (op. cit.) states: "If pyrite occurs with sphalerite or galena in shale, feldspar or limestone gangues, air-water processes alone will cause precipitation of limonite."

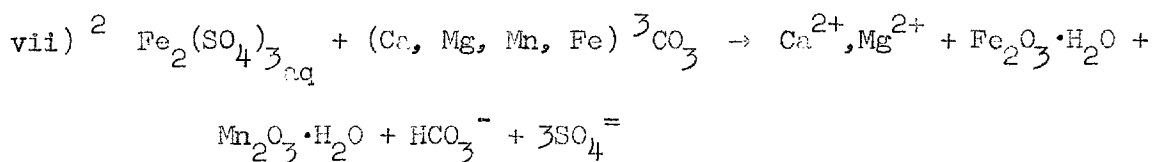
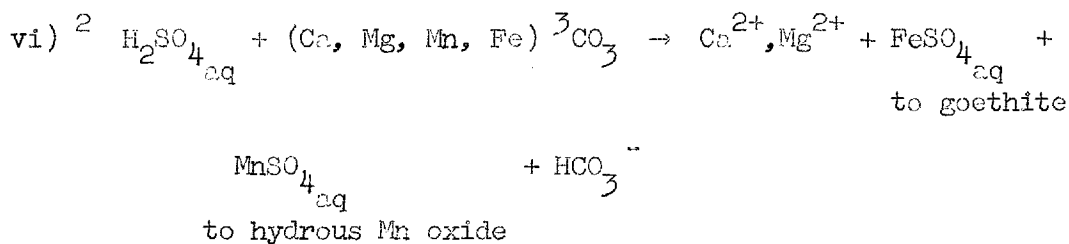
Sphalerite will go into solution on prolonged contact with  $\text{Fe}_2(\text{SO}_4)_3$  and some additional free  $\text{H}_2\text{SO}_4$  and  $\text{FeSO}_4$  generated. With the presence of a neutralizing gangue (at Keel, calcareous-dolomitic sandstones) the reactions now become exceedingly complex and an idealized geochemical reaction scheme is presented below.



and



Subsequently, sulphuric acid and ferric sulphate would react with carbonates as follows:




---

<sup>1</sup> generated by equations (i) and (ii)

<sup>2</sup> equations not balanced

<sup>3</sup>  $\text{Ca} > \text{Mg} \geq \text{Fe} \geq \text{Mn}$

Obviously, the chemical reactions required to produce hydrous iron and manganese oxides are not as completely simple as given above, and the introduction of additional elements would certainly add to the complexity. The above equations are presented only to idealize the geochemical phenomena of hydrous iron and manganese oxide formation by precipitation of ionic Fe and Mn through neutralization.

Of further interest, a slightly acid residual environment has been determined on Decomposed Zone -80 mesh fines using "regenerated" pH's. A range of 5.4 to 7.3 and a mean value of 6.5 were determined on selected deionized water slurries.

### 3.5.3 A Comparison with Genesis of the Tynagh Residual Deposit

Morrissey and Whitehead (1966) have studied the residual oxide and sulphide accumulation of base metals at Tynagh. They suggest aerial oxidation of sulphide ore to leached outcrop in pre-glacial times, incubation and water saturation during glacial and post-glacial times and further alteration of the original secondary products. A fluctuating water-table (and reducing environment) has produced conditions favourable for the formation of some secondary sulphides. Mass chemical changes have been accompanied by some mechanical re-working of the residuum. In comparison with Keel, the Tynagh oxides and secondary sulphides are situated vertically above the primary massive sulphides; hence, the original Tynagh leached outcrop was probably a gossan and not a capping as believed existed at Keel in pre-glacial time.

### 3.5.4 Base Metal Retention

It is during the stage of iron and manganese precipitation that interest in the Keel Decomposed Zone as a trace metal reservoir arises. Normally, an acid environment would aid migration and loss of dissolved metals such as Zn and Cd and, perhaps, Pb and Hg.

The writer believes that the large surface areas created by the formation of collomorphic Fe and Mn oxides (Jenne, 1968 and others) effectively sequestered base metals from solution. Sources of metals include both soluble sulphates from oxidized disseminated sulphides and soluble ionic species and complexes released from calcareous and dolomitic sandstones and shales during leaching.

### 3.6 METALS IN THE DECOMPOSED ZONE

#### 3.6.1 Introduction

Hawkes and Webb (op. cit.) state "Chemical composition as a basis for appraising secondary limonitic material can be put on a quantitative basis much more easily than studies of colour and texture." This quotation refers to the time-honoured practice of distinguishing metalliferous gossans from transported (exotic) gossans by study of diagnostic textures (cellular pseudomorphs and colour characteristics). Although a worthy avenue of research, the approach tends to be subjective and Kelly (op. cit.) and Blanchard (op. cit.) both note difficulties in application.

Cellular pseudomorphs have been identified in leached subcrop (Table 7) and some are suggestive of a sphalerite origin. Millman (op. cit.) identified boxwork structures after pyrite. Some ochrous stained voids observed by the writer appeared to be of a pyritic origin. Colour has not been attempted as an assessment of origin or metalliferous nature as staining tends to change quickly over short lengths (see Plates 3 and 4). This probably reflects remnant compositions and bedding planes of the original Mixed Beds lithologies.

As an alternative approach, multi-element analysis for selected trace metals and associated elements has been applied to oxidized and leached material with three main aims:

- i) Additional data to support genesis hypothesis
- ii) Ore and trace element ranges, means, and their influence on soil anomaly formation
- iii) Ore and trace element retention properties of hydrous Fe-Mn oxides

Hawkes and Webb (op. cit.) are of the opinion that leached capping and gossan formed from the weathering of ores of Cu, Co, Mo, and Ni and other metals that are commonly co-precipitated with Fe hydroxides can often be recognized by their high ore metal content as compared with lateritic limonites, bog iron ores, and the weathering products of barren syngenetic sulphides and Fe-bearing carbonates. Examples given include Cu, Co, Ni, Pb, Zn, Mo, Au, and Ag retention and/or accumulation by gossans and "pseudogossans". In addition, they quote Sindeyeva (1958) noting that gossans covering epigenetic sulphides are characterized by high contents of Se.

Blanchard (op. cit.) has determined selected metals in leached and oxidized material over Australian Pb-As deposits and recorded the retention of Pb and As with lesser amounts of Cu and Zn.

Krauskopf (1956) has noted Hg and other metals can be absorbed by  $\text{Fe}(\text{OH})_3$ . Erickson et al. (1966) report anomalously high concentrations of Hg in Pb and Zn-rich gossans in carbonate terrane in Nevada, U.S.A. Donovan (1965) records anomalous values of Hg, Zn, Pb, and Cu associated with limonitic muds at the Tynagh deposit, Co. Galway.

Jenne (op. cit.) has proposed that hydrous oxides of Mn and Fe furnish the principal control on the fixation of Co, Ni, Cu, and Zn (heavy metals) in soils and fresh water sediments. Sorption and desorption occurs in response to aqueous concentrations of Fe, Mn, and heavy metals, pH and the presence of organic and inorganic complexing agents in solution.

### 3.6.2 Metal Enrichment Ratios

At Keel, metal enrichment in the Decomposed Zone has been studied by analysis of partially, moderately, and totally leached material. A total of 106 samples from the Decomposed Zone were analyzed for As, Sb, Hg, Cd, Pb, Zn, Mn, Fe, Ca, Mg, Cu, Ag, Ba, Sr, Ni, Co, Cr, Ga, V, Mo, and Ti. An associated study including 30 mineralized tills to investigate vertical/lateral dispersion of elements and enrichment is also reported.

Unweathered rock from drillcore was analyzed to ascertain the degree of relative metal enrichment in the Decomposed Zone. This aspect of the study is not completely comprehensive as only 30 rock samples were collected. A more thorough study of element distribution in Keel carbonate and clastic rocks is currently under investigation by J. Watling (pers. comm.).

Tables A6, A7, and A8 (Appendix Six) contain the analyses used to tabulate data shown in Table 8. Simply, element levels in rock, till, and Decomposed Zone are compared and contrasted using arithmetic mean values to establish relative metal enrichment ratios. The Decomposed Zone samples for Table 8 (31 in number) were selected from three continuously oxidized and leached sections.

### 3.6.3 Discussion on Tables 8 and 9

The principal ore elements found in Keel sulphide ore (Zn, Cd, and Pb) are enriched in the Decomposed Zone relative to enclosing rocks and overlying tills. Mercury and Ba also show similarly high enrichment coefficients. Manganese and Fe are not as highly enriched in leached material as the ore metals and Ba.

Decalcification and dedolomitization are both overly evident while minor concentration of As, Sb, Cu, Mo, Ni, and Ti (sources include carbonate-leached residues and, perhaps, pyrite) is weakly

Table 8. Relative enrichment ratios

| Element | D. Z./Rocks<br>(all rock<br>samples) | D. Z./Rocks<br>(Mixed Beds<br>only) | D. Z./Tills | Tills/Rocks |
|---------|--------------------------------------|-------------------------------------|-------------|-------------|
| As      | 1.9                                  | 1.2                                 | 2.0         | 0.9         |
| Sb      | 1.7                                  | 1.2                                 | 0.8         | 2.0         |
| Hg      | 14                                   | 10                                  | 2.5         | 5.5         |
| Cd      | 16                                   | 15                                  | 11          | 1.5         |
| Pb      | 16                                   | 11                                  | 3.0         | 5.4         |
| Zn      | 12                                   | 8.3                                 | 5.9         | 2.0         |
| Mn      | 9                                    | 6.1                                 | 3.7         | 2.4         |
| Fe      | 4.3                                  | 4.1                                 | 2.6         | 1.7         |
| Ca      | 0.02                                 | 0.03                                | 0.16        | 0.13        |
| Mg      | 0.14                                 | 0.11                                | 0.51        | 0.27        |
| Cu      | 2.9                                  | 2.6                                 | 1.1         | 2.6         |
| Ag      | 5.0                                  | 2.9                                 | 5.5         | 0.9         |
| Ba      | 14                                   | 11                                  | 2.6         | 5.5         |
| Sr      | 0.4                                  | 0.5                                 | 0.8         | 0.5         |
| Ni      | 1.6                                  | 1.5                                 | 1.1         | 1.4         |
| Co      | 0.7                                  | 0.7                                 | 0.6         | 1.3         |
| Cr      | 0.4                                  | 0.4                                 | 0.5         | 0.8         |
| Ga      | 0.7                                  | 0.7                                 | 0.7         | 1.0         |
| V       | 0.9                                  | 0.9                                 | 0.6         | 1.6         |
| Mo      | 2.6                                  | 2.2                                 | 1.8         | 1.5         |
| Ti      | 1.4                                  | 1.3                                 | 1.0         | 1.4         |

D. Z. = Decomposed Zone



Table 9. Basic statistical data on total element levels in the Decomposed Zone (106 samples)

| Element |     | Range                    | Arithmetic Mean | Standard Deviation | <u>S.D.</u><br>Mean |
|---------|-----|--------------------------|-----------------|--------------------|---------------------|
| As      | ppm | 3 - 750                  | 94              | 116                | 1.2                 |
| Sb      | ppm | 0.5 - 50                 | 15.8            | 13.5               | 0.9                 |
| Hg      | ppb | 20 - 160000              | 5347            | 15874              | 3.0                 |
| Cd      | ppm | <1 - 5000                | 263             | 589                | 2.2                 |
| Pb      | ppm | 30 - 24000               | 2469            | 4516               | 1.8                 |
| Zn      | ppm | 300 - 125000             | 13606           | 18883              | 1.4                 |
| Mn      | ppm | 100 - 132000             | 34416           | 28207              | 0.8                 |
| Fe      | %   | 0.5 - 30                 | 10.0            | 5.9                | 0.6                 |
| Ca      | ppm | <100 - 124000            | 2992            | 1057               | 0.4                 |
| Mg      | ppm | 100 - 68000              | 5014            | 726                | 0.1                 |
| Cu      | ppm | <5 - 400                 | 42              | 59                 | 1.4                 |
| Ag      | ppm | <0.2 - 100               | 8.5             | 12.1               | 1.4                 |
| Ba      | ppm | 100 - 17000 <sup>1</sup> | 7135            | 6291               | 0.9                 |
| Sr      | ppm | 15 - 1000                | 67              | 107                | 1.6                 |
| Ni      | ppm | 5 - 400                  | 90              | 74                 | 0.8                 |
| Co      | ppm | <5 - 400                 | 21              | 42                 | 2.0                 |
| Cr      | ppm | 8 - 160                  | 35              | 27                 | 0.8                 |
| Ga      | ppm | <2 - 40                  | 10              | 6.8                | 0.7                 |
| V       | ppm | 10 - 160                 | 44              | 27                 | 0.6                 |
| Mo      | ppm | <2 - 20                  | 4.7             | 4.4                | 0.9                 |
| Ti      | ppm | 500 - 4000               | -               | -                  | -                   |

<sup>1</sup> Many values over 1% (upper limit of spectrographic method). Extrapolated distribution curve suggests 1.7% probable average value of samples >1%.

evident. Silver shows relatively high enrichment in the Decomposed Zone and metal contribution from both sulphide ore and acid insoluble residues and/or pyrite sources seems possible.

Overall, enrichment ratios would seem to support Hg, Zn, Cd, and Pb sources from disseminated sphalerite-galena. Other enriched elements would appear to be derived from residual or scavenged sources originally in carbonate rocks or in disseminated pyrite.

Although not included in the enrichment and statistical study, Se, Au, Zr, K, Rb, and organic carbon were determined on some selected samples to study enrichment (or depletion).

Selenium and Au were not detected in any samples (less than 1 ppm and 50 ppb, respectively). As pyrite is also deficient in these elements (to the same degree), the results are not surprising.

Phosphorus ranges from 140 to 500 ppm in leached material with no distinguishable pattern (from limited data) observable.

Potassium and Rb were determined on a number of Decomposed Zone samples and rocks and while good correlation exists between the two elements, concentration was only observed in the bleached samples absent of ferric or manganese staining. As the mineralogy of these samples has been established to be primarily hydrous micas (illites), above average K and Rb values are consistent with geochemical data on the mineral.

Organic carbon was determined on a few leached samples and yielded totally negative results.

#### 3.6.4 Correlation Pairs

Correlation coefficients for selected elements have been determined for all 106 samples in the Decomposed Zone as well as for all rock and till samples. The computer programme used to calculate correlation coefficients was written by R. J. Howarth of the Applied

Geochemistry Research Group and the writer gratefully acknowledges Dr. Howarth's help.

Table 10 shows correlation pairs of metals in two ranges. Rocks and tills exhibit many of the classic metal paragenetic associations while the Decomposed Zone is seemingly "washed" of most correlation pairs (over the selected coefficient ranges). The reason for this is not known, but it is speculated that acid leaching has effectively redistributed and/or modified metal associations.

The Hg-Ag, Zn-Cd, and Fe-Mn pairs are very strong, reflected in each media. The Hg-Ag association may be a naturally-occurring amalgamation.

### 3.7 METAL DISPERSION THROUGH GLACIAL TILL AT KEEL

#### 3.7.1 Introduction

Figure 9 shows selected element levels in glacial till and Decomposed Zone from two drillhole profiles at Keel. In each instance, the area approximating the contact between the Decomposed Zone and till shows some metal enrichment of the till. Generally, ore metals, Hg, and S show a sympathetic relationship with Fe and Mn while Ca and Mg exhibit an antipathetic relationship with Fe-Mn. To understand more fully the levels of elements involved in vertical (capillary) dispersion, cold-extractable determinations were employed for Zn, Cd, Pb, Mn, and Fe, on both tills and the Decomposed Zone.

#### 3.7.2 Cold-Extractable Metals in Decomposed Zone and Till

Investigation of the chemical movement and upward migration of metals has been attempted through "availability" studies using cold-extractable solutes (see Appendix Two for analytical details). An abstracts publication entitled "Determination of Zinc and Zinc Availability in Soils, 1956-1969" (Commonwealth Bureau of Soils)

Table 10. Correlation pairs for selected elements<sup>1</sup>  
in Decomposed Zone<sup>2</sup>, rocks<sup>3</sup>, and tills<sup>4</sup>.

| Correlation<br>Coefficient<br>Range | >+ .700                          | .500 - .700                                                                                                                                           |
|-------------------------------------|----------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|
| Rocks                               | Hg-As<br>Hg-Ag<br>Zn-Ag<br>Pb-Sb | Hg-Sb<br>Hg-Cd<br>Hg-Pb<br>Hg-Zn<br>Zn-As<br>Zn-Cd<br>Cd-Ag<br>Pb-Ag<br>Fe-Mn<br>Ag-As<br>Ag-Sb                                                       |
| Tills                               | Hg-Sb<br>Zn-Cd<br>Fe-Mn<br>Fe-Ba | Hg-As<br>Hg-Zn<br>Hg-Ag<br>Zn-As<br>Zn-Pb<br>Zn-Mn<br>Zn-Ag<br>Cd-As<br>Cd-Pb<br>Cd-Mn<br>Fe-Ag<br>Mn-As<br>Mn-Ag<br>Mn-Ba<br>Ag-Sb<br>Ba-Ag<br>As-Sb |
| Decomposed Zone                     | Hg-Ag<br>Zn-Cd                   | Fe-Mn                                                                                                                                                 |

<sup>1</sup> Hg, Zn, Cd, Pb, Fe, Mn, Ag, Ba, As, Sb

<sup>2</sup> 106 samples, .250 99% significant

<sup>3</sup> 30 samples, .500 99% significant

<sup>4</sup> 30 samples, .500 99% significant

indicates that many different buffer extractants have been used to determine "available" zinc and other metals in soils. Among these include 0.1N HCl, EDTA<sup>1</sup>, NH<sub>4</sub>OH, KCl, CaCl<sub>2</sub>, KNO<sub>3</sub>, 0.1N HNO<sub>3</sub>, MgSO<sub>4</sub>, and a host of acetate and/or citrate buffer mixtures.

Little work has been reported on cold leaching of mixtures of colloidal iron-manganese minerals for the determination of trace metals. Hence, some preliminary experiments were performed to test prospective cold-extractable solutions.

Three extractants were selected for testing.

- i) 0.1M EDTA (diammonium salt)
- ii) 3 per cent (0.5M) acetic acid
- iii) 1N KCl

Table 11 briefly outlines solution properties and conditions expected during a three hour leach period.

Table 12 shows results of cold leaching experiments with selected Decomposed Zone samples for Zn, Cd, Pb, and Mn. EDTA extractions prove by far the most efficient (relative to total levels), particularly with Pb and Mn, but less marked with Zn and Cd (relative to acetic acid extractions). Two Pb determinations on EDTA leaches are greater than the total values suggesting the hot acid attack may be ineffective on some naturally-occurring Pb compounds or may have rendered the Pb passive during digestion.

Overall, Table 12 suggests certain metallic elements in the Decomposed Zone may have some migration potential in a moderately acid environment and/or are readily chelatable. Presumably, solution mechanisms involve metal release during neutralization of Fe(OH)<sub>3</sub> or liberation from positively charged clay minerals in the case of acetic acid and complex formation in the case of EDTA.

As EDTA was shown to be the most effective cold extractant,

<sup>1</sup> Ethylene Diamine Tetracetic Acid

Table 11. Cold extraction buffer mixtures

| Cold extractant                                  | Solution                                                                                 | Element release mechanism                                                                              | Extracted element form                                                  | Notes                                                                                                                                 |
|--------------------------------------------------|------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|
| 0.1M EDTA (Di-NH <sub>4</sub> salt) <sup>4</sup> | Active chelating agent (pH 10-11)                                                        | Chelates many transition metals <sup>1</sup> and their cationic and anionic complexes                  | Readily available <u>plus</u> chelatable forms at pH > 8 ≤ 12           | EDTA may dissolve metal oxides on prolonged contact                                                                                   |
| 3% (0.5M) acetic acid                            | Moderately acid (pH < 3.0)                                                               | Moderately acid soluble metals, some release from Fe(OH) <sub>3</sub> and cation exchange from illites | Readily available <u>plus</u> moderately acid-extractable forms.        | 2.5% normally used in soil availability studies. 3.0% used here as added buffer capacity for potential CO <sub>3</sub> .              |
| 1N KCl                                           | Neutral solution, no hydrolysis with equi-dimensional K <sup>+</sup> and Cl <sup>-</sup> | Ideally, a return to water-saturated conditions with little pH shift.                                  | Readily available elements (water soluble, ionic species and complexes) | Autocomplexation of chlorides (and other halides) may solubilize more Pb, Zn, and Cd <sub>2</sub> than readily available <sup>2</sup> |

<sup>1</sup> (Hg<sup>++</sup>) > Pb<sup>++</sup> > Zn<sup>++</sup> = Cd<sup>++</sup> > Fe<sup>++</sup> > Mn<sup>++</sup> (after Fisher Scientific Co. TD-104)

<sup>2</sup>  $\text{MCl}_2 + (2)\text{Cl}^- \rightarrow \text{MCl}_4^{=}, \text{MCl}_3^-$

Table 12. Comparison of cold extractants on selected samples from the Decomposed Zone

| Drillhole/<br>Footage | Total     |           |           |         | 1N KCl    |           |           |           | 3% Acetic Acid |           |           |           | 0.1M EDTA |           |           |         |
|-----------------------|-----------|-----------|-----------|---------|-----------|-----------|-----------|-----------|----------------|-----------|-----------|-----------|-----------|-----------|-----------|---------|
|                       | Zn<br>ppm | Cd<br>ppm | Pb<br>ppm | Mn<br>% | Zn<br>ppm | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Zn<br>ppm      | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Zn<br>ppm | Cd<br>ppm | Pb<br>ppm | Mn<br>% |
| K86, 61'              | 1600      | 30        | 3600      | 0.6     | 17        | <1.0      | 90        | 38        | 38             | 3.0       | 375       | 135       | 320       | 1.0       | 2000      | 0.3     |
| K86, 116'             | 4130      | 70        | 7800      | 3.9     | 25        | 3.0       | 30        | 63        | 231            | 7.5       | 645       | 765       | 960       | 26        | 4500      | 0.2     |
| K91, 105-109'         | 4500      | 39        | 200       | 1.6     | 17        | 6.0       | <10       | 45        | 292            | 18        | <10       | 525       | 620       | 22        | 150       | 0.9     |
| K91, 110-114'         | 5500      | 43        | 90        | 4.9     | 13        | 6.0       | <10       | 25        | 360            | 27        | <10       | 795       | 1020      | 31        | 130       | 1.3     |
| K94, 122-126'         | 11500     | 239       | 110       | 4.0     | 60        | 43        | <10       | 16        | 2490           | 125       | <10       | 1020      | 6100      | 198       | 70        | 2.3     |
| K94, 154-158'         | 9500      | 263       | 400       | 7.6     | 4         | 3.0       | <10       | 6         | 2020           | 102       | <10       | 720       | 2360      | 199       | 630       | 5.5     |
| K120, 75-77'          | 4400      | 16        | 4150      | 0.5     | 46        | 2.0       | 30        | 72        | 253            | 4.5       | <10       | 210       | 560       | 9.0       | 3000      | 0.3     |
| K120, 86'             | 4350      | 17        | 2250      | 0.6     | 50        | 1.0       | 10        | 25        | 216            | 6.0       | 375       | 120       | 600       | 10        | 2500      | 0.4     |

continued investigations on metal dispersion through tills were undertaken using this solution.

Table 13 shows selected element determinations on glacial till and on the Decomposed Zone. Both total and cold-extractable levels increase with depth suggesting a "capillary" (chemical) dispersion of metals. It should be noted that the drillholes are not vertical (inclined at 60 degrees) and the dispersions are those at 30 degrees from the normal. Also, poor core recovery has limited sampling, resulting in an incomplete study of drillholes K82 and K83.

Secondary dispersion through glacial tills is also examined in Chapter Four in discussion of the link between soil anomalies and selected metal levels in glacial tills.

### 3.8 SUMMARY

From limited observations and geochemical analyses, the Decomposed Zone is attributed to be a leached outcrop (subcrop now), perhaps modified by incubation during glacial periods and subsequent ground water saturation. A number of points require recapitulation.

i) An iron and manganese-rich capping has formed at the expense of the porous, chemically reactive carbonates in the Mixed Beds (including the Bioclastic Dolomites) and now occupies a large subsurface zone laterally displaced from the massive sulphide mineralization.

ii) Disseminated sphalerite and galena and unknown amounts of pyrite have been subjected to oxidation both above and below the water-table. Sulphuric acid and ferrous sulphate solutions have attacked and leached calcareous and dolomitic sandstones, mudstones, and shales. The net result was to precipitate hydrous Fe and Mn oxides and the eventual loss to ground water of Ca, Mg, and alkali metals.



Table 13. Secondary dispersion of selected metals through glacial till covering the Decomposed Zone

| Drillhole<br>and Footage | Descrip-<br>tion | Total     |           |           |           |         | EDTA Extractable |           |           |           |           |
|--------------------------|------------------|-----------|-----------|-----------|-----------|---------|------------------|-----------|-----------|-----------|-----------|
|                          |                  | Zn<br>ppm | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Fe<br>% | Zn<br>ppm        | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Fe<br>ppm |
| K82, 18"                 | Clay             | 910       | 10        | 800       | 300       | 2.3     | 97               | 6.0       | 370       | 690       | 430       |
| K82, 3'                  | Clay             | 1190      | 20        | 2600      | 6500      | 2.8     | 166              | 5.0       | 1240      | 230       | 230       |
| K82, 5'                  | Clay             | 3000      | 30        | 6500      | 2300      | 3.8     | 870              | 8.0       | 2400      | 620       | 620       |
| K82, 32-39'              | D. Z.            | 2500      | 20        | 3000      | 6000      | 10.8    | 68               | 1.0       | 720       | 850       | 60        |
| K83, 12-13½'             | Till             | 1650      | 7.0       | 440       | 1000      | 2.9     | 32               | 3.5       | 220       | 640       | 350       |
| K83, 20'                 | Till             | 6500      | 101       | 10200     | 48200     | 6.2     | 1035             | 34        | 1800      | 8750      | 800       |
| K83, 25'                 | Till/D. Z.       | 490       | 5.0       | 6450      | 8500      | 2.8     | 75               | <1.0      | 760       | 850       | 100       |
| K117, 12-15'             | Till             | 190       | 3.0       | 100       | 500       | 2.7     | 19               | 1.0       | 95        | 285       | 425       |
| K117, 15-18'             | Till             | 250       | 5.0       | 130       | 600       | 2.7     | 13               | 2.0       | 50        | 385       | 205       |
| K117, 18-21'             | Till             | 410       | 7.0       | 180       | 900       | 3.2     | 25               | 3.0       | 85        | 785       | 175       |
| K117, 21-23'             | Till             | 660       | 6.0       | 240       | 1200      | 1.9     | 53               | 3.0       | 155       | 685       | 175       |
| K117, 31-32'             | Till             | 25000     | 4.0       | 980       | 9500      | 4.5     | 50               | 2.0       | 590       | 800       | 150       |
| K117, 33-36'             | D. Z.            | 11250     | 84        | 8750      | 64000     | 15.0    | 2800             | 48        | 1300      | 31000     | 8500      |
| K117, 38-42'             | D. Z.            | 3750      | 88        | 820       | 34000     | 6.5     | 350              | 26        | 1370      | 8730      | 2780      |
| K117, 58'                | D. Z.            | 17300     | 31        | 2900      | 1400      | 30.0    | 960              | 7.0       | 1270      | 1340      | 250       |

D. Z. = Decomposed Zone

iii) Metallic trace elements (sulphide and acid insoluble residue sources) have been retained by the large surface area hydrous Fe-Mn oxides thus creating a metal-rich reservoir. Some enrichment is probably due to an overall loss of rock volume.

iv) Metals noticeably enriched in the Decomposed Zone include Zn, Cd, Pb, and Ag. Ba is also highly enriched. As, Sb, Cu, Mo, Ni, and Ti have been slightly concentrated relative to enclosing rocks and their origin is believed to be an accumulation derived from the acid insoluble residues and pyritic sources.

v) Mercury enrichment is marked in Fe and Mn-rich material at Keel. An arithmetic mean of 5.3 ppm has been calculated for 106 samples. A high degree of correlation is shown between Hg and Ag in rock, till, and the Decomposed Zone.

vi) Metals (Zn, Cd, Pb, Mn) may be released from hydrous Fe-Mn oxides using 3 per cent acetic acid or 0.1M EDTA. Of the two, EDTA is the more effective agent. One N KCl extractions released little metal to solution.

vii) EDTA-extractable metals have been employed to demonstrate potential element levels available for vertical (capillary) dispersion from the Decomposed Zone through the covering glacial till.

viii) Although not discussed in this chapter, the Decomposed Zone may have some eventual economic potential. Johnson and Bhappu (1969) have investigated cold leaching agents for Zn and Pb oxide ores. They conclude that a NaCl-saturated solution is suitable for extracting Zn and Pb from low grade, calcareous, semioxidized ores. The writer envisages an "in-situ" leaching process whereby extractants would be pumped into the porous, oxidized material at subcrop sites and metal-containing leach recovered from the 400 and 500 levels of the existing exploratory tunnels. Of course, additional experimental work and feasibility studies are necessary requirements before such a venture could be undertaken.

## CHAPTER 4

### SECONDARY DISPERSION OF SELECTED METALS.

#### KEEL AND ARDAGH AREAS

##### 4.1 GENERAL

Secondary dispersion halos of selected elements in soils over the Keel deposit are presented and discussed with particular reference to the influence of the Decomposed Zone as the source of metals. Environmental factors such as organic scavenging and retention of base metals, certain soil conditions, and topographic features are included as important secondary controls on element dispersion.

Soil traverses have also been undertaken in the Ardagh area to study known anomalies.

Shorter investigations on stream sediments (Ardagh area), biogeochemistry at Keel and levels of selected metals in water are also presented and discussed.

##### 4.2 PHYSIOGRAPHY

Discussion on secondary dispersion of selected elements is preceded by a brief outline of general environmental conditions in Ireland and the Longford District.

###### 4.2.1 Ireland

Although a relatively small island, Ireland exhibits a complex morphology and an involved physiographic history leading to its present shape and topography.

Today, the central lowland of Ireland is essentially a broad, gently-rolling plain occasionally broken by rises and hills. Prominent topographic rises can usually be attributed to Caledonian and American folding of pre-Carboniferous and Carboniferous units into

anticlinal and dome-like structures (Chapter Two). Smaller local elevations can usually be related to kames, eskers, drumlins, and other glacial features (Synge and Stephens, 1960).

#### 4.2.2 The Longford District

The physiography of the Longford District is essentially dominated by the underlying geology. The northern (Longford) inlier and the Keel inlier are the highest points within the District. Both are crests of anticlinal structures cored with pre-Carboniferous rocks. Topographic elevations range from 659 ft. O.D. at the crest of the Keel inlier to 125 ft. O.D. at Lough Ree in the west. Apart from the inliers, the Keel area is an undulating to flat-lying area with local relief not usually fluctuating beyond  $\pm 50$  ft.

#### 4.3 GLACIAL GEOLOGY AND GEOMORPHOLOGY

Any discussion of secondary environment in central Ireland must inevitably begin (or end) with the mantle of glacial drift which blankets the country.

During the Pleistocene epoch, glaciers advanced from sources in the northwest and northeast of the country, the latter probably linked to spreading continental glaciation from Scotland. Ireland has experienced continental glaciation at least twice, probably three times (Synge and Stephens, op. cit.). The last glacial cycle, the Weischel (Wurm) glacial period, reached a maximum stade about 21,000 B.P. and covered approximately 80 per cent of the Irish land mass (Mitchell in Meenan and Webb, 1958).

Counties Longford, Roscommon, and West Meath all exhibit excellent evidence of glacial activity. Pot-hole lakes abound in north Roscommon and north Longford while topographic lineations, parallel and sub-parallel drainages, and crenulating lake shorelines

are other features indicative of mass glacial action. Synge and Stephens (op. cit.) describe the area to the north and west of Lough Ree as being within a drumlin field and the writer endorses their opinion from his own limited field observations. Just east of the Keel shaft site, an elongate, southeast-trending, above-average thickness of drift suggests the presence of a small, flat-lying drumlin.

Till composition in the Keel area is thought to reflect a local source origin. X-ray diffraction analyses of selected samples from drillcore contained abundant quartz and illite with lesser amounts of calcite, dolomite, kaolinite, and feldspars.

#### 4.4 SOILS

Since 1959, a soil mapping programme has been underway in Ireland with an aim to classifying lands for agricultural purposes (Gardiner and Ryan, 1969). Recently, a General Soil Map (1969) was released and shows the wide diversity of soil types found in the Irish environment. Discussion here is limited to those soils encountered in the Keel and Ardagh areas.

The above-mentioned soil map places the area of study within a region classified as Reclaimed Podzols. Such soils were originally Podzols that have been ploughed under sufficiently to break up and mix both the "A" and "B" horizons. Podzolization as a soil-forming process is very much in evidence in the Keel area, but few Podzols (as a Great Soil Group) have been observed.

The field classification of Irish soils is complicated by the confusing problem that many podzolized profiles possess twin characteristics (Ryan and Walsh, 1966). Most well-drained profiles developed on tills covering Carboniferous clastic rocks and limestones closely resemble either Grey-Brown Podzolics or Podzols. It follows that such soils are not fully classified under the Great Soil Group

classification scheme, but are of intergrade soil types.

A considerable variety of soil types have been encountered in the Keel and Ardagh areas and tentatively classified by the writer. Lithosols have been recognized near and around the crest of the Keel inlier where subcrop is very close to the surface. Shallow Brown Earths-? or Brown Podzolics-? have been observed in association with the Lithosols and in some areas to the west of Keel. Basin peats (including Interdrumlin peats) are in evidence in some topographic depressions. Gleysolic soils and peaty gleysolics are found in areas fringing peats and in poorly-drained areas.

The soil type most commonly encountered has been the Grey-Brown Podzolics (including Modified Grey-Brown Podzolics). These soils are recorded as the prevalent soil types found in Central Ireland (General Soil Map, 1969).

The importance of soil type in geochemical exploration in Ireland has received comment by Donovan (op. cit.), Larsson (1970), and Butt (1971). Each has demonstrated the importance of soil conditions in controlling the dispersion of selected elements. The writer has continued research on soil type-metal distribution relationships in applied geochemical studies. Results in this chapter indicate that some knowledge of soil type and soil conditions is required for a meaningful interpretation of metal anomalies. Also, the belief that thicknesses of glacial till can hide or depress secondary geochemical expressions of dispersed metals is evident at Keel. Some results suggest that metal anomalies form more readily in poorly-drained soils.

#### 4.5 PREVIOUS WORK

The Longford District mineral exploration licences presently held by Riofinex have been explored by reconnaissance, orientation,

and detailed geochemical studies on soil and stream sediment; hence, a certain amount of information was available to the writer.

During surface assessment of the mineral potential in the Keel area, personnel of Anglo-Austral Mines Ltd. (eventually renamed Riofinex) collected soils in two phases. The first collection included detailed grids over and around the apparent source areas of the Zn anomalies found during the regional stream sediment survey (Chapter One). One plot (a  $1\frac{1}{2}$  x 1 mile block) was centered approximately around the present shaft site at Keel. A second grid was positioned near Drumming Cross Roads, Ardagh area and covered a  $2 \times \frac{2}{3}$  mile block. In each case, sampling centres of 100 ft. with 400 ft. line intervals were employed. Sample depths have been recorded as "B" horizons or bottom of the "B" horizon (J. Patterson, pers. comm.).

This programme established the presence of soil anomalies with some areas of highly anomalous levels of Zn and Pb. Coverage was then extended to the entire flanks of the Keel inlier and reconnaissance sampling employing 800 ft. line intervals and 200 ft. sampling stations was carried out. This additional data revealed little in the way of mineral finds, but has confirmed the widespread secondary dispersion of the mobile metals.

Zinc, Cd, Pb, and Cu were determined on all samples, but Hg was determined only on selected samples immediately around the Keel prospect.

The presence of an intense mercury in soil anomaly at Keel had been reported as early as 1964 (James and Webb, 1964). In addition, they were the first to note a high degree of correlation between Hg and Pb, a feature characteristic of Keel and Ardagh soil anomalies.

Continued research on the extent and origin of the Keel-Ardagh anomalies was undertaken by Donovan (op. cit.) as part of a programme

of study on secondary dispersion of base metals from mineralized occurrences in West-Central Ireland. Three soil traverses were laid out and sampled in the Keel area and two more near Ardagh. Analysis for Zn, Pb, Cu, and Hg confirmed metal distribution and levels found by Riofinex. A coincident Hg-Pb anomaly was found near Garrycam.

Unfortunately, Donovan's study was of a very brief nature, and perhaps, hampered by a limited knowledge of geology, mineralization, and soils. However, he did conclude a number of noteworthy points:

- i) Soil anomalies are characterized by widespread dispersion of Zn and relatively confined Pb patterns.
- ii) There is an apparently close association between Pb and Hg in near-surface soils.
- iii) A variety of soil types are to be found in the Keel and Ardagh areas. Their possible influence on secondary dispersion of metals warrants additional study.
- iv) Solifluction and cryoturbation are possibly important mechanical dispersion mechanisms.

#### 4.5.1 Use and Examination of Previous Work

The original geochemical results of Riofinex have been re-examined and contoured as a basis for discussion of regional geochemical patterns and for further detailed studies. Five Figures (10 through 14) show the areas covered by sampling and corresponding Zn, Cd, Pb, and Hg maps denoting weakly anomalous, moderately anomalous, and strongly anomalous soils. Table 14 outlines the criteria used for establishing contouring levels. Simply, a background plot of 40 samples south of Drumming Cross Roads was selected and an arithmetic mean and standard deviation calculated for each element. Successive contouring of mean plus 2, 5, and 10 times the standard deviation correspond to weakly, moderately, and strongly anomalous classifications.



Table 1.4. Contouring data for regional soils

| Element |     | n  | Range (A values) | Arithmetic Mean | Standard <sup>1</sup> Deviation | Weakly <sup>2</sup> Anomalous | Moderately <sup>3</sup> Anomalous | Strongly <sup>4</sup> Anomalous | Analytical Method                     |
|---------|-----|----|------------------|-----------------|---------------------------------|-------------------------------|-----------------------------------|---------------------------------|---------------------------------------|
| Zn      | ppm | 38 | 50-465           | 145             | 90                              | >325<br>(330)                 | >595<br>(600)                     | >1045<br>(1000)                 | Atomic absorption, nitric acid leach  |
| Cd      | ppm | 42 | <1-12            | 2.4             | .7                              | >3.8<br>(4)                   | >5.9<br>(6)                       | >9.4<br>(10)                    | Atomic absorption, nitric acid leach  |
| Pb      | ppm | 40 | 10-120           | 55              | 80                              | >205<br>(200)                 | >455<br>(450)                     | >855<br>(850)                   | Atomic absorption, nitric acid leach  |
| Hg      | ppb | 40 | 80-320           | 195             | 70                              | >335<br>(340)                 | >545<br>(550)                     | >895<br>(900)                   | Lemaire detector (filtered volatiles) |

$$^1 \text{ S.D.} = \sqrt{\frac{(A - \bar{A})^2}{n}}$$

<sup>2</sup> Mean plus (2 x standard deviation)

<sup>3</sup> Mean plus (5 x standard deviation)

<sup>4</sup> Mean plus (10 x standard deviation)

N.B. Figures in parenthesis used in contouring

## 4.6 REGIONAL GEOCHEMICAL PATTERNS

### 4.6.1 Introduction

Contouring at three anomalous classifications reveals a variety of geochemical signatures. The most noticeable is the U-shaped pattern of metal anomalies around the northeast end of the Keel inlier, particularly evident with Zn. Also, Zn anomalies appear to closely approximate the drainage catchments west and northwest of Ardagh. Cadmium values generally show good correlation with Zn, but lateral dispersion appears relatively restricted.

Lead anomalies are less widespread than Zn and seemingly reflect both the immobility of the element and lack of galena in mineralized occurrences.

The limited Hg analyses show good correlation with Pb values and faulting systems, and indicate an apparently widespread lateral dispersion halo.

The source of metals for the Keel anomaly should be noted here. Metal in tills/soils is thought to be derived primarily from the Decomposed Zone. The areal information indicates little positive definition of the narrow, subcropping sulphide orebodies.

### 4.6.2 Zinc (Fig. 11)

Zinc anomalies are commonly developed in transported overburden covering Zn mineralization (Hawkes and Webb, op. cit.). The Keel and Ardagh area zinc anomalies can be loosely classified under three headings:

- i) Clastic-syngenetic anomalies in till modified by ground water movement
- ii) "Organically accumulated and fixed" anomalies
- iii) Lateral hydromorphic dispersion anomalies, adjacent to anomalous streams

Zinc has dispersed widely in the Keel area. Clastic-syngenetic (modified by ground water) anomalies are developed over both the Decomposed Zone and the mineralized faults. Discrimination between either source seems difficult, if not impossible.

Strongly anomalous areas are usually found in association with peaty soils, peats, and low-lying, poorly-drained soils. Such environments are generally topographically low areas and field observations indicate that the importance of a few tens of feet in elevation cannot be under-estimated as being locally insignificant in anomaly formation.

A small basin peat below the Keel shaft is the best example of the "organic retention-type" anomaly. Sequestering of Zn by humic acids has been reported by Randhawa and Broadbent (1965a, 1965b) and its influence in geochemical exploration is well documented (Cannon, 1955 and Salmi, 1956). The study by Cannon of Zn accumulation in peats over mineralized (sphalerite) dolomites in New York State, U.S.A. bears some resemblance to the highly anomalous Zn values encountered in peat at Keel. A detailed sampling traverse (two depths) and pitting have been employed in a further investigation in this chapter.

The high mobility of Zn is demonstrated by an examination of anomalies in the Ardagh area. Originally, disseminated mineralization (mainly sphalerite) had been observed in stream cuttings by Riofinex personnel (Patterson, op. cit.). Pitting and drilling yielded little more than some sub-economic disseminated sulphides. It would appear that Zn from such sources is being actively (chemically and mechanically) dispersed along streams coincident with lateral dispersion into directly associated tills and soils. Note the close association of Zn soil anomalies with streams west of Ardagh town (Fig. 11).

The phenomena is not without local parallel as J. Sample (pers. comm.) has indicated similar Zn accumulation in soils adjacent to anomalous streams in north Longford. Hawkes and Webb (op. cit.) also note that lateral hydromorphic dispersion is an important secondary process in anomaly formation and cite both idealized and case history examples (p. 157 and 192).

The Zn soil anomaly at Keel appears to be modified by lateral hydromorphic dispersion about the anomalous stream draining mineralized peats and soils east of the shaft site.

Laterally dispersed hydromorphic anomalies have been studied by traverse sampling, total element analysis and cold-extractable methods for Zn and Cd.

#### 4.6.3 Cadmium (Fig. 12)

Cadmium patterns at Keel and Ardagh closely reflect those of Zn. A high degree of retention of the metal by organic-rich soils and peats is also evident and up to 0.66 per cent has been recorded in the mineralized peat at Keel. Like Zn, Cd anomalies appear to be topographically controlled and lateral dispersion processes are again evident.

Literature sources indicate little research or application of Cd geochemistry in mineral exploration. Ginzburg (1960) suggests Cd:Zn ratios may be useful in prospecting if a Cd:Zn ratio has become established. Apparently, the Cd:Zn ratio would shift in favour of Zn at distance from the Zn anomaly, if the source is chiefly sphalerite. This would indicate Cd less mobile than Zn.

Hawkes and Webb (op. cit.) quote Polikarpochkin, 1958 that Cd may be useful as a pathfinder for Zn. Also, they report Cd following Zn in weathering except during the oxidation of Zn sulphide. Here, the secondary Cd sulphides tend to remain behind after oxida-

tion of sphalerite.

Salmi (op. cit.) has reported finding up to 30 ppm Cd in mineralized peats in Finland.

Cadmium has been identified in mineralized soils in the Bathurst District, New Brunswick, Canada (Presant, 1966).

Clearly, little seems known of Cd abundance in soils and its application to geochemical prospecting. As Keel sulphide ore exhibits a nearly constant Cd:Zn ratio (Chapter Two), some effort has been made to establish secondary environmental controls on Cd dispersion relative to those of Zn.

#### 4.6.4 Lead (Fig. 13)

Lead is considerably less mobile than Zn in naturally-occurring environments (Hawkes and Webb, op. cit.) and soil anomalies tend to be restricted to source areas.

At Keel, the relatively low content of galena in the sulphide orebodies has undoubtedly influenced the magnitude of the Pb in soil levels. However, Pb anomalies do show good association with the known faults and fault systems.

Lead patterns in the Ardagh area are more confined than those of the Keel area. Again, some association with known faults is suggested.

Lead shows a preference for near-surface enrichment, particularly in gleyed soils. Although accumulating in organic-rich horizons, Pb does not appear to concentrate in peats as do Zn and Cd. Donovan and James (1966) also note this phenomena.

At Keel, Pb anomalies developed in glacial till show little lateral displacement (glacial smearing) from the underlying metal sources. Donovan and James (op. cit.) conclude that Pb (as well as Cu, Zn, and Hg) form syngenetic anomalies in glacial till approximating

the Tynagh deposit, Co. Galway and have been little modified by any secondary mobilization processes.

#### 4.6.5 Mercury (Fig. 14)

As can be seen in Figure 14, mercury analyses are much more limited in number than Zn, Cd, and Pb; hence, a comparative regional examination of Hg dispersion is not possible. As mercury gains most support as a pathfinding and "secondary support" geochemical search tool, the regional approach may be of minor importance. Fortunately, analyses here cover the critical sites at Keel.

Of particular note is the widespread pattern (weakly anomalous classification) of Hg relative to other elements. As primary dispersion has not yet been defined at Keel (J. Watling, pers. comm.), other factors must account for the extensive soil halo. The writer is of the opinion that dispersion from oxidizing sulphides and the Decomposed Zone may be supplemented by mercury sources (disseminated sphalerite) in the subcropping Basal Clastic Group and Mixed Beds Group.

Good association is shown between mercury and faulting at Keel, and an intense (strongly anomalous), narrowly-defined anomaly suggests additional faulting and/or the presence of the Decomposed Zone near Garrycam.

As found by previous investigators (James and Webb, op. cit., Donovan, op. cit.), anomalous Hg-containing soils at Keel correlate more closely with Pb anomalies than with Zn-Cd anomalies. Most primary Hg appears to be associated with sphalerite (Chapter Two); hence, mass secondary separation and movement would seem evident.

Generally, Hg pathfinding has had success in aiding geochemical surveys searching for Zn and Pb (Erickson *et al.*, 1966, Fursov, 1958, Hawkes and Williston, 1962, Baily and Barnes, 1968, and Jolly and Heyl, 1968).

In Ireland, Donovan (op. cit.) successfully defined subcropping mineralization at Tynagh and some other sulphide occurrences using mercury pathfinding, but noted some undesirable secondary accumulation characteristics of the element. Elsewhere in Ireland, mercury anomalies in soil and/or stream sediments have been found in association with mineralization at Cortdrum, Co. Tipperary (A.G.R.C., unpublished information), Aherlow, Co. Tipperary (D. S. Evans, unpublished information) and Avoca, Co. Wicklow (C. Wheatley, pers. comm.).

#### 4.7 ADDITIONAL SOIL SAMPLING AND RESULTS

##### 4.7.1 Keel Area

An area partly covering the soil anomalies at Keel was resampled with the following aims:

- i) To establish favourable sites for soil gas (Hg) studies
- ii) To confirm Riofinex data and to extend analyses for other elements of concern (As, Sb, Fe, Mn, Ag, Ba, etc.)
- iii) To investigate the known Hg-Pb correlation and environmental associations and the Zn-Cd correlation and environmental associations

Field geometry and size in the Keel area is such that a "sampling per field programme" (usually one or two sites per field) was employed during follow-up work. Accordingly, soils were collected at 18 to 24 inches (see Appendix One) to complement the original Company work.

Sample sites were selected to cover the area with known geological control. Background sites were collected north and south of the anomaly and, in addition, all samples were taken well away from ditches and fences to avoid any local water-table effects or contamination. Separate soil sampling was employed to supplement soil-air studies.

Figure 15 shows the area resampled by the writer. Briefly, Zn-Cd-Pb levels and areal patterns were confirmed, but a slightly lower background for mercury (calculated at 165 ppb) was established using the James-Webb Hg spectrophotometer as opposed to the background obtained from the "Lemaire detector" results used by Riofinex (about 195 ppb). The writer's mercury in soil map is presented in Chapter Seven (Fig. 45).

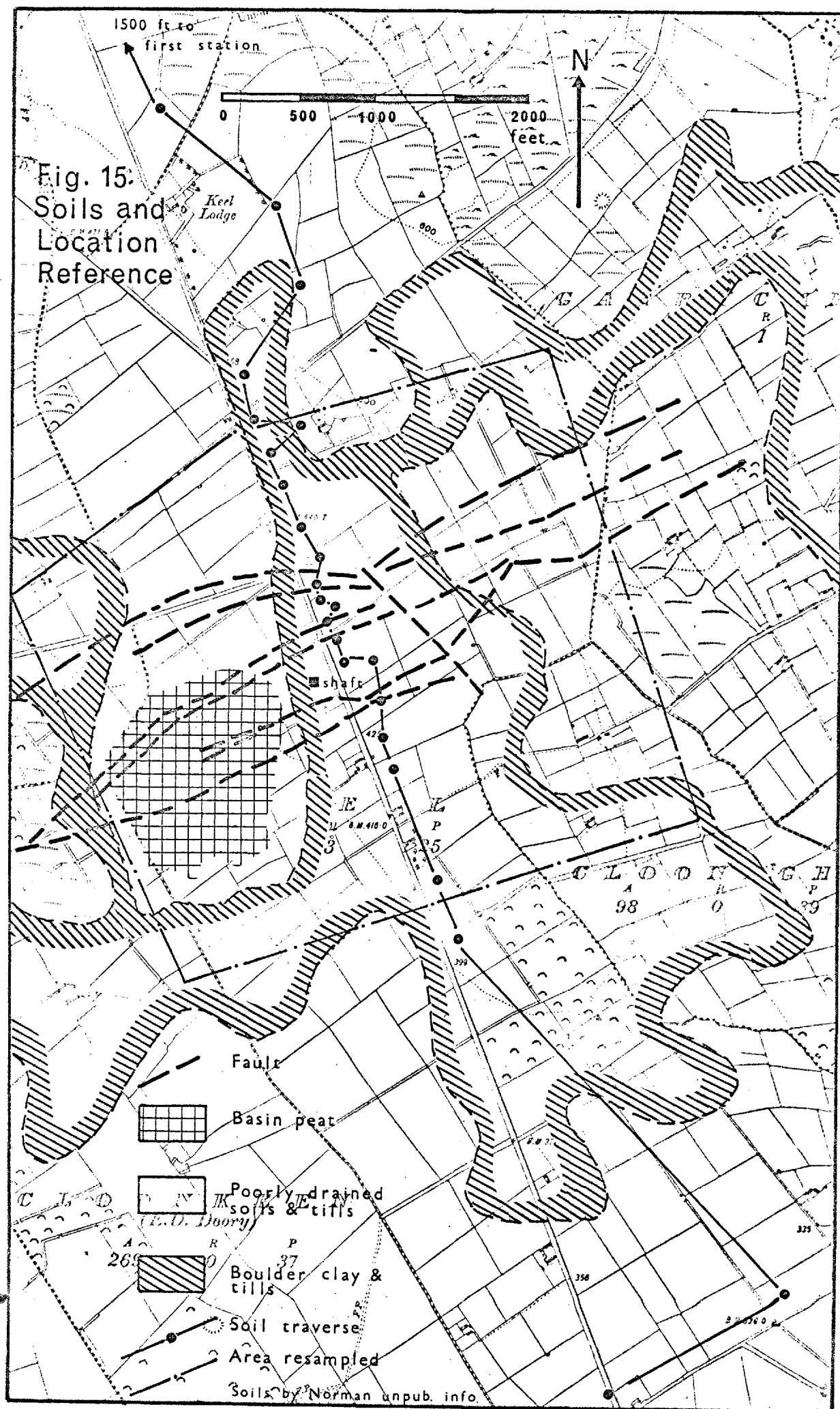
A traverse of sample sites incorporating the flanking, widely-spaced background sites and centrally located anomalous sites was selected over the Keel deposit (see Fig. 15). Figure 16 shows element profiles for 14 metals (total levels), EDTA-extractable Zn, Cd, and Pb, and organic carbon for this traverse.

Table 15 shows mean background values, the number of samples greater than mean background plus two and five times the standard deviation (moderately and strongly anomalous) and maximum anomaly relief values for selected elements from Figure 16. Samples used to calculate background levels were selected from 20 assumed background sites near Keel (Hg, Cd, Zn, Pb, Mn, and Fe) and from 10 apparently background sites from Figure 16 for the limited spectrographic and colorimetric analyses (Ba, Ag, As, Sb). Calcium, Mg, K, Rb, EDTA-extractable Zn, Cd, and Pb have not been treated statistically and are presented in Figure 16 only for relative comparison purposes.

Road-side sampling is a commonly-used geochemical reconnaissance exploration technique in Ireland (C. Morley, pers. comm. and Schultz, 1971). Figure 16 and Table 15 have been used jointly to evaluate the suitability and applicability of selected metals for this prospecting technique in the Longford District.

Interpretation of Table 15 follows that columns 6 and 7 have been used to establish the mobility and dispersion characteristics of each element. Simply, column 6 is the total number of moderately





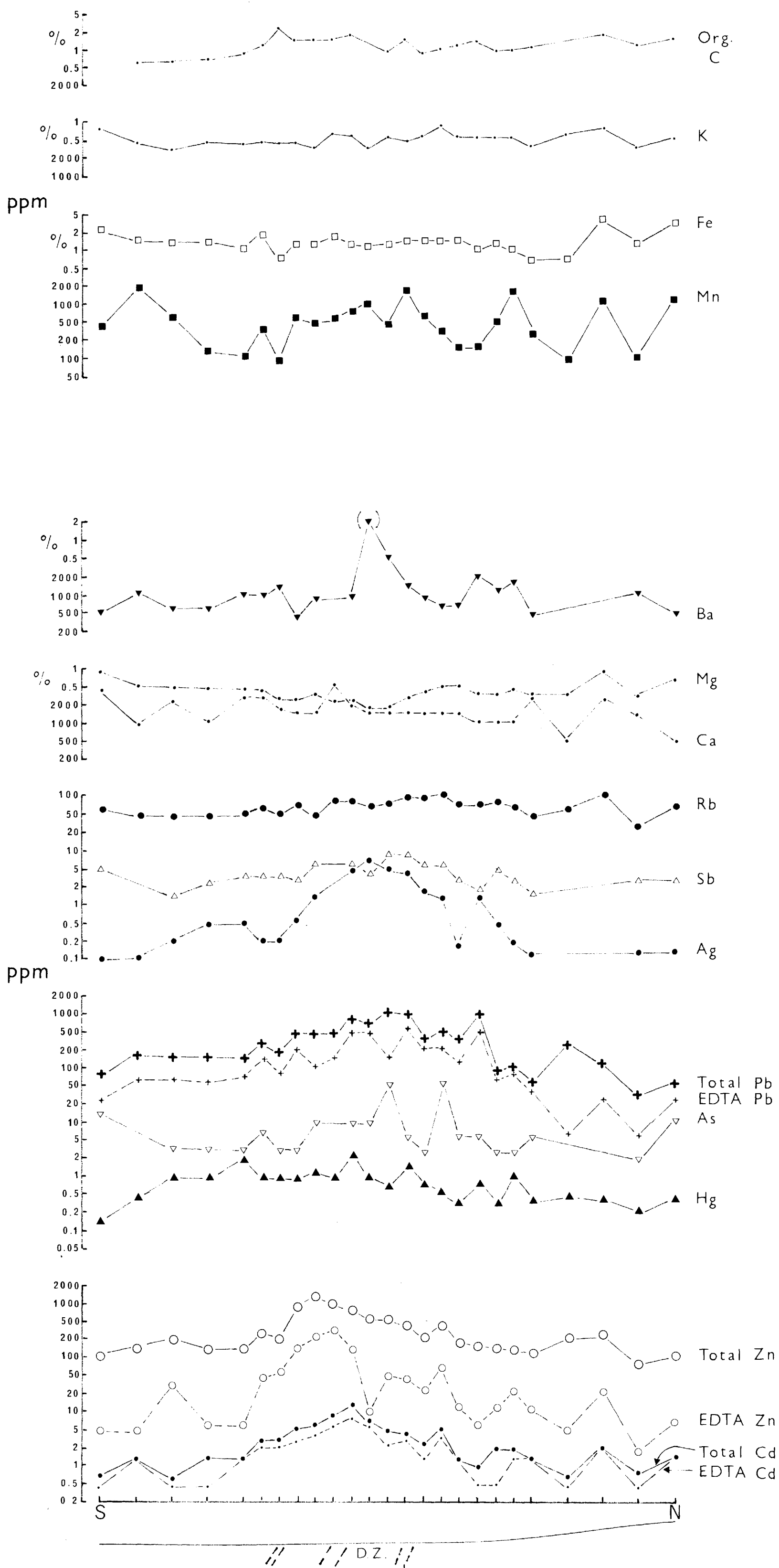


Fig. 16 Selected elements in soil over the Keel deposit

18 to 24 in.

D.Z. = Decomposed Zone

Table 15. Statistical data to accompany Figure 16

|         |     | 1  | 2        | 3               | 4                  | 5                    | 6                    | 7                                 |                        |
|---------|-----|----|----------|-----------------|--------------------|----------------------|----------------------|-----------------------------------|------------------------|
| Element |     | n  | Range    | Arithmetic Mean | Standard Deviation | Mean plus (2 x S.D.) | Mean plus (5 x S.D.) | Sites $\geq$ mean plus (5 x S.D.) | Maximum Anomaly Relief |
| Hg      | ppb | 20 | 72-320   | 165             | 125                | 415                  | 790                  | 5                                 | 7.3                    |
| Zn      | ppm | 20 | 70-360   | 160             | 70                 | 300                  | 510                  | 6                                 | 7.0                    |
| Cd      | ppm | 20 | <0.5-3.0 | 1.3             | 0.7                | 2.7                  | 4.8                  | 6                                 | 9.1                    |
| Pb      | ppm | 20 | 5-240    | 75              | 70                 | 2.5                  | 420                  | 4                                 | 12                     |
| Mn      | ppm | 20 | 50-1200  | 295             | 290                | 875                  | 1745                 | 1                                 | 6.2                    |
| Fe      | %   | 20 | 0.6-4.5  | 2.5             | 1.1                | 4.7                  | 8.0                  | Nil                               | 1.3                    |
| Ag      | ppm | 10 | <0.2-3.0 | 0.8             | 0.5                | 1.8                  | 3.3                  | 3                                 | 7.5                    |
| As      | ppm | 10 | <2.5-43  | 9               | 11                 | 31                   | 64                   | Nil                               | 4.8                    |
| Sb      | ppm | 10 | 1.5-6.2  | 3.8             | 1.7                | 7.2                  | 12.3                 | Nil                               | 2.1                    |
| Ba      | ppm | 10 | 300-2000 | 960             | 400                | 1940                 | 3410                 | 2                                 | >11 <sup>1</sup>       |

<sup>1</sup> Highest site greater than 1%

Maximum Anomaly Relief =  $\frac{\text{Highest sample along road}}{\text{Mean}}$

anomalous sites encountered on the road-side traverse while column 7 establishes the maximum "geochemical relief" of any one metal. Ideally, a mobile and/or diffuse ore or pathfinding element should exhibit a greater number of anomalous sites than an immobile element for a given number of analyses, while an immobile metal should exhibit high local "geochemical relief". Data here suggests the following mobility sequence of the ore and pathfinding elements at Keel.



Iron and Mn levels are somewhat erratic and may only reflect podzolization and leaching processes in soils rather than the Fe and Mn-rich Decomposed Zone.

The limited As and Sb data shows no sites above mean background plus five times the standard deviation and few sites above mean background plus two times the standard deviation. The use of As-Sb pathfinding seems somewhat limited for defining mineralization and/or As and Sb-rich sources in the Keel area. Both arsenic and antimony mobilities have been reported as low by Hawkes and Webb (op. cit.).

Generally, Zn, Cd, Hg, Pb, Ag, and Ba are all relatively effective geochemical aids when applying road-side sampling in the Keel area.

#### 4.7.2 Relationship of Soil Anomalies with the Decomposed Zone

Figure 17 shows selected metal profiles across soils covering known subcropping Decomposed Zone. It is openly evident that metal halos reflect the presence of the leached subcrop more readily than the relatively unweathered massive sulphides in faults. Inconsistencies in metal levels may possibly be related to glacial smearing of the syngenetic source, ground water modification of the clastic anomaly, and occasional peaks from sulphide occurrences.

Although the anomalous metal levels do not define the sulphide-

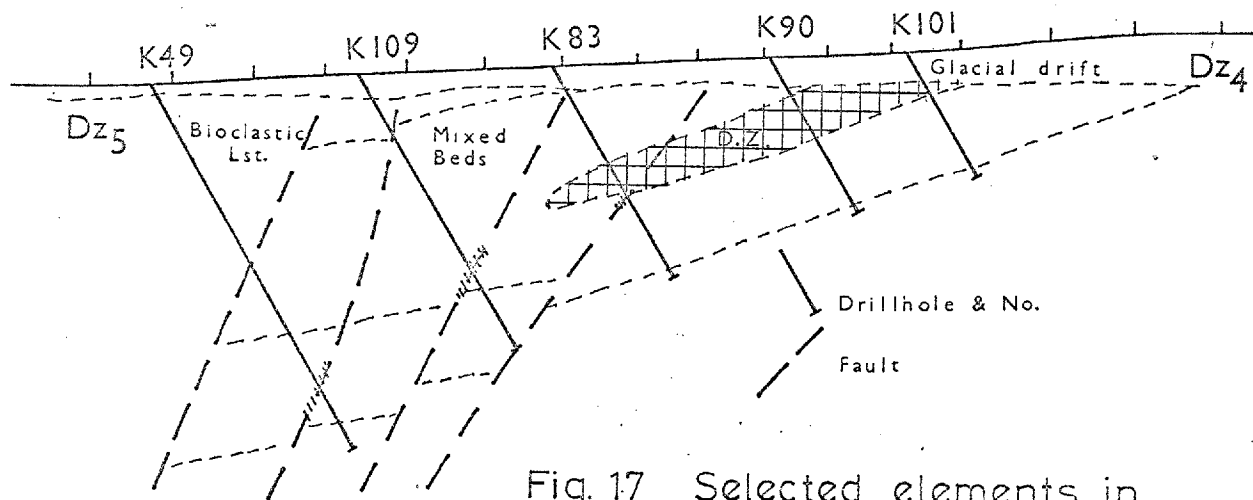
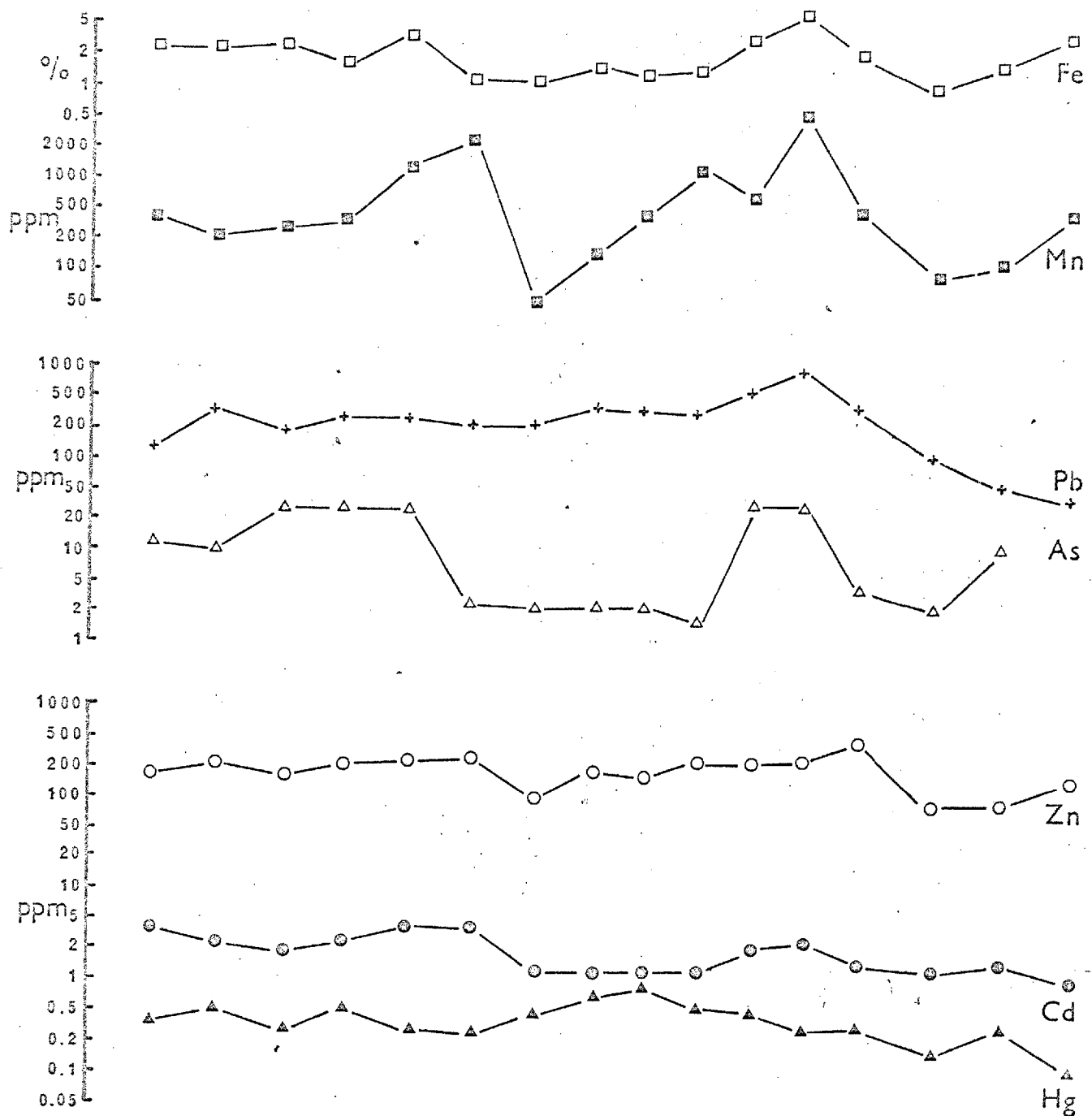


Fig. 17 Selected elements in soil overlying the Decomposed Zone and mineralized faults at Keel

18 to 24 in.

bearing faults at Keel, the use of geochemical techniques for prospecting should not be considered a failure. As has been discussed in Chapter Three, the metalliferous oxidized-leached subcrop appears to be partially derived from disseminated sulphides (probably genetically related with the massive orebodies) and the measurement of soil anomalies here reflects weathered products of sulphide origin. In addition, valuable information on metal dispersion from an Fe and Mn-rich source has been obtained.

#### 4.7.3 Other Areas

Other anomalous soil metal patterns have been investigated by traverse sampling from indicated backgrounds across the maximum "geochemical relief" of known enriched areas. Such samples were collected over soil anomalies near Garrycam, Drumming Cross Roads, Ardagh Hill, Kenagh, Moydow and the proposed laterally dispersed anomalies about mineralized streams southeast of Keel and west of Ardagh Town (see Fig. 10 for traverse locations). All samples were collected at 18 to 24 inch depths unless specifically noted otherwise.

Results from traverse sampling are presented as metal profiles to contrast and compare levels of selected metals with a view to extending geochemical aids in the search for Keel-type mineralization and to establish important secondary environmental controls on metal dispersions.

##### 4.7.3.1 Garrycam

The Garrycam soil anomaly is regarded as an extension of the Keel anomaly (see Figs. 13 and 14 and Fig. 10 for traverse location reference).

Figure 18 shows selected element levels across this anomaly. A Mn anomaly (possibly reflecting the Decomposed Zone), a coincident

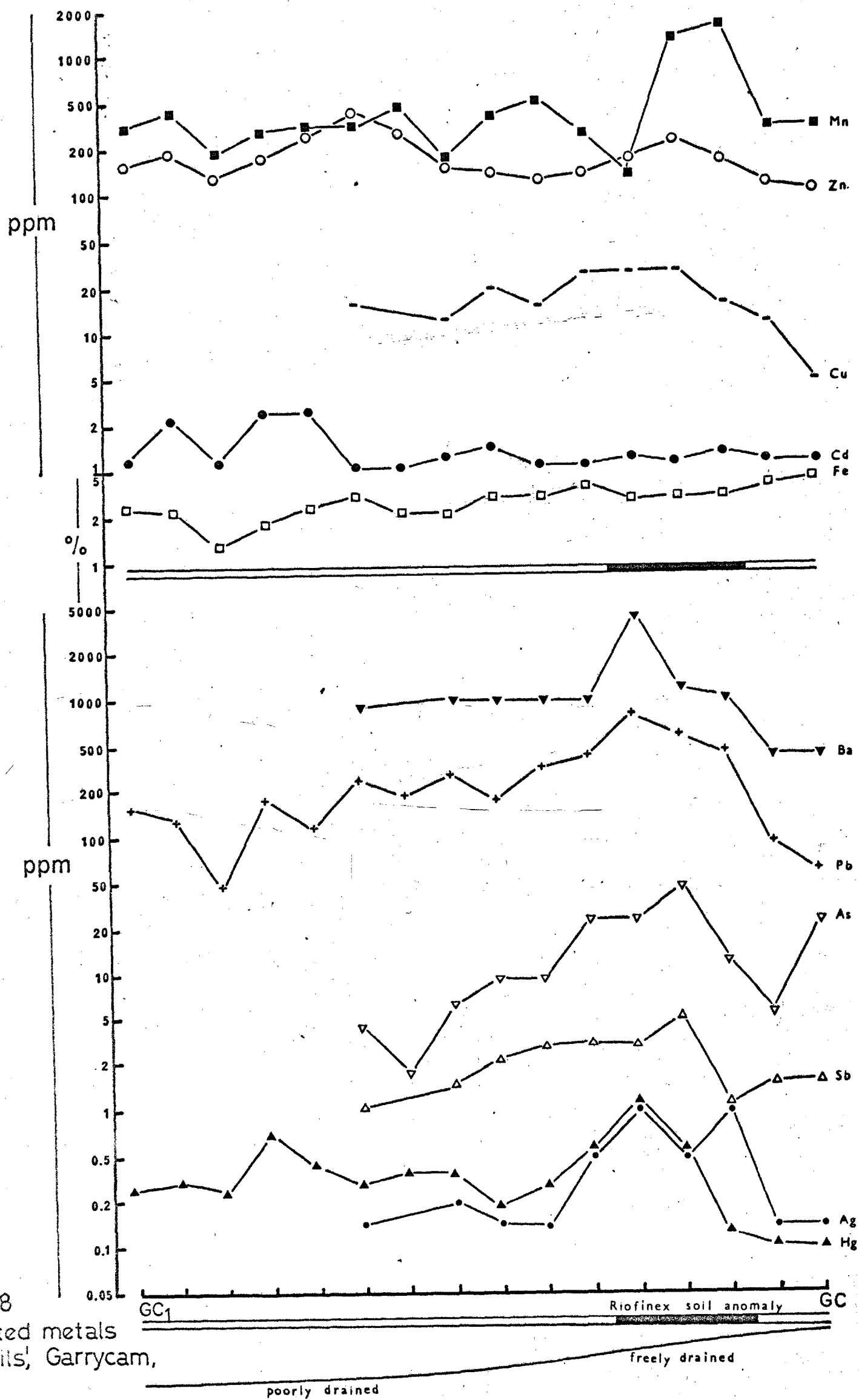


Fig. 18  
Selected metals  
in soils, Garrycam,  
Keel  
18 to 24 in.

Hg-Pb-Ba anomaly, and low order Ag-As-Sb-Cu anomalies are noteworthy features.

The southern half of the traverse crosses projected extensions of the Keel sulphide mineralization. However, the deep glacial drift in this region (up to 150 ft.) has probably obscured any useful metal patterns.

#### 4.7.3.2 Drumming Cross Roads (Ballygar)

Figure 19 shows results (Zn, Cd, Pb, Hg, Ba, Sb, and Ag) across the southern extension of the main Zn-Cd-Pb anomaly near Drumming Cross Roads (see Fig. 10 for location reference).

At the anomalous sites, element levels show coincident Zn, Cd, Pb, Hg, and Pb peaks. Low order Sb and Ag anomalies are also present. Arsenic, Mn, and Fe analyses gave no positive results.

The area enclosed by the highly anomalous classification for Zn (see Fig. 11) has received previous attention. Riofinex did considerable pitting and trenching in an attempt to establish the source of the anomaly. Near the anomalous sites on the writer's traverse, abundant pyrite mineralization with some galena and yellow Cd bloom on joints was observed in subcrop exposed by the pitting. Nearby, a trench revealed two small faults with some Pb, Zn, and Ba mineralization.

The low-lying, peaty area just north of the writer's traverse has been sampled at two depths (Table 16). Metals here show a preference for accumulation in the near-surface horizon. As will be demonstrated later in this chapter, poorly-drained, organic-rich environments accentuate surficial retention of certain metals.

#### 4.7.3.3 Ardagh Hill

The Ardagh Hill soil anomaly is again a coincident Zn-Cd-Pb pattern. As shown in Figure 11, the Zn anomaly is continuous with a larger dispersion halo, but the Ardagh Hill pattern is treated as



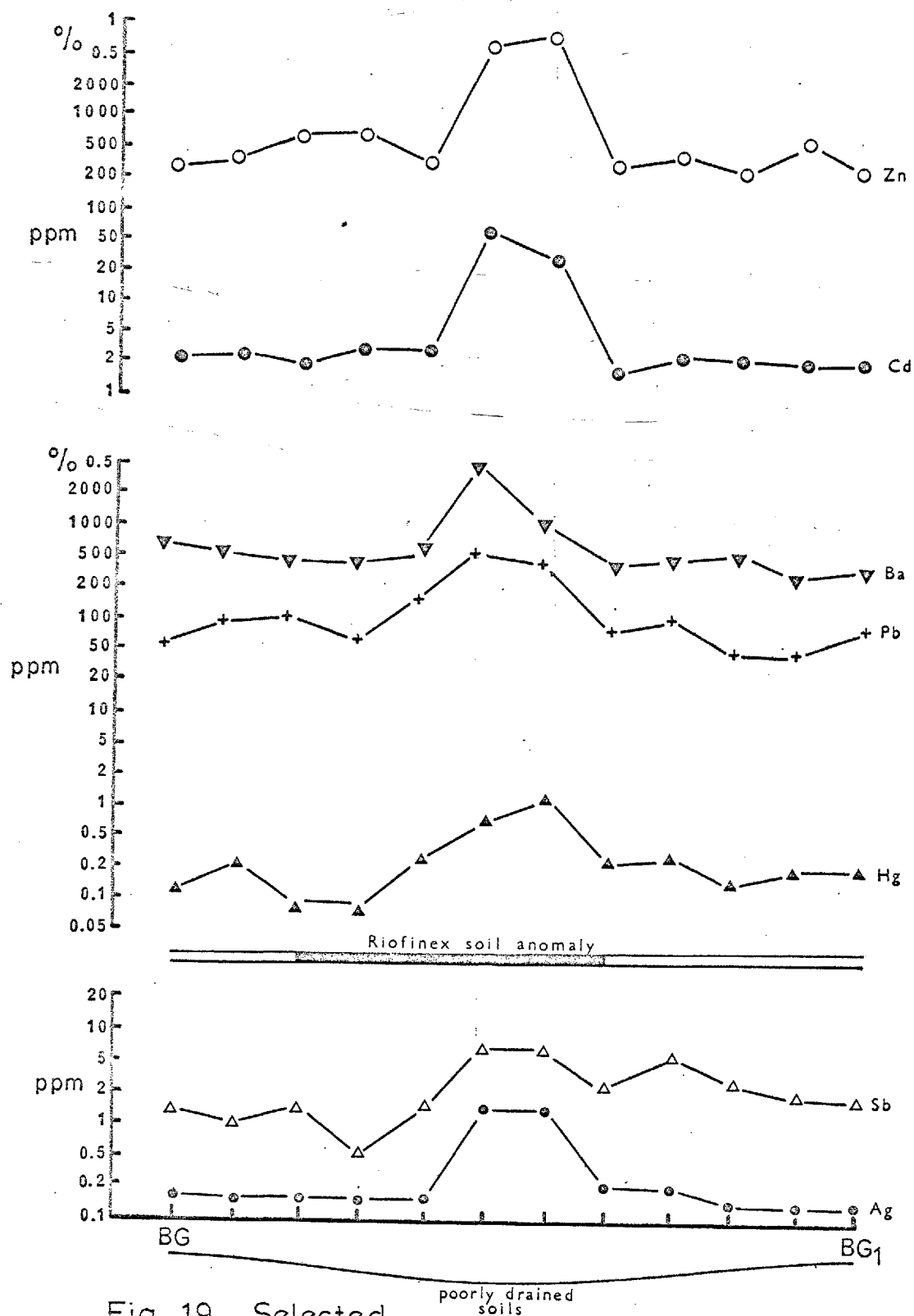


Fig. 19 Selected metals in soil, Drumming Cross Roads, Ardagh area

18 to 24 in.

Table 16. Selected metals in anomalous, poorly-drained soils near Drumming Cross Roads

| Sample No. | Depth (inches) | Description       | As ppm | Hg ppm | Cd ppm | Zn ppm | Pb ppm | Fe % | Mn ppm | pH <sup>1</sup> |
|------------|----------------|-------------------|--------|--------|--------|--------|--------|------|--------|-----------------|
| BG-21      | 0-10           | Dark brown loam   | 33     | 420    | 22     | 1370   | 240    | 2.9  | 630    | -               |
|            | 32             | Gleyed clay       | 8      | 288    | 6      | 287    | 80     | 4.0  | 200    | 7.5             |
| BG-22      | 0-10           | Dark brown loam   | 43     | 352    | 11     | 1080   | 100    | 4.0  | 1020   | -               |
|            | 34             | Gleyed sandy clay | 13     | 158    | 7      | 310    | 60     | 1.5  | 300    | 7.7             |
| BG-23      | 0-10           | Black peaty loam  | 50     | 460    | 50     | 25100  | 100    | 6.0  | 2950   | -               |
|            | 36             | Gleyed sandy clay | 8      | 188    | 13     | 2770   | 90     | 1.4  | 1020   | 7.6             |
| BG-24      | 0-10           | Peaty loam        | 58     | 448    | 25     | 8000   | 240    | 7.2  | 1200   | -               |
|            | 38             | Black muck        | 23     | 280    | 27     | 7800   | 140    | 2.9  | 750    | 6.2             |

<sup>1</sup> Regenerated deionized water slurry

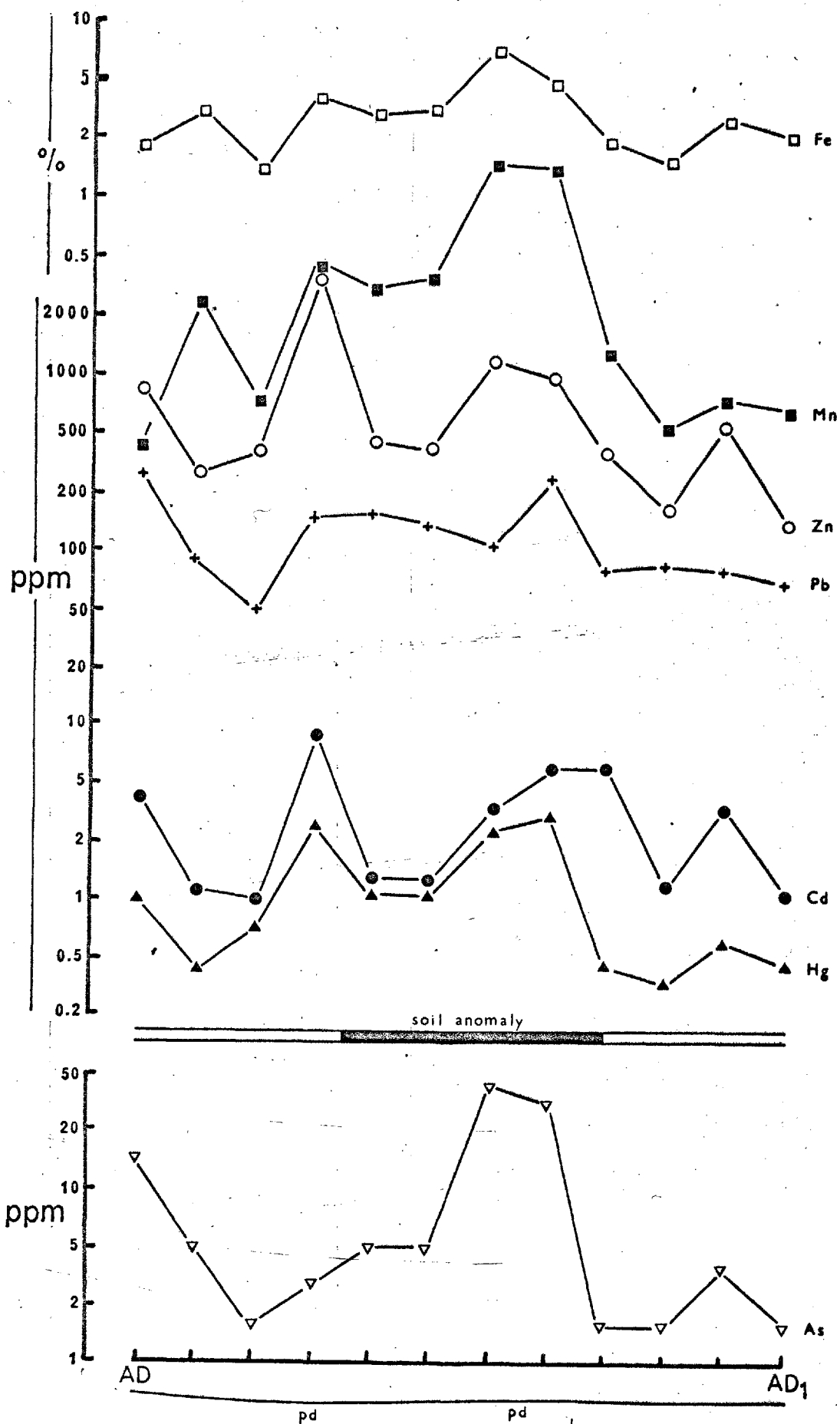


Fig. 20 Selected metals in soil,  
Ardagh Hill, Ardagh

1 18 to 24 in.  
pd poorly drained areas

being separate.

A soil traverse over the maximum geochemical relief area (Fig. 20) shows a high degree of correlation between Pb, Mn, Fe, Cd, Zn, Hg, and As. Maximum Zn and Cd (displaced from other metal maxima) is associated with a marshy depression encountered on the traverse.

Pitting around the Ardagh Hill anomaly by Riofinex revealed that Zn and Pb increased with depth and some minor faulting with disseminated sub-economic mineralization was encountered. High metal values in pits were observed to broadly correlate with surface anomalies and were considered highly encouraging by the Company although limited drilling was unsuccessful.

The writer equates the Ardagh Hill anomaly with the Drumming Cross Roads anomaly and further investigation would probably reveal additional sub-economic, disseminated sulphide mineralization (sphalerite and perhaps pyrite). Also, the Ardagh Hill anomaly may have been magnified by gleying and/or surficial accumulation processes in soil.

#### 4.7.3.4 Kenagh and Moydow

Although not shown in Figure 10, two broad soil anomalies were outlined by Riofinex near Kenagh Town and Moydow (see Figure 1 for an approximate location reference), both flanking the southeast extension of the Keel inlier. These anomalies appear to be similar to the Keel-Ardagh anomalies with confined Pb patterns and widespread Zn dispersion. A few samples were collected near the indicated anomaly maxima but revealed little more than the known Pb and Zn. Mercury values were all less than 300 ppb.

Of additional interest, both anomalies are transected by streams suggesting lateral hydromorphic dispersion processes may have played some part in anomaly formation.

Studies on both areas were discontinued as initial observations

and analyses indicated that metal may have been chemically transported from unknown sources.

#### 4.7.4 Lateral Hydromorphic Dispersion of Zinc and Cadmium

In the discussion on regional soil patterns, lateral hydromorphic dispersion of the mobile elements (principally Zn and Cd) was observed in stream bank tills and soils adjacent to anomalous streams west of Ardagh Town. Similarly occurring patterns are suspected at Kenagh and Moydow and part of the Zn-Cd soil anomaly at Keel appears to halo a stream draining an area covered by mineralized soils and peats.

Samples from a traverse (Zn-Zn<sub>1</sub> in Fig. 10) across the proposed laterally dispersed anomaly at Keel were analyzed for total and EDTA-extractable Zn and Cd. EDTA-extractable Zn, Cd, and other metals have been determined on tills and Fe and Mn-rich leached material with some success (Chapter Two). The method has been extended here for use with soils and stream sediments.

Results are depicted in Figure 21 and show complementing total and EDTA-extractable Zn-Cd halos flanking the mineralized stream. A lateral hydromorphic dispersion operating via local ground water and/or stream waters is strongly suggested.

Lateral hydromorphic dispersion studies have been less definitive on anomalous soils flanking mineralized streams west of Ardagh Town. Traverse CG-CG<sub>1</sub> (Fig. 22) crosses a known Zn-Cd-Pb anomaly adjacent to a stream course in a low-lying, poorly-drained environment. Peats and peaty gleys seem to be the prevalent soil types. Figure 22 shows total element levels and the corresponding EDTA-extractable values for Zn-Cd. Overall, the anomaly appears modified by surficial accumulation of Zn-Cd although EDTA-extractable levels of both elements would seem sufficient to produce a lateral hydromorphic dispersion pattern.

Source of the metal in this instance is believed to be the mineralized occurrence in a stream cutting north of Drumming Cross

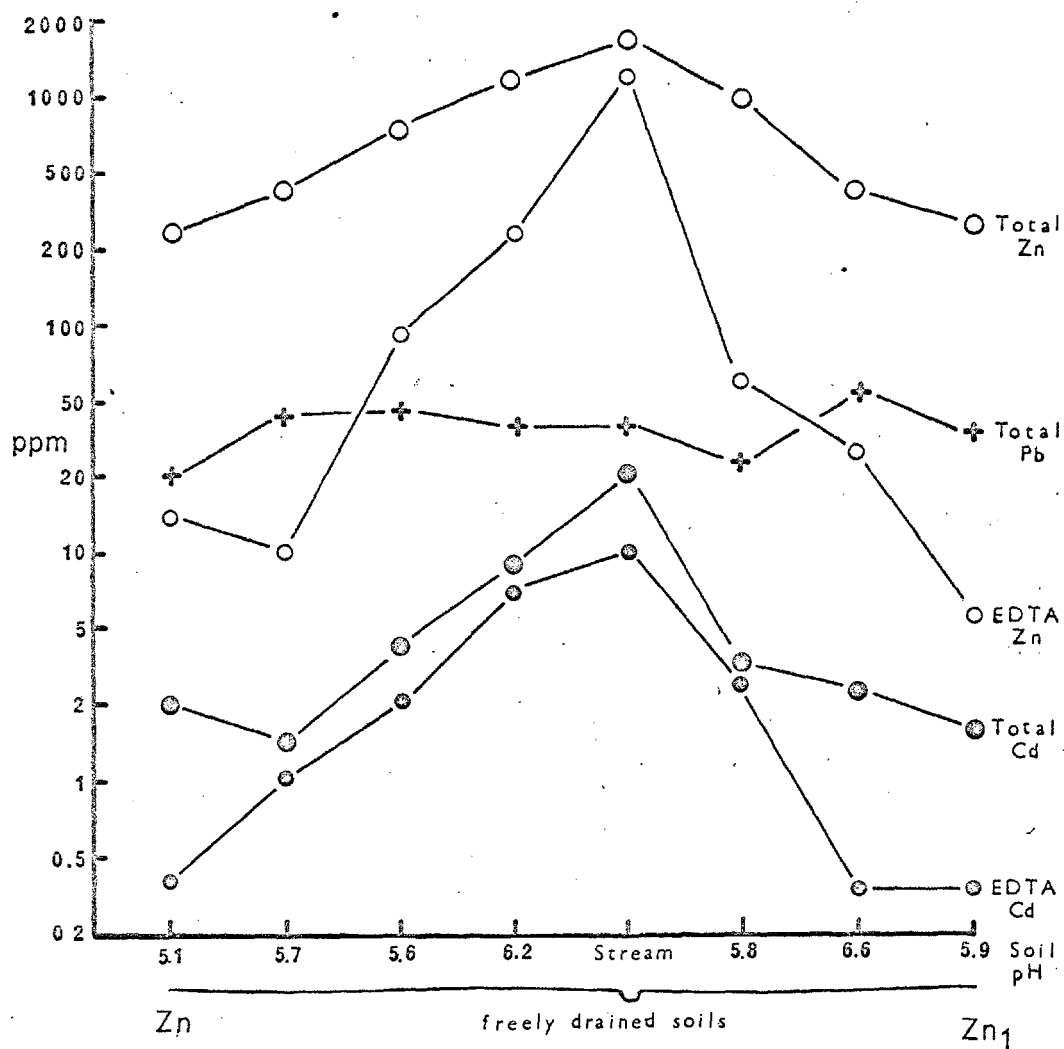


Fig. 21 Lateral hydromorphic dispersion of zinc and cadmium from a mineralized stream to adjacent soils, Keel

18 to 24 inches

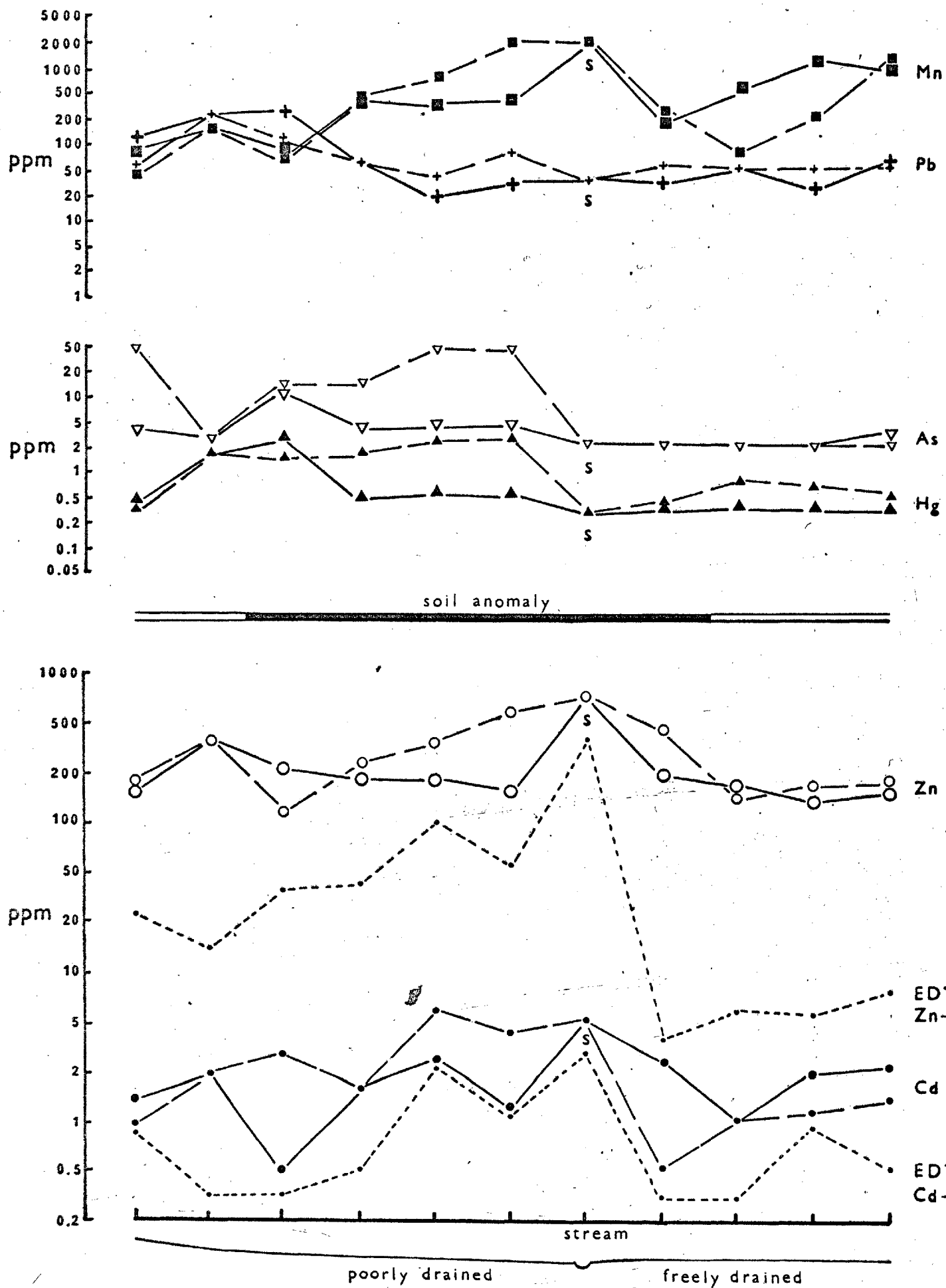


Fig.22 Lateral hydromorphic dispersion of Zn and Cd in soils<sup>1,2</sup> adjacent to an anomalous stream, Ardagh area. Pattern modified by surficial accumulation of metals in peaty, poorly-drained soils.

1 ——— 10 in.  
2 ——— 24 in.

Roads found by Riofinex geologists during surface exploration.

Disseminated sulphides from the Ardagh Hill area may constitute another source. ASARCO geologists have apparently recorded some mineralization in the immediate vicinity of the traverse (E. Yarrow, pers. comm.)

Other soil traverses (BM-BM<sub>1</sub> and MF-MF<sub>1</sub> in Fig. 10) cross anomalous streams and results of total and EDTA-extractable Zn and Cd are presented in Figure 23. Like traverse CG-CG<sub>1</sub>, the results are not as definitive as at Keel, but levels of Zn and Cd are certainly above background levels.

Although total analyses and partial extraction studies employed to chemically investigate lateral hydromorphic dispersion processes have not been wholly definitive in the areas west of Ardagh Town, the evidence from the regional geochemical maps strongly supports an intimate relationship between anomalous streams and their flanking soils and tills.

#### 4.7.4.1 Geochemical considerations of lateral hydromorphic dispersion

That Zn and Cd and other metals are present in stream and mine waters (carbonate-rich and pH greater than 7) and possibly available for lateral hydromorphic dispersion is known from direct (see Table 17) and indirect evidence.

A small number of stream sediments were collected in the Ardagh area and analyzed for total and EDTA-extractable metals (Table 18). Of principal interest here is that of Mn, as a good proportion of the element is released to solution by the cold leach. As oxides of Mn can selectively scavenge heavy metals from solution (Jenne, op. cit.), and up to 70 per cent of the total Zn and Cd can also be released by this same EDTA extraction, aqueous migration of metals appears to be an active process in alkaline streams. The aspect of Mn oxide



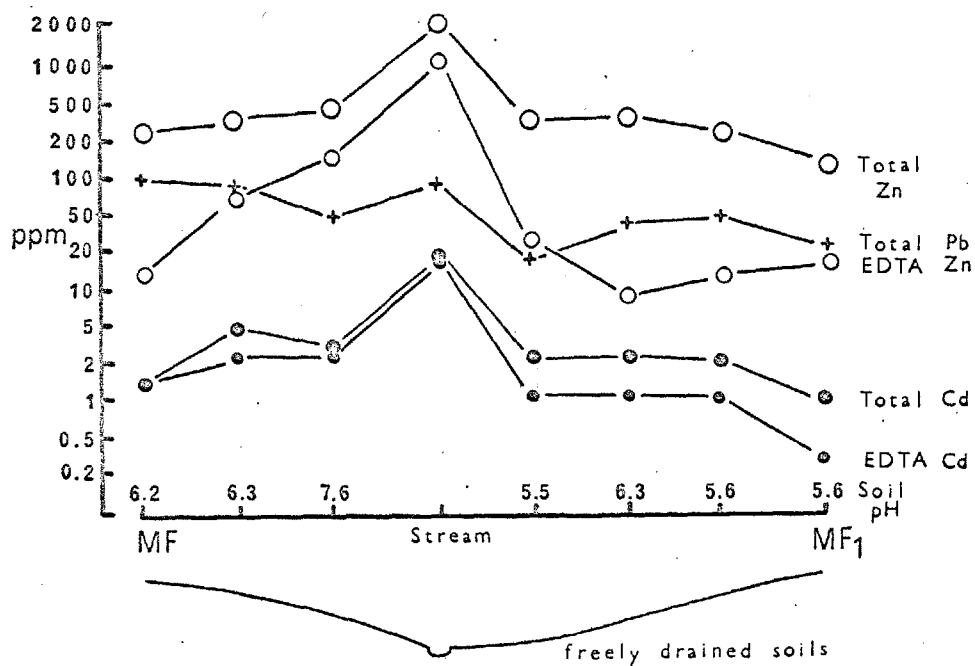
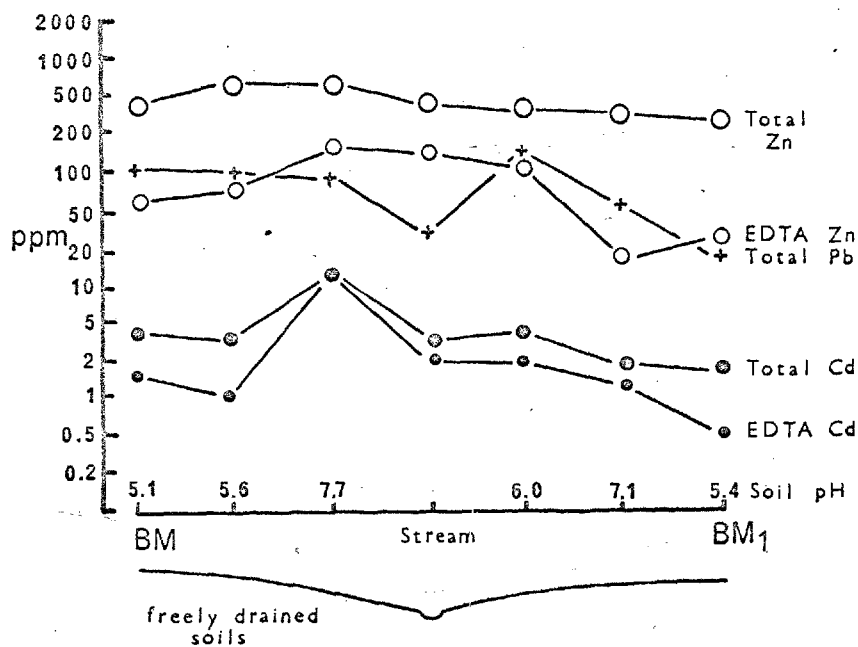


Fig. 23 Lateral hydromorphic dispersion of zinc and cadmium in soils<sup>1</sup> about mineralized streams, Ardagh area

<sup>1</sup> 18 to 24 inches

Table 17. Selected metals in waters, Keel and Ardagh Areas

| Sample Site                     | Date    | Hg <sup>1</sup><br>ppb | Zn <sup>2</sup><br>ppm | Cd <sup>2</sup><br>ppb | Pb <sup>2</sup><br>ppm | Fe <sup>2</sup><br>ppm | Mn <sup>2</sup><br>ppb | Ca <sup>2</sup><br>ppm | Mg <sup>2</sup><br>ppm | pH <sup>3</sup> |
|---------------------------------|---------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|-----------------|
| Keel shaft                      | 18/5/71 | 0.77                   | 2.70                   | 58                     | < 50                   | 0.25                   | 77                     | 96                     | 25                     | 7.5             |
| Keel shaft                      | 28/5/71 | 1.84                   | 2.45                   | 51                     | < 50                   | 0.20                   | 50                     | 86                     | 22                     | 7.5             |
| Peat water, Keel                | 20/5/71 | 0.69                   | 700                    | 1150                   | 120                    | 80                     | 4000                   | 288                    | 60                     | 2.9             |
| Peat water, Keel                | 29/5/71 | 1.60                   | 700                    | 1060                   | 140                    | 60                     | 3600                   | 290                    | 56                     | 2.9             |
| Well near Druming               | 22/5/71 | 0.93                   | 2.14                   | ≤ 2                    | < 50                   | 1.1                    | 290                    | 102                    | 20                     | 7.1             |
| Anomalous stream, Ardagh        | 22/5/71 | 0.69                   | 0.08                   | ≤ 2                    | < 50                   | 0.4                    | 90                     | 91                     | 13                     | 7.9             |
| Anomalous stream, Druming       | 22/5/71 | 0.29                   | 0.14                   | ≤ 2                    | < 50                   | 0.3                    | 30                     | 66                     | 11                     | 7.8             |
| Weakly anomalous stream, Ardagh | 22/5/71 | 0.32                   | 0.12                   | ≤ 2                    | < 50                   | 0.4                    | 50                     | 106                    | 13                     | 8.0             |
| Weakly anomalous stream, Ardagh | 22/5/71 | 0.26                   | 0.14                   | ≤ 2                    | < 50                   | 0.5                    | 50                     | 32                     | 5                      | 7.8             |
| Anomalous stream, Keel          | 22/5/71 | 0.53                   | 1.02                   | 12                     | < 50                   | 0.3                    | 100                    | 92                     | 19                     | 7.1             |

<sup>1</sup> Determinations on unfiltered samples

<sup>2</sup> Determinations on filtered samples

<sup>3</sup> On-site measurements

Table 18. Total and EDTA-extractable metals in stream sediments, Ardagh area.

| Location              | Total     |           |           |           |           |           |           |         | EDTA-extractable |           |           |
|-----------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|---------|------------------|-----------|-----------|
|                       | As<br>ppm | Sb<br>ppm | Hg<br>ppb | Zn<br>ppm | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Fe<br>% | Zn<br>ppm        | Cd<br>ppm | Mn<br>ppm |
| Ardagh Town           | < 5       | <0.5      | 540       | 500       | 6.0       | 90        | 1620      | 1.3     | 251              | 3.5       | 1250      |
| Ardagh Hill           | < 5       | <0.5      | 648       | 390       | 4.0       | 40        | 1000      | 0.7     | 68               | 0.5       | 1000      |
| BM traverse           | < 5       | -         | 510       | 305       | 2.7       | 35        | 1250      | 1.2     | 122              | 2.0       | 1010      |
| Drumming Cross Roads  | 25        | 1.0       | 302       | 510       | 6.0       | 200       | 1400      | 1.5     | 222              | 3.5       | 1150      |
| MF traverse           | 10        | -         | 1800      | 2100      | 17.3      | 95        | 1300      | 1.8     | 900              | 12.0      | 1250      |
| Below MF traverse     | < 5       | <0.5      | 92        | 760       | 7.0       | 70        | 750       | 0.9     | 414              | 5.0       | 650       |
| CG traverse           | < 5       | -         | 280       | 765       | 5.0       | 30        | 2300      | 1.8     | 370              | 3.0       | 2290      |
| Below CG traverse - 1 | < 5       | -         | 630       | 765       | 6.0       | 50        | 2050      | 1.9     | 380              | 6.0       | 1970      |
| Below CG traverse - 2 | 8         | <0.5      | 240       | 530       | 6.0       | 40        | 1250      | 1.6     | 249              | 2.5       | 1150      |
| Zn traverse, Keel     | 3         | -         | 620       | 1750      | 20.0      | 30        | 605       | 1.2     | 765              | 10.0      | 460       |

retention of metals is consistent with field observations as thin black coatings have been found on carbonate pebbles in stream beds.

Butt (op. cit.) has recorded coincident Fe-Mn-Co-Zn stream sediment patterns in Northern Ireland. Detailed field and experimental studies showed intimate soil-stream relationships responsible for mobilization and precipitation of metals.

The widespread movement of Zn-Cd into a calcareous till ( $\text{pH} > 7$ ) presents some geochemical difficulties. According to Schofield (1950), an alkaline pH creates negatively charged clay particles, an unfavourable environment for ionic Zn and Cd migration. Also, metal hydroxides of Zn and Cd may precipitate at alkaline pH.

Zn-Cd migration into stream bank tills and associated soil may be enhanced during infrequent floodings of streams in low-lying areas, thus saturating the flanking soil profiles with metal-bearing water. However, the magnitude of the laterally dispersed anomalies and the levels of Zn and Cd in stream waters (Table 17) suggest that periodic flooding may contribute only a minor amount of metal.

According to Udo et al. (1970), that while Zn adsorbs to  $\text{CaCO}_3$ , the role of clay and organic matter retention may be equally important. Randhawa and Broadbent (1965a) report that humic acid can retain quantities of divalent Zn up to pH 8.6. They also report (1965b) that ionic Zn is more strongly bound than ionic Ca and can only be removed using dilute nitric acid. Ravikovitch et al. (1968) investigated "plant available" Zn in calcareous soils and reported measurable levels of the element.

The above references suggest that while ground water fluctuations may create hydrological conditions suitable for lateral movement of metals into calcareous tills and soils, chemical dispersion mechanisms to form Zn-Cd hydromorphic halos about anomalous streams (at alkaline pH) may be aided or enhanced by clay minerals and organic complex

movement of metals. As Zn and Cd become diluted at a distance from the stream, precipitation and/or sorption processes would tend to become more important and effectively "fix" the metal.

#### 4.8 ENVIRONMENTAL MAGNIFICATION OF SOIL ANOMALIES AT KEEL

##### 4.8.1 Introduction

Ore and pathfinding metal distribution in the secondary environment at Keel is both widespread and geochemically complex. It has been postulated that hydromorphic dispersion processes have transported Zn and Cd through soils to expand the areal distribution of the clastic anomalies. In addition, other environmental controls appear equally important in accumulation and magnification of soil anomalies.

Two soil traverses (P-P<sub>1</sub> and AF-AF<sub>1</sub> in Fig. 10) cross the peak Zn-Cd anomaly and Pb-Hg anomaly found at Keel. Results show the importance of investigating soil conditions and metal distribution within the soil profile during orientation studies in geochemical exploration in the Longford District.

Peaty gleysolic soils and gleyed environments at Keel have chemically mobilized Hg, Pb, and Ag for eventual accumulation in near-surface humic horizons while a basin peat overlying gleyed, mineralized tills has retained unusually high amounts of Zn and Cd (dry weight matter) and considerable amounts of Ag, Mo, Sn, Ni, Ba, Sr, and Sb (ashed samples). In contrast, well-drained Grey-Brown Podzolic (Modified) profiles overlying the Decomposed Zone show relatively little enrichment of ore and pathfinding metals.

Thinly-overburdened areas usually show better anomaly relief (note traverse AF-AF<sub>1</sub> on Fig. 24) ~~than~~ do thickly-covered areas. Since topography can vary sympathetically with overburden depth, hydromorphic gravity and capillary movement of mobile and immobile

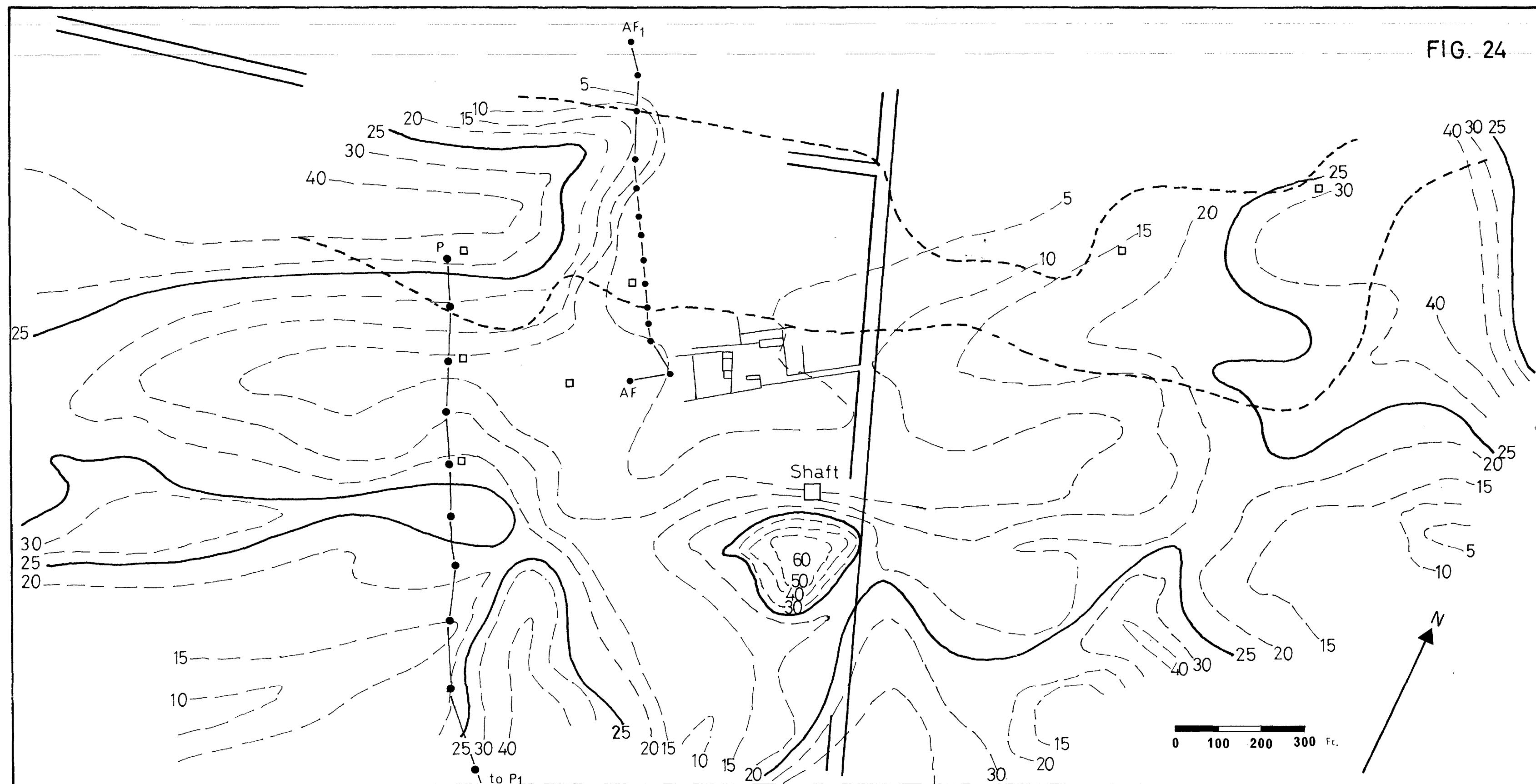


FIG. 24

FIG. 24 Thickness of glacial drift, Keel

- 20 glacial drift isopachs (ft.)
- 25
- - - plan outline of the Decomposed Zone
- pit
- — • soil traverse

metals in unconsolidated surficial deposits must be considered important metal dispersion processes in the Longford District.

#### 4.8.2 Metal Anomalies in Peaty Gleys and Gleysolic Soils at Keel

Gleying occurs in those soils subjected to impeded drainage which normally results in a relatively reducing and/or anaerobic environment. At Keel, gleyed profiles are characterized by a blue-gray till at depth and some accompanying ferric iron mottling.

It is well known that gleying can cause extensive mobilization of iron (Bloomfield, 1952). Bloomfield reports from experimental work (Ng and Bloomfield, 1962) that considerable Zn, Pb, Mn, Fe, Mo, and Ni can be readily mobilized when soils are flooded and incubated anaerobically with plant material.

Swaine and Mitchell (1960) report that during impeded drainage, conditions differ markedly from those in freely drained soils and certain trace elements can be mobilized, among them Co, Ni, Cu, V, Fe, and Pb. Further, they state restricted drainage may in extreme instances mobilize up to 50 per cent of the total content of the element in question, while the effects of other pedological processes such as podzolization are (by methods employed in their investigations) of a much smaller order. Hence, minor local changes in drainage conditions are quite liable to obscure efforts of other factors.

The anomalies in gleysolic soils investigated at Keel are primarily Hg-Pb-Ag anomalies. Figure 25 shows results on a soil traverse (two depths) of these elements and organic carbon in gleyed fields directly north of the shaft site. Earlier studies had confirmed the presence of an intense and coincident Pb-Hg anomaly.

Of particular interest in Figure 25 are the following:

- i) The similar, near-surface accumulations of Hg-Pb-Ag suggesting organo-metallic concentrating mechanisms

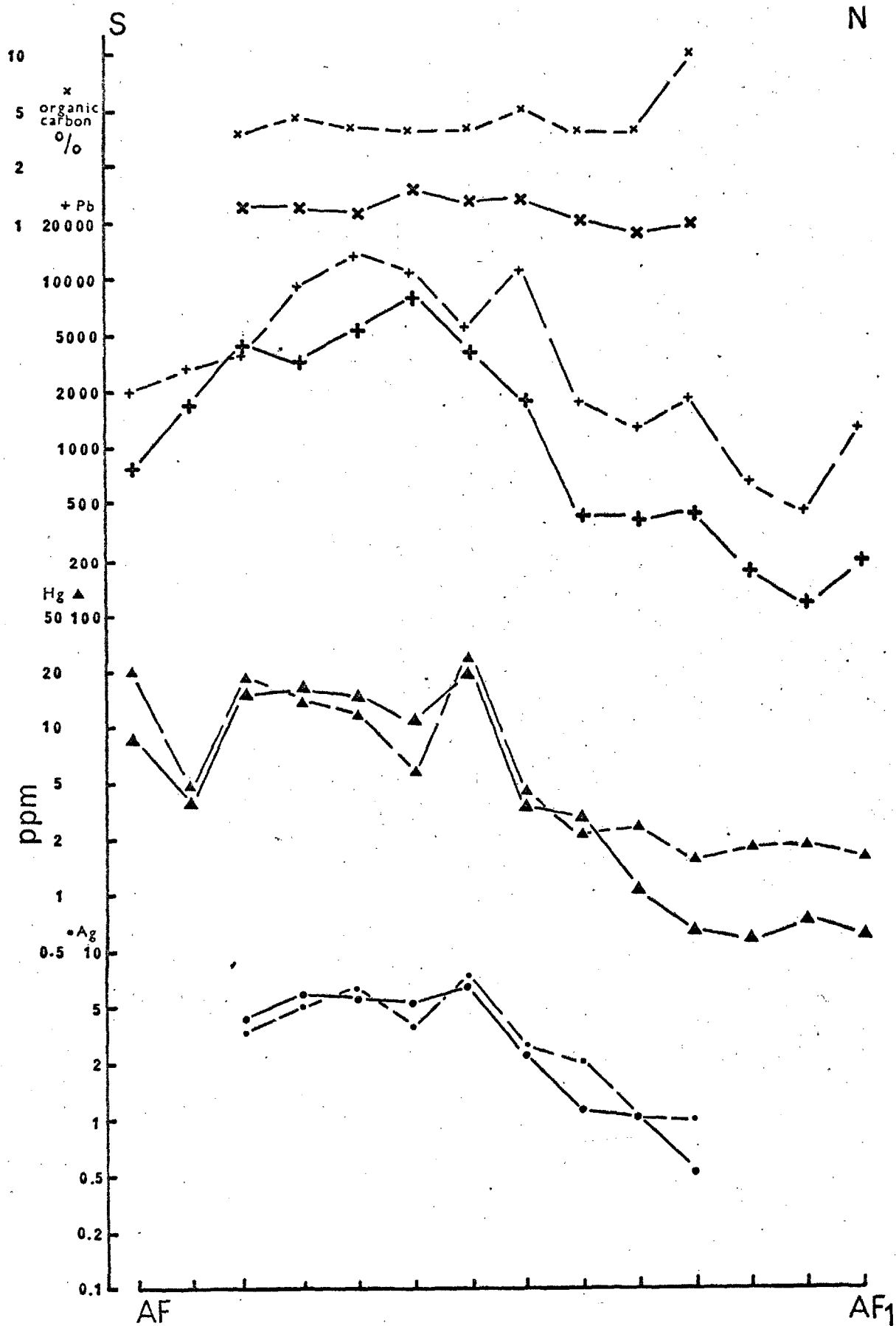


Fig. 25 Pb, Hg, and Ag in mineralized, peaty gleysolic soils, Keel



# ii) The proximity of the Decomposed Zone

Metal accumulation in near-surface humic horizons overlying sulphide mineralization and/or their oxidized products has been reported by Hornbrook (1970), Boyle (1968), and Reed and Miller (1971). In each instance, the investigators report that the content of Ag in "A" horizon reflects subcropping mineralization.

Anomalous levels of mercury have also been recorded in near-surface soil horizons overlying mineral deposits (Barakso et al., 1969, Barakso and Tarnocai, 1970, and Warren et al., 1966).

In most of the above-quoted references, Pb enrichment accompanies Ag and Hg. Warren and Delavault (1960) mention "lead tends to accumulate in a particular soil horizon, usually the A<sub>1</sub>. Forest litter and peat may also accumulate lead." Warren et al. (1966) report accumulation of Pb in A<sub>0</sub> and A<sub>1</sub> horizons covering Pb-Zn mineralization in British Columbia.

The extraordinary levels of Pb encountered in some near-surface horizons at Keel (up to 3.2%) must be considered true (bio)geochemical enrichments as no mining history has been recorded in the Longford District (Patterson, op. cit.) and contamination seems unlikely. The nearby road is lightly travelled and Pb from petrol combustion products seems improbable, although vegetation and humus respond positively to such pollution (Warren, 1966 and Lagerwerff and Specht, 1970).

Two pits were excavated in this highly anomalous area for visual examination and sampling purposes. Plate 7 shows the profile development in one of these pits and Table 19 shows selected element distributions.



Plate 7    Anomalous peaty, gleyed, and podzolized soil profile, Keel. Note dark gray clasts in bleached horizon. Scale 1:12

Table 19. Metal distribution in an anomalous peaty, gleyed, and podzolized profile, Keel

| Depth<br>(in.)     | Description                   | As<br>ppm | Sb<br>ppm | Hg<br>ppm | Zn<br>ppm | Cd<br>ppm | Pb<br>% | Mn<br>ppm | Fe<br>% | Ca<br>% | Mg<br>% | Cu <sup>1</sup><br>ppm | Ag <sup>1</sup><br>ppm | Ba <sup>1</sup><br>ppm | L.O.I. <sup>2</sup><br>% | Eh<br>mV | pH <sup>3</sup> |
|--------------------|-------------------------------|-----------|-----------|-----------|-----------|-----------|---------|-----------|---------|---------|---------|------------------------|------------------------|------------------------|--------------------------|----------|-----------------|
| 0-6                | Dk. br. loam                  | 20        | 5         | 4.2       | 650       | 9         | 2.9     | 120       | 1.6     | 0.4     | 0.4     | 500                    | 20                     | 5000                   | 33                       | +540     | 5.5             |
| 6-12               | Dk. br. loam                  | 10        | 2.5       | 4.4       | 600       | 8         | 3.2     | 60        | 1.2     | 0.5     | 0.4     | 500                    | 16                     | 5000                   | 35                       | +460     | 5.7             |
| 12-16              | Dk. br. gray<br>plastic clay  | < 5       | 2.5       | 20        | 500       | 4         | 2.4     | 40        | 1.0     | 0.1     | 0.5     | 200                    | 16                     | 5000                   | 13                       | +500     | 5.5             |
| 16-28              | Bleached clays<br>and sands   | < 5       | 2.5       | 0.6       | 420       | 4         | 0.4     | 80        | 1.5     | 0.1     | 0.6     | 50                     | 0.8                    | 850                    | 3                        | +500     | 5.7             |
| 16-28 <sup>4</sup> | Dk. gray clasts               | < 5       | 1.0       | 0.5       | 250       | 2         | 0.3     | 50        | 1.7     | 0.1     | 1.3     | 50                     | 0.8                    | 1000                   | 3                        | -        | 5.8             |
| 28-36              | Ferric-mottled<br>gleyed clay | 5         | 6.0       | 1.1       | 300       | 4         | 0.3     | 100       | 2.2     | 0.1     | 0.7     | 50                     | 1.6                    | 850                    | 3                        | +580     | 5.5             |
| 36-48              | Boulder clay,<br>gleyed       | 20        | 1.0       | 2.0       | 330       | 6         | 0.2     | 330       | 2.8     | 0.3     | 1.0     | 50                     | 1.0                    | 1000                   | 4                        | +440     | 6.5             |
| 48-60              | Boulder clay                  | 23        | 3.0       | 0.9       | 180       | 4         | 0.06    | 330       | 2.6     | 0.3     | 0.7     | 50                     | 1.0                    | 1000                   | 4                        | -140     | 7.8             |

<sup>1</sup> Results on ignited portions

<sup>3</sup> Regenerated deionized water slurry

<sup>2</sup> Loss On Ignition

<sup>4</sup> Clasts in 16-28 inch horizon

surface and Fe sesquioxide accumulation at depth. Zinc and Cd, although anomalous, show less geochemical relief than Pb, Ba, Cu, Hg, and Ag. Slightly anomalous Sb levels seemingly follow Fe. The dark gray shaley clasts (see Plate 7) in the 16-28 inch horizon contain 3100 ppm Pb and suggest a possible source of metals.

The writer believes that the thinly-covered, subcropping Decomposed Zone and till have been "geochemically homogenized" by ground water gleying and podzolization. Such processes have produced conditions enabling the metal reserves of the Decomposed Zone to enter into chemical and biogeochemical reactions leading to surficial accumulation of Hg-Pb-Ag.

Analyses on size-fractions approximating sand, fine sand, and silt-clay fractions (Table 20) show metal build-up with finer fractions. Iron is particularly concentrated in the silt-clay fraction. Considering dispersion processes, the relative differences are sufficient to suggest metal association with clay minerals and, possibly, with colloidal hydrous Fe oxides.

One N KCl, three per cent acetic acid, and 0.1M EDTA extractions (Table 21) on the silt-clay fractions show some readily available metal (KCl extract), considerable potentially available metal (acetic acid extract), and even greater amounts of chelatable metal (EDTA extract). Levels of cold-extractable metals support a hypothesis of mixed organic matter and clay mineral mechanisms operating within the profile being responsible for the mobilization and near-surface accumulation of metals.

#### 4.8.3 Metals in Peat at Keel

The small, metalliferous peat at Keel is of the "fen" type as described by Newbould (1958). A fen peat usually develops in a topographic depression underlain by mineral soils or tills which are

Table 20. Metal distribution in selected size fractions<sup>1</sup> for an anomalous, peaty gleysolic profile, Keel

| Depth<br>(in.) | Description                        | Fractions             | Hg<br>ppb | Zn<br>ppm | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Fe<br>% | Ca<br>% | Mg<br>% | O.C.<br>% |
|----------------|------------------------------------|-----------------------|-----------|-----------|-----------|-----------|-----------|---------|---------|---------|-----------|
| 0-8            | Dark brown organic-rich loam       | -38 +80 <sup>2</sup>  | 4890      | 620       | 5.9       | 3800      | 740       | 1.6     | 0.28    | 0.37    | 3.9       |
|                |                                    | -80 +197 <sup>3</sup> | 4900      | 630       | 11.6      | 4800      | 680       | 1.9     | 0.30    | 0.39    | 4.1       |
|                |                                    | > -197 <sup>4</sup>   | 6200      | 780       | 15.6      | 5600      | 730       | 2.0     | 0.37    | 0.48    | 4.4       |
| 8-18           | Gray clay, dark gray mottle        | -38 +80               | 2410      | 510       | 2.9       | 1470      | 120       | 1.4     | 0.16    | 0.66    | 0.4       |
|                |                                    | -80 +197              | 2480      | 550       | 3.6       | 1590      | 110       | 1.6     | 0.18    | 0.74    | 0.5       |
|                |                                    | > -197                | 3040      | 770       | 4.7       | 1600      | 120       | 3.6     | 0.24    | 0.92    | 0.6       |
| 18-28          | Gray clay, Fe <sup>3+</sup> mottle | -38 +80               | 950       | 230       | 2.4       | 340       | 110       | 1.5     | 0.44    | 0.69    | 0.2       |
|                |                                    | -80 +197              | 1070      | 310       | 3.9       | 390       | 250       | 2.1     | 0.57    | 0.91    | 0.3       |
|                |                                    | > -197                | 1070      | 400       | 6.1       | 530       | 320       | 2.8     | 0.73    | 1.16    | 0.3       |
| 28-36          | Orange-brown sandy clay            | -38 +80               | 200       | 73        | 1.8       | 20        | 610       | 2.7     | 6.08    | 0.76    | 0.1       |
|                |                                    | -80 +197              | 200       | 83        | 2.3       | 20        | 1100      | 3.4     | 6.78    | 0.89    | 0.1       |
|                |                                    | > -197                | 204       | 200       | 2.0       | 60        | 1500      | 3.9     | 7.47    | 1.09    | 0.2       |

<sup>1</sup> Dry sieved

<sup>2</sup> Sand

<sup>3</sup> Fine sand

<sup>4</sup> Silt, clay

Table 21. Results of partial extraction experiments on an anomalous peaty gleysolic profile <sup>1</sup>, Keel

| Depth (in.) | Extraction Method   | Zn ppm | Cd ppm | Pb ppm | Mn ppm | Fe ppm |
|-------------|---------------------|--------|--------|--------|--------|--------|
| 0-8         | Total <sup>2</sup>  | 780    | 15.6   | 5600   | 730    | 2.0%   |
|             | 0.1M EDTA           | 195    | 13.0   | 4400   | 520    | 2500   |
|             | 3% HAC <sup>3</sup> | 195    | 13.5   | 1450   | 180    | 53     |
|             | 1N KCl              | 124    | 10.0   | 1700   | 84     | < 10   |
| 8-18        | Total               | 770    | 4.7    | 1600   | 120    | 3.6%   |
|             | 0.1M EDTA           | 44     | 3.0    | 1490   | 10     | 320    |
|             | 3% HAC              | 62     | 4.5    | 790    | 15     | 60     |
|             | 1N KCl              | 16     | 1.0    | 500    | 5      | < 10   |
| 18-28       | Total               | 400    | 6.1    | 530    | 320    | 2.8%   |
|             | 0.1M EDTA           | 30     | 3.0    | 370    | 110    | 200    |
|             | 3% HAC              | 29     | 6.0    | 195    | 67     | 15     |
|             | 1N KCl              | < 3    | < 1.0  | 10     | < 5    | < 10   |
| 28-36       | Total               | 200    | 2.0    | 60     | 1500   | 4.9%   |
|             | 0.1M EDTA           | 11     | 3.0    | 30     | 560    | 810    |
|             | 3% HAC              | 6      | 3.0    | 22     | 135    | 455    |
|             | 1N KCl              | < 3    | < 1.0  | < 10   | < 5    | < 10   |

<sup>1</sup> Results on > -197 mesh

<sup>2</sup> HNO<sub>3</sub>/HClO<sub>4</sub> digestion

<sup>3</sup> 3% Glacial acetic acid

alkaline-rich (i.e. substantial concentrations of cations such as Ca, Mg, K, Na). The organic accumulation is usually black in colour, moderately decomposed, and has an ash content always greater than 10 per cent, frequently greater than 50 per cent. The term basin peat (as used on the General Soil Map, 1969) is a preferred term as it describes more fully the environment of the peat bog.

The basin peat covers an area underlain by faults, subcropping mineralization, and the Decomposed Zone, thus represents an ideal locale for investigation of selected organo-metallic relationships. A line of samples traversing the peat was collected (P-P<sub>1</sub> in Fig. 10) and analyses for Zn, Cd, Pb, Fe, Mn, As, and Hg are presented in Figure 26.

Accumulations of Zn and Cd are truly unique to the Keel area. Mercury levels correlate more closely with the Group IIB elements than with Pb, which shows erratic distribution. Iron levels are relatively stable across the traverse while Mn and As are rejected from and/or reject the organic environment. The highly anomalous peaks and levels of metal (Zn-Cd-Hg-Pb) are smeared over both Decomposed Zone and subcropping veins, but dispersion from sulphide is suggested by peak Zn-Cd values over known mineralized faults. Within the peat, Zn and Cd show little relative difference between near-surface and at depth sites, but appear to exhibit a preferential partition with surface humic horizons in the flanking, poorly-drained inorganic soils.

Pitting was employed to examine vertical distribution and accumulation of Zn-Cd and other selected elements in basin peat. Two pits (Tables 22 and 23) were excavated in areas fringing the peat and metal levels approximate element distributions found in anomalous gleysolic profiles.

Two other pits (Tables 24 and 25) are over the known Zn-Cd maxima from Figure 26. Plate 8 shows profile development in one of

Table 22. Metal distribution in a gleyed profile fringing an anomalous basin peat, Keel

| Depth<br>(in.) | Description                    | Hg<br>ppb | Zn<br>ppm | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Fe<br>% | L.O.I.<br>% | pH <sup>1</sup> |
|----------------|--------------------------------|-----------|-----------|-----------|-----------|-----------|---------|-------------|-----------------|
| 0-10           | Black peaty loam               | 2240      | 1150      | 18        | 640       | 400       | 2.2     | 32          | 6.5             |
| 10-20          | Bleached, gray sands and clays | 200       | 190       | 4         | 60        | 200       | 2.3     | 4           | 7.8             |
| 20-28          | Ferric mottled, gray clay      | 92        | 150       | 3         | 50        | 660       | 3.1     | 7           | 7.9             |
| 28-36          | Boulder clay                   | 96        | 130       | 3         | 50        | 560       | 2.5     | 3           | 8.0             |

Table 23. Metal distribution in a gleyed profile fringing an anomalous basin peat, Keel

| Depth<br>(in.) | Description                    | Hg<br>pp | Zn<br>ppm | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Fe<br>% | L.O.I.<br>% | pH <sup>1</sup> |
|----------------|--------------------------------|----------|-----------|-----------|-----------|-----------|---------|-------------|-----------------|
| 0-8            | Black peaty loam               | 9600     | 2280      | 43        | 2500      | 180       | 2.0     | 21          | 5.8             |
| 8-18           | Gray sands and clays           | 1400     | 900       | 8         | 160       | 90        | 1.6     | 3           | 6.6             |
| 18-28          | Ferric mottled, brown sands    | 480      | 460       | 7         | 130       | 90        | 2.0     | 3           | 6.7             |
| 28-36          | Ferric mottled clays and sands | 304      | 550       | 7         | 70        | 200       | 2.6     | 4           | 7.9             |
| 36-48          | Brown clays and sands          | 180      | 2240      | 41        | 60        | 240       | 2.8     | 3           | 8.1             |

<sup>1</sup> Regenerated deionized water slurries



Table 24. Metal distribution in an anomalous basin peat, Keel

| Depth<br>(in.) | Description                                 | As <sup>1</sup><br>ppm | Sb <sup>2</sup><br>ppm | Hg <sup>1</sup><br>ppb | Zn <sup>1</sup><br>ppm | Cd <sup>1</sup><br>ppm | Pb <sup>1</sup><br>ppm | Mn <sup>1</sup><br>ppm | Fe <sup>1</sup><br>% | Ca <sup>1</sup><br>% | Mg <sup>1</sup><br>% | L.O.I.<br>% |
|----------------|---------------------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|----------------------|----------------------|----------------------|-------------|
| 0-4            | Mixed peat and inorganic layer <sup>3</sup> | 20                     | <1.0                   | 448                    | 1390                   | 17                     | 350                    | 220                    | 1.8                  | 0.5                  | 0.4                  | 20          |
| 5-10           | Black peat                                  | 25                     | 17.5                   | 400                    | 14200                  | 122                    | 90                     | 520                    | 1.8                  | 2.6                  | 0.1                  | 85          |
| 10-20          | Black peat                                  | 20                     | 20                     | 472                    | 18000                  | 156                    | 100                    | 300                    | 1.1                  | 2.6                  | 0.1                  | 83          |
| 20-30          | Black peat                                  | 25                     | 5.0                    | 328                    | 1220                   | 26                     | 110                    | 20                     | 3.7                  | 0.8                  | 0.1                  | 85          |
| 30-34          | Mixed black muck and brown clay             | 75                     | 1.2                    | 480                    | 1420                   | 42                     | 110                    | 30                     | 2.0                  | 5.0                  | 0.4                  | 54          |
| 34-40          | Blue-gray till                              | 10                     | <1.0                   | 180                    | 150                    | 1.0                    | 40                     | 580                    | 2.3                  | 4.1                  | 1.0                  | 2.5         |
| 40-50          | Blue-gray clays                             | 20                     | <1.0                   | 232                    | 130                    | 3.0                    | 40                     | 440                    | 2.2                  | 3.8                  | 0.9                  | 3.0         |

<sup>1</sup> Results on air-dried portions

<sup>2</sup> Results on ignited portions

<sup>3</sup> Not a natural horizon, probably contaminated by farming practices



Plate 8 Highly anomalous basin peat overlying gleyed till, Keel. Light and dark brown horizons above the till can contain up to 17.9% Zn and 0.66% Cd. Scale 1:25

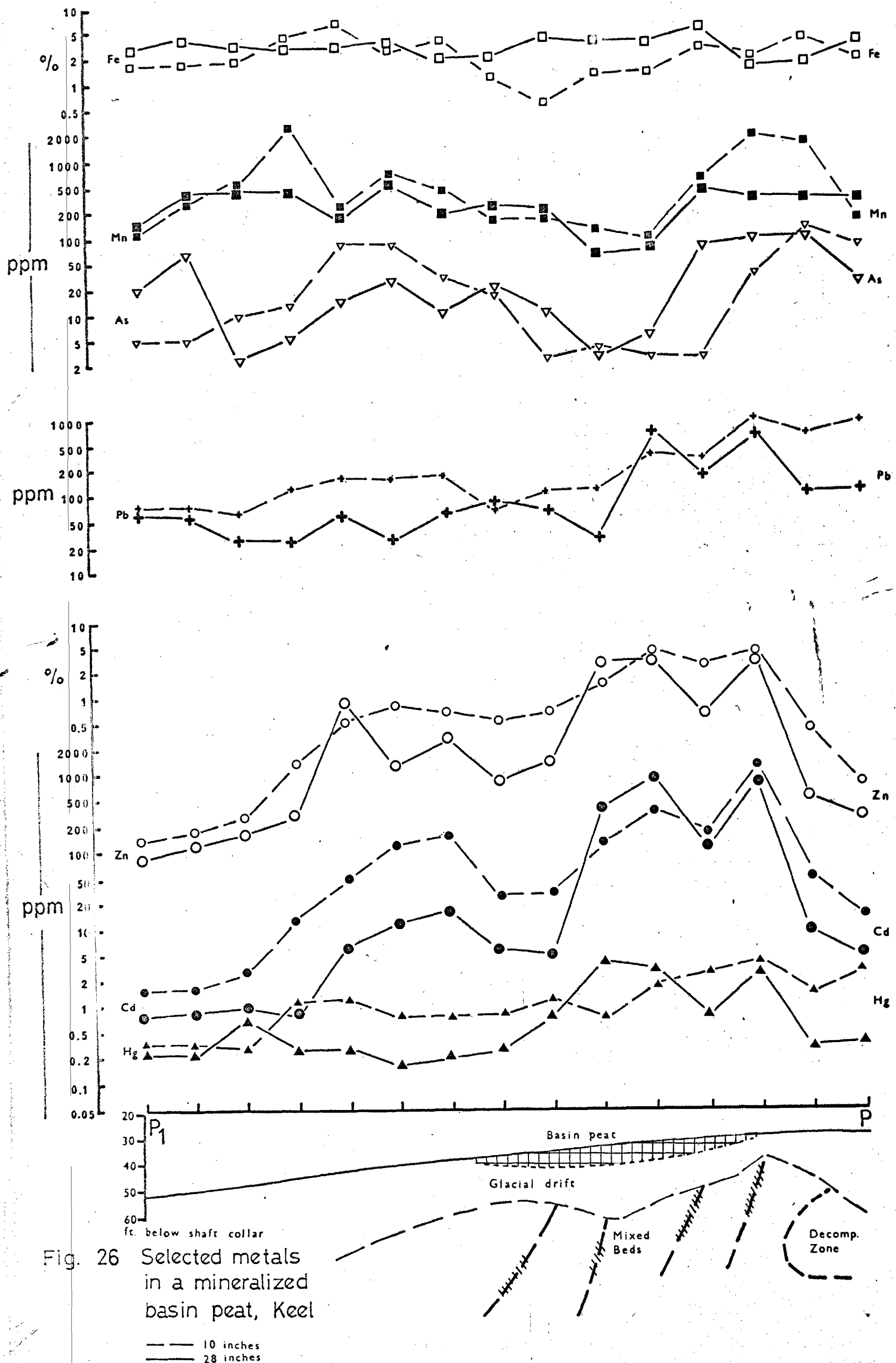


Fig. 26 Selected metals in a mineralized basin peat, Keel

Table 25. Metal distribution in a highly anomalous basin peat, Keel

|                |                               | Total                  |                        |                        |                      |                        |                        |                        |                      |                      |                      |                        |                        |                        |                        |                        |                        |                        |                        |                        |             | EDTA - extractable   |                        |                        |                        |                      | Eh <sup>3</sup><br>mV | pH <sup>3</sup> |
|----------------|-------------------------------|------------------------|------------------------|------------------------|----------------------|------------------------|------------------------|------------------------|----------------------|----------------------|----------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|-------------|----------------------|------------------------|------------------------|------------------------|----------------------|-----------------------|-----------------|
| Depth<br>(in.) | Description                   | As <sup>1</sup><br>ppm | Sb <sup>2</sup><br>ppm | Hg <sup>1</sup><br>ppb | Zn <sup>1</sup><br>% | Cd <sup>1</sup><br>ppm | Pb <sup>1</sup><br>ppm | Mn <sup>1</sup><br>ppm | Fe <sup>1</sup><br>% | Ca <sup>1</sup><br>% | Mg <sup>1</sup><br>% | Sn <sup>2</sup><br>ppm | Ga <sup>2</sup><br>ppm | Mo <sup>2</sup><br>ppm | Cu <sup>2</sup><br>ppm | Ti <sup>2</sup><br>ppm | Ag <sup>2</sup><br>ppm | Ni <sup>2</sup><br>ppm | Ba <sup>2</sup><br>ppm | Sr <sup>2</sup><br>ppm | L.O.I.<br>% | Zn <sup>1</sup><br>% | Cd <sup>1</sup><br>ppm | Pb <sup>1</sup><br>ppm | Mn <sup>1</sup><br>ppm | Fe <sup>1</sup><br>% |                       |                 |
| 0-4            | Dark brown immature peat      | 20                     | 20                     | 532                    | 3.1                  | 409                    | 490                    | 90                     | 0.9                  | 1.5                  | 0.09                 | 8                      | 8                      | 6                      | 200                    | 2000                   | 40                     | 200                    | >5000                  | 600                    | 82          | 1.5                  | 113                    | 370                    | 90                     | 0.6                  | +560                  | 5.0             |
| 6-18           | Black peat                    | 20                     | 5                      | 376                    | 2.6                  | 285                    | 200                    | 90                     | 1.3                  | 2.0                  | 0.1                  | < 5                    | 5                      | 30                     | 60                     | 600                    | 4.0                    | 400                    | >5000                  | 1600                   | 85          | 1.3                  | 97                     | 170                    | 90                     | 0.9                  | +500                  | 5.4             |
| 18-26          | Black peat                    | 20                     | 35                     | 328                    | 1.4                  | 169                    | 120                    | 70                     | 2.4                  | 2.6                  | 0.08                 | 200                    | 5                      | 40                     | 60                     | 600                    | 2.0                    | 400                    | >5000                  | 2000                   | 87          | 0.9                  | 77                     | 100                    | 70                     | 1.5                  | +540                  | 4.9             |
| 26-34          | Mixed black and brown peat    | 25                     | 48                     | 312                    | 2.3                  | 502                    | 140                    | 50                     | 5.7                  | 5.0                  | 0.09                 | 400                    | 4                      | 50                     | 60                     | 600                    | 0.5                    | 500                    | 5000                   | 2000                   | 81          | 0.9                  | 87                     | 90                     | 40                     | 2.1                  | +580                  | 4.5             |
| 34-40          | Light and dark humic horizons | 43                     | 60                     | 280                    | 17.9                 | 6600                   | 840                    | 100                    | 4.1                  | 2.8                  | 0.2                  | < 5                    | 4                      | 20                     | 60                     | 400                    | 2.0                    | 300                    | 3000                   | 1300                   | 67          | 2.0                  | 28                     | 240                    | 60                     | 1.1                  | +620                  | 3.8             |
| 40-50          | Dark brown humic horizons     | 105                    | 48                     | 224                    | 8.7                  | 300                    | 30                     | 80                     | 10.0                 | 2.2                  | 0.2                  | 300                    | 4                      | 40                     | 50                     | 300                    | < 0.2                  | 850                    | 3000                   | 1600                   | 68          | 1.6                  | 26                     | 40                     | 50                     | 2.5                  | +550                  | 2.9             |
| 50-56          | Dark gray gleyed clay         | 45                     | < 1                    | 192                    | 1.4                  | 256                    | 240                    | 130                    | 2.2                  | 4.2                  | 1.5                  | < 5                    | 16                     | 2                      | 40                     | 2000                   | 1.0                    | 85                     | 600                    | 100                    | 8           | 0.2                  | 17                     | 100                    | 40                     | 0.2                  | +350                  | 6.1             |
| 56-66          | Gray-blue boulder clay        | < 5                    | < 1                    | 368                    | 0.1                  | 15                     | 60                     | 300                    | 1.8                  | 5.0                  | 1.6                  | < 5                    | 16                     | < 2                    | 40                     | 2000                   | < 0.2                  | 85                     | 300                    | 100                    | 6           | 0.04                 | 5                      | 50                     | 150                    | 0.2                  | -40                   | 6.6             |

<sup>1</sup> Results on air-dried portions;    <sup>2</sup> Results on ignited portions;    <sup>3</sup> On-site measurements

these pits. Of particular interest in Plate 8 are the light and dark brown humic horizons directly over the blue-gray boulder clay. These horizons can contain up to 17.9 per cent Zn (Table 25) and 0.66 per cent Cd (both dry weight). Lead and Hg are only slightly enriched, but ashed portions of mineralized peat contain relatively abundant levels of As, Sb, Ba, Sr, Sn, Mo, Ni, and Ag. EDTA extractions (also Table 25) indicate a decreasing level of extraction (Zn-Cd) with depth suggesting that most metal in deeper organic horizons may have become permanently fixed.

As noted earlier, the accumulation of metals in such an environment is not an isolated instance. Cannon (op. cit.) reports similarly high Zn values (up to 16 per cent) in peat and muck overlying a mineralized (sphalerite) dolomite in the United States. Further, she states that Zn, Pb, and other metals have been leached from the dolomites, transported to the bog site and precipitated (as sulphides) and/or entered into biogeochemical accumulating processes through plants.

Donovan (1965) reports values up to 1900 ppm Cu, 77,500 ppm Zn, 4200 ppm Pb, and 4200 ppb Hg in peats in the immediate vicinity of the Tynagh deposit. Accumulation here is related to an "unlimited" amount of available metal derived from the underlying till, initially by vegetation growing directly on anomalous soils, and subsequently by leaching of the waterlogged calcareous till by acid ground water which is sucked upwards due to high loss of water from the surface of the bog, particularly during hot spells. Surface flooding may also have contributed some metal.

Salmi (1956) investigated peats overlying pyrite and sphalerite mineralization in Finland and noted concentration of Ag, Cu, Zn, Cd, Ni, Co, Cr, and Pb in peats and in twigs and leaves of Ledum palustre growing on the bog. He reports that metal accumulation originates

through acidic water rich in dissolved metals being taken up by plants and retained on perishing.

Walsh and Barry (1958) researched major, minor, and trace elements in Irish blanket and raised bogs. They report a relatively high level of Pb, Cu, and Ni in the surface layers of some profiles as well as that of Sn. Of further interest, they conclude that atmospheric precipitation of elements both in the form of sea derived salts and dust are important sources of metals in bog development. The surficial accumulation of Ti in the Keel peat may reflect wind-blown dust as a partial source of some elements.

Larsson (1971) has studied selected metal distribution in unmineralized blanket peats in the west of Ireland and recognizes the following metal variations regardless of underlying bedrock-type:

- i) Top zone of peat profile: Enhanced contents of Pb, Sn, Mn, Mo, and to a lesser extent Zn
- ii) Central zone of peat profile: Enhanced contents of Co, Cu, and Ni
- iii) Basal zone of peat profile: Tendency for enhanced contents of V

At Keel, the writer believes that metal sources, principally Zn and Cd, below and/or flanking the basin peat have migrated inward and upward by simple gravity and capillary movements of ground waters. An acid, slightly reducing environment retains metals in solution near the gley/peat contact. Metals are then introduced to active biochemical processes. Once entered into an organic environment, the metal becomes semi-permanently fixed. Of course, metals are still provided from lateral and sub-till sources to continue the enriching processes. Evaporation would tend to keep the peat solute concentrated (i.e. low in pH and high in organic complexes). Thus, metals are easily accommodated and provided in a form suitable for plants.

It is known that metals occur in peat waters at Keel, as a sample collected from an old pit filled with rain water (pH 2.9) contained 700 ppm Zn, 1.1 ppm Cd, and 1.6 ppb Hg (Table 17).

Other metals appear to have responded differently to the organic environment. Anomalous Pb levels are displaced to the north end of the peat traverse where the Decomposed Zone is thought to subcrop. The erratic levels of Pb shown in Figure 26 are probably due to the mixed secondary environmental chemistries usually found in areas fringing swampy ground (Hawkes and Webb, *op. cit.*). Lead does not appear to migrate into and/or upward in mineralized peats as it does in the nearby anomalous gleysolic soils. Arsenic and manganese appear to have rejected and/or have been rejected by the peaty environment. Iron probably enters into organic complex transport and biochemical mechanisms and thus exhibits little variation from inorganic to organic environments.

The basin peat at Keel has been contrasted with an immature, weakly mineralized basin peat west of Ardagh Town. Near-surface auger samples are compared in Table 26 to evaluate shallow sampling of small basin peats as a prospective geochemical exploration aid in the Longford District. It would seem encouraging that Ag, Pb, Zn, and Cd are noticeably enriched (particularly Zn-Cd) in the anomalous peat. Mercury exhibits little enrichment in the mineralized peat. Arsenic, Mn, and Fe are relatively depleted in the anomalous peat, but this may reflect the immaturity of the weakly mineralized peat rather than being indicative of a "negative" anomaly. Selenium analyses indicate some organic retention of the element, but the limited data is not conclusive for speculation on Se pathfinding for Keel-type ore.

Overall, the anomalous levels of Zn and Cd in basin peat have demonstrated the aqueous mobility of both elements to migrate to such an environment and their affinity for natural organo-metallic

Table 26. A comparison of metal levels in the near-surface horizons of a weakly mineralized basin peat<sup>1</sup> and a highly anomalous basin peat<sup>2</sup>

|                                        | Depth<br>(in.) | Description                 | As<br>ppm | Se<br>ppm | Hg<br>ppb | Ag<br>ppm | Cd<br>ppm | Zn<br>ppm | Pb<br>ppm | Mn<br>ppm | Fe<br>% |
|----------------------------------------|----------------|-----------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|---------|
| Weakly<br>mineralized<br>basin<br>peat | 8              | Black peat                  | 175       | 4.0       | 248       | < 1.0     | 8         | 630       | 80        | 170       | 2.8     |
|                                        | 12             | Black peaty muck            | 135       | 4.5       | 272       | 1.0       | 16        | 393       | 60        | 130       | 2.3     |
|                                        | 16             | Black muck bedrock at depth | 90        | -         | 328       | < 1.0     | 16        | 209       | 60        | 250       | 3.8     |
|                                        | 12             | Black muck bedrock at depth | 115       | 3.5       | 272       | < 1.0     | 7         | 117       | 140       | 280       | 2.0     |
|                                        | 18             | Black muck bedrock at depth | 75        | -         | 420       | 1.0       | 6         | 244       | 120       | 760       | 4.0     |
| Mean                                   |                |                             | 118       | -         | 308       | < 1.0     | 11        | 298       | 92        | 318       | 2.9     |
| Highly<br>anomalous<br>basin<br>peat   | 10             | Black peat                  | 30        | -         | 320       | 2.0       | 393       | 11300     | 380       | 100       | 2.2     |
|                                        | 10             | Black peat                  | < 5       | 2.0       | 360       | 4.0       | 485       | 20600     | 440       | 85        | 0.5     |
|                                        | 10             | Black peat                  | < 5       | -         | 288       | 2.0       | 380       | 20400     | 240       | 50        | 0.3     |
|                                        | 10             | Black peaty muck            | < 5       | 8.0       | 420       | 2.2       | 223       | 52000     | 720       | 70        | 1.1     |
|                                        | 10             | Black peaty muck            | 10        | -         | 560       | 1.2       | 333       | 24000     | 180       | 360       | 1.7     |
|                                        | 10             | Dark brown loam             | 10        | -         | 204       | < 1.0     | 10        | 2120      | 60        | 230       | 1.6     |
| Mean                                   |                |                             | 9         | -         | 358       | 1.9       | 304       | 21735     | 336       | 149       | 1.2     |

<sup>1</sup> West of Ardagh Town, near CG traverse

<sup>2</sup> At Keel



enrichment. Mercury and Pb levels are relatively deficient in mineralized peats. Tin, Ni, Ba, Sr, Mo, and Ag are enriched in ashed portions of the mineralized basin peat.

#### 4.8.4 Metal Levels in Anomalous Freely-drained Soils

Two additional pits were excavated at Keel in soils thought to be freely-drained sites. One pit (a modified Grey-Brown Podzolic profile) approximates the crest of the slight topographic elevation believed to be a flat-lying drumlin (see Glacial Geology and Geomorphology). Nearby, drillhole K96 intersects totally oxidized and leached metal-rich material covered by 20 ft. of glacial drift. Table 27 shows selected metal levels in the writer's pit to a depth of almost six feet coupled with analytical data on selected samples taken from drillhole K96. Other than a muddy and mottled horizon at about three feet (believed to be an Fe sesquioxide accumulation) and accompanying anomalous levels of Zn-Cd, the profile shows relatively little near-surface metal enrichment (other than Ba) relative to the mineralized till and the Decomposed Zone. Mercury values are somewhat depressed and there is no obvious evidence of gaseous (or saline) dispersion of the element through the unconsolidated overburden.

A second pit (Table 28) was excavated in an anomalous area east of Keel thought to be a freely-drained site. The locale is relatively low-lying and covers subcropping Decomposed Zone. Mercury and lead levels are more encouraging here, but the profile is moderately acidic in all horizons suggesting less than freely-drained conditions prevail. Topography has seemingly shown its influence on metal distribution and Zn-Cd-Pb-Hg sources here are believed to be derived from both the subcropping Decomposed Zone and laterally dispersed elements from flanking and unslope mineralized soils.

Table 27. Metal distribution in a freely-drained Modified Grey-Brown Podzolic profile overlying mineralized till<sup>1</sup> and the Decomposed Zone<sup>1</sup>, Keel

| Depth  | Description                 | Total     |           |           |           |           |           |           |         |           |           |                 | EDTA-extractable |           |           |           |           |
|--------|-----------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|---------|-----------|-----------|-----------------|------------------|-----------|-----------|-----------|-----------|
|        |                             | As<br>ppm | Sb<br>ppm | Hg<br>ppb | Zn<br>ppm | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Fe<br>% | Ag<br>ppm | Ba<br>ppm | pH <sup>2</sup> | Zn<br>ppm        | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Fe<br>ppm |
| 0-6"   | Brown loam                  | 23        | 1.0       | 240       | 360       | 3.0       | 160       | 1100      | 1.9     | 0.2       | 500       | 5.0             | 48               | 1.5       | 85        | 700       | 650       |
| 6-14"  | Br. stoney clay             | 13        | <1.0      | 176       | 360       | 1.0       | 120       | 1160      | 2.0     | 0.2       | 600       | 4.8             | 27               | 0.5       | 45        | 300       | 400       |
| 14-26" | Br. stoney clay             | 8         | 1.0       | 295       | 470       | 2.0       | 120       | 1380      | 3.2     | <0.2      | 400       | 4.9             | 23               | 0.5       | 35        | 210       | 200       |
| 28-36" | Br. stoney clay             | 25        | 1.0       | 300       | 350       | 3.0       | 150       | 1620      | 3.0     | <0.2      | 600       | 5.3             | 19               | 1.0       | 65        | 500       | 250       |
| 36-46" | Br. clay,<br>muddy mottling | 20        | 1.5       | 312       | 610       | 12        | 200       | 7200      | 4.5     | <0.2      | 1600      | 5.9             | 107              | 11.5      | 90        | 6600      | 2950      |
| 46-56" | Br. sandy clay              | 25        | 1.5       | 144       | 230       | 3.0       | 180       | 1220      | 3.0     | <0.2      | 1600      | 6.2             | 13               | 0.5       | 85        | 850       | 350       |
| 56-70" | Br. sandy clay              | 20        | <1.0      | 96        | 180       | 3.0       | 130       | 1630      | 3.3     | <0.2      | 1600      | 6.8             | 12               | 1.0       | 60        | 1600      | 750       |
| 8-12'  | Brown till                  | 40        | <1.0      | 1240      | 300       | 13        | 260       | 550       | 2.6     | 1.6       | 2000      |                 |                  |           |           |           |           |
| 12-15' | Brown till                  | 85        | 43        | 1860      | 2420      | 22        | 250       | 16800     | 8.5     | 4.0       | 5000      |                 |                  |           |           |           |           |
| 15-18' | Decomposed<br>Zone/till     | 70        | 23        | 1270      | 2500      | 22        | 100       | 84000     | 19.5    | 10.0      | >1%       |                 |                  |           |           |           |           |
| 18-25' | Decomposed Zone             | 113       | 48        | 1230      | 4000      | 54        | 2500      | 50000     | 12.5    | 10.0      | >1%       |                 |                  |           |           |           |           |
| 25-32' | Decomposed Zone             | 100       | 45        | 4400      | 2250      | 33        | 400       | 40000     | 11.0    | 3.0       | 5000      |                 |                  |           |           |           |           |
| 32-39' | Decomposed Zone             | 75        | 43        | 15200     | 2500      | 96        | 200       | 65000     | 17.5    | 16.0      | >1%       |                 |                  |           |           |           |           |

<sup>1</sup> Drillhole K96

<sup>2</sup> Regenerated deionized water slurry

Table 28. Metal distribution in a mineralized, Modified Grey-Brown Podzolic profile, Keel

| Depth<br>(in.) | Description               | As<br>ppm | Sb<br>ppm | Hg<br>ppb | Zn<br>ppm | Cd<br>ppm | Pb<br>ppm | Mn<br>ppm | Fe<br>% | pH <sup>1</sup> |
|----------------|---------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|---------|-----------------|
| 0-8            | Brown and gray loamy clay | <5        | <0.5      | 640       | 220       | 1.0       | 380       | 600       | 1.7     | 4.7             |
| 8-18           | Gray and brown sandy clay | 15        | 3.5       | 520       | 440       | 1.0       | 400       | 460       | 3.3     | 4.7             |
| 18-30          | Brown sandy till          | 23        | <0.5      | 480       | 330       | 1.0       | 350       | 2010      | 3.8     | 4.7             |
| 30-40          | Gray and brown sandy till | 30        | 2.0       | 532       | 330       | 1.0       | 280       | 900       | 3.1     | 4.7             |
| 40-50          | Brown sandy till          | 20        | 0.5       | 460       | 440       | 6.0       | 420       | 4150      | 3.2     | 4.7             |

<sup>1</sup> Regenerated deionized water slurry

#### 4.9 BIOGEOCHEMISTRY AT KEEL

Biogeochemistry as a mineral exploration aid has had some success in glaciated environments (Warren, 1962). When combined with the closely associated science of Geobotany, the approach is an appealing one and can be considered a potentially useful "remote-sensing" search tool.

Biogeochemical prospecting has been investigated by a number of research institutions but to date, little active interest seems shown by mining companies. H.L. Cannon of the U.S.G.S. and H.V. Warren and R.E. Delavault of the University of British Columbia, Canada have been the principal proponents in Western research and application. Of the the Soviet investigators, the name of Malyuga is probably best known.

Geobotany and biogeochemistry in the Keel and Ardagh areas has been studied in a preliminary (orientation) investigation by Cole (1968). She concludes the Zn content of plant samples outline Zn-Pb mineralization at Keel more effectively than do near-surface soil samples.

Species sampled by Cole included hawthorn (Crataegus monogyna Jacq), ash (Fraxinus excelsior L.), and limited collection of gorse (Ulex europea L.) and bracken (Pteridium aquilinum L.).

Hawthorn appears to have a favourable accumulating mechanism for Zn while analysis of gorse may be useful in defining Pb-rich soils (Figs. 27, 28, 29). Further, Cole suggests that the Zn content of plants may define faults at Keel. A third conclusion indicates a general relationship between plant Zn content and total soil Zn content for sites over certain lithological units. Fourthly, the higher mobility of Zn relative to Pb was confirmed.

Cole's work has added new and interesting data on the applicability of biogeochemistry to mineral exploration in the glaciated

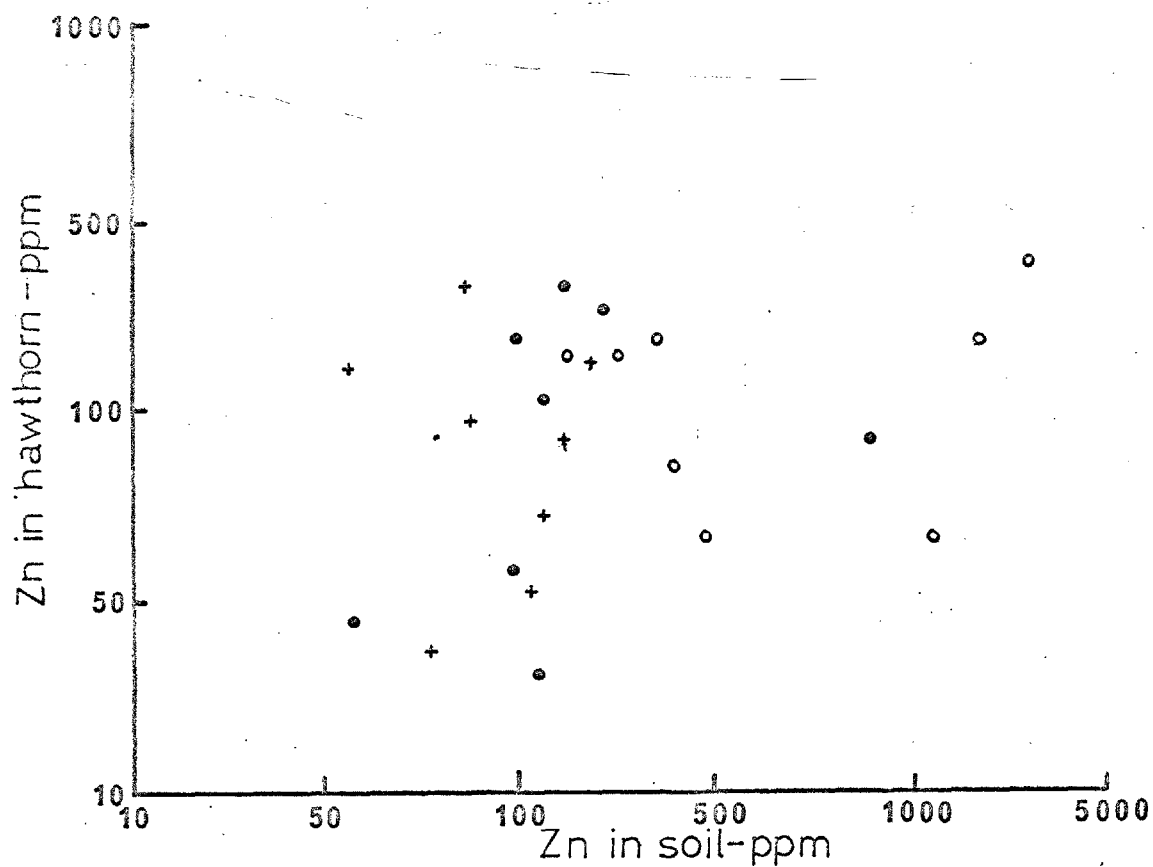


Fig. 27 Relationship between Zn in hawthorn and Zn in soil, Keel

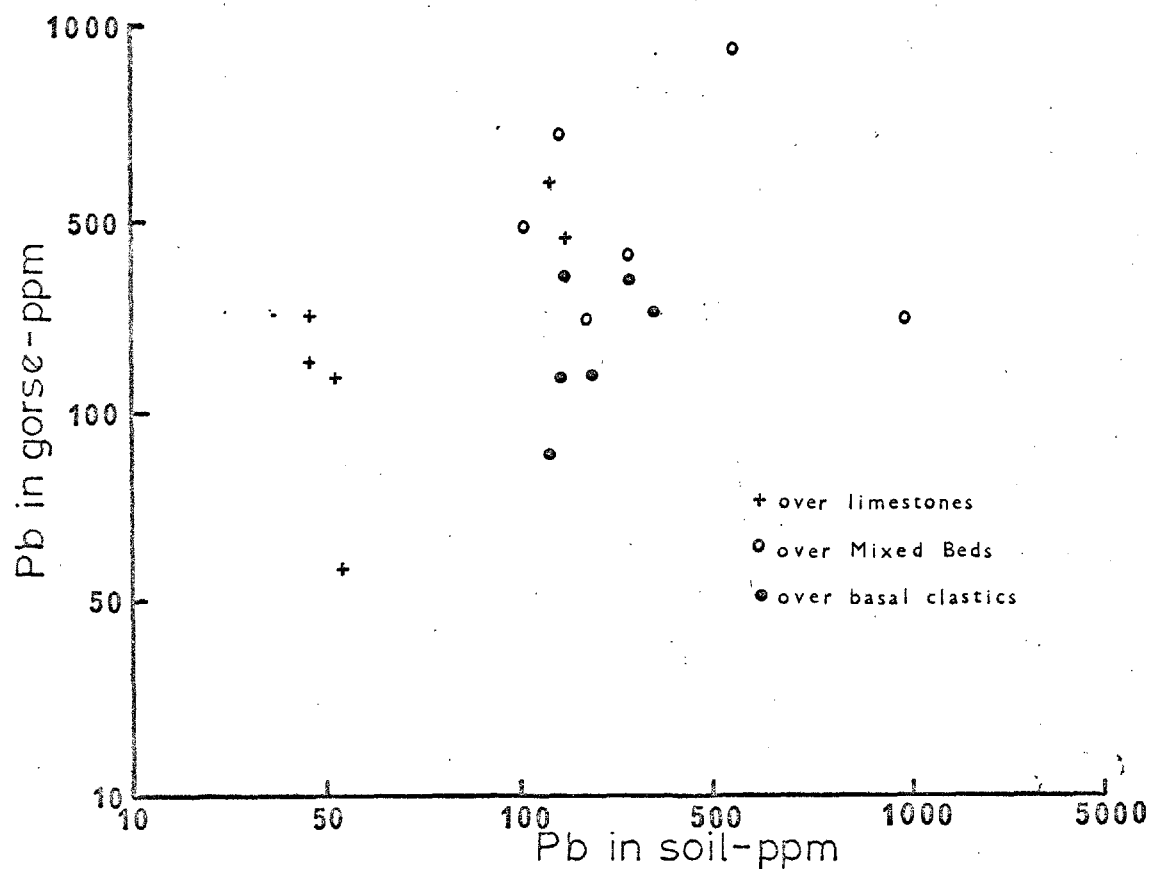


Fig. 28 Relationship between Pb in gorse and Pb in soil, Keel

both after Cole, unpub. info.

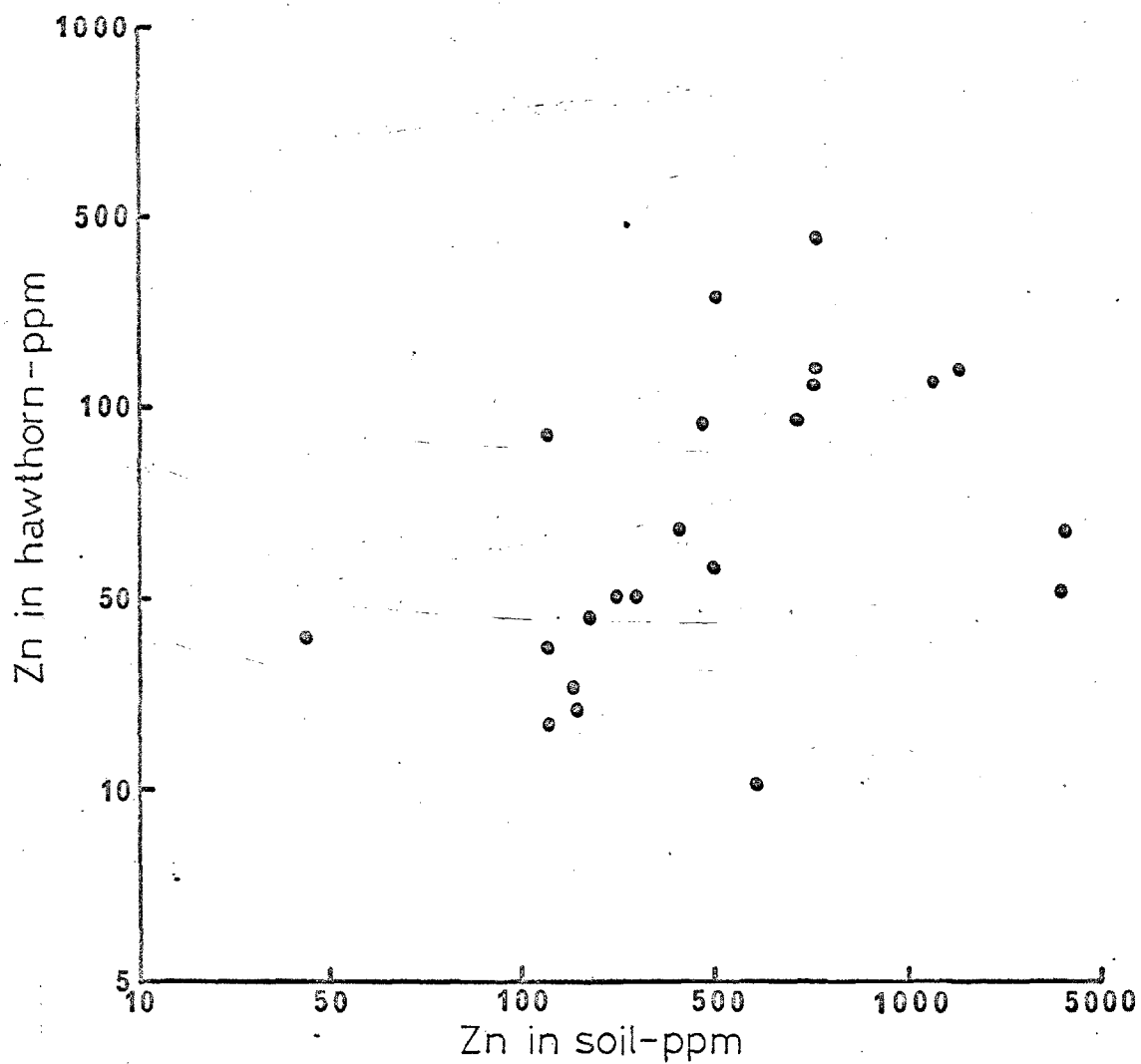


Fig. 29 Relationship between Zn in soil and Zn in hawthorn, Ardagh

after Cole, unpub. info.

environment. However, this study may exhibit some of the shortcomings of the technique.

As the Keel area (and essentially most of Ireland) is a patchwork of fields and pastures, shrubs and trees are normally found along field margin boundaries. This feature biases sampling to the hedgerows. The writer wishes to point out that some environmental factors here may influence metal uptake by plants. As most fields at Keel are surrounded by ditches which contain water at least part of the year, drainage problems could result in fluctuating redox potentials in the associated soils. This may affect trace metal availability to roots over the course of a growing season. As first and second year twigs are normally selected for analyses, metal levels in plants may reflect either a suppressing or an enhancing effect of element accumulation and not the true secondary dispersion halo of the metal sought.

Further, Cole has made no mention of soil pH, soil type or the Decomposed Zone. These factors have all been shown to have some effect (to a certain degree) on metal values in Keel soil profiles. These same factors may influence metal distribution in plants.

The writer embarked on a short biogeochemical investigation at Keel primarily to supplement the study of relative mobilities of the metals of concern, viz. Cd, Hg, Zn, and Pb. Manganese was also included in the study. Pasture grasses were selected as they represent the sole vegetation in most fields (Cole is critical of shallow rooting plants for prospecting purposes). Two collections were made, one in March and the other in July of the same year. Figure 30 shows the element levels found in the July collection across the Keel deposit. If Figure 30 is compared with the soil results in Figure 16, the Zn content of grass appears to vary sympathetically with Zn soil values. The nature of soil appears to be of some importance as poorly-drained, gleyed sites seem to have mobilized metals such as Pb, and perhaps,

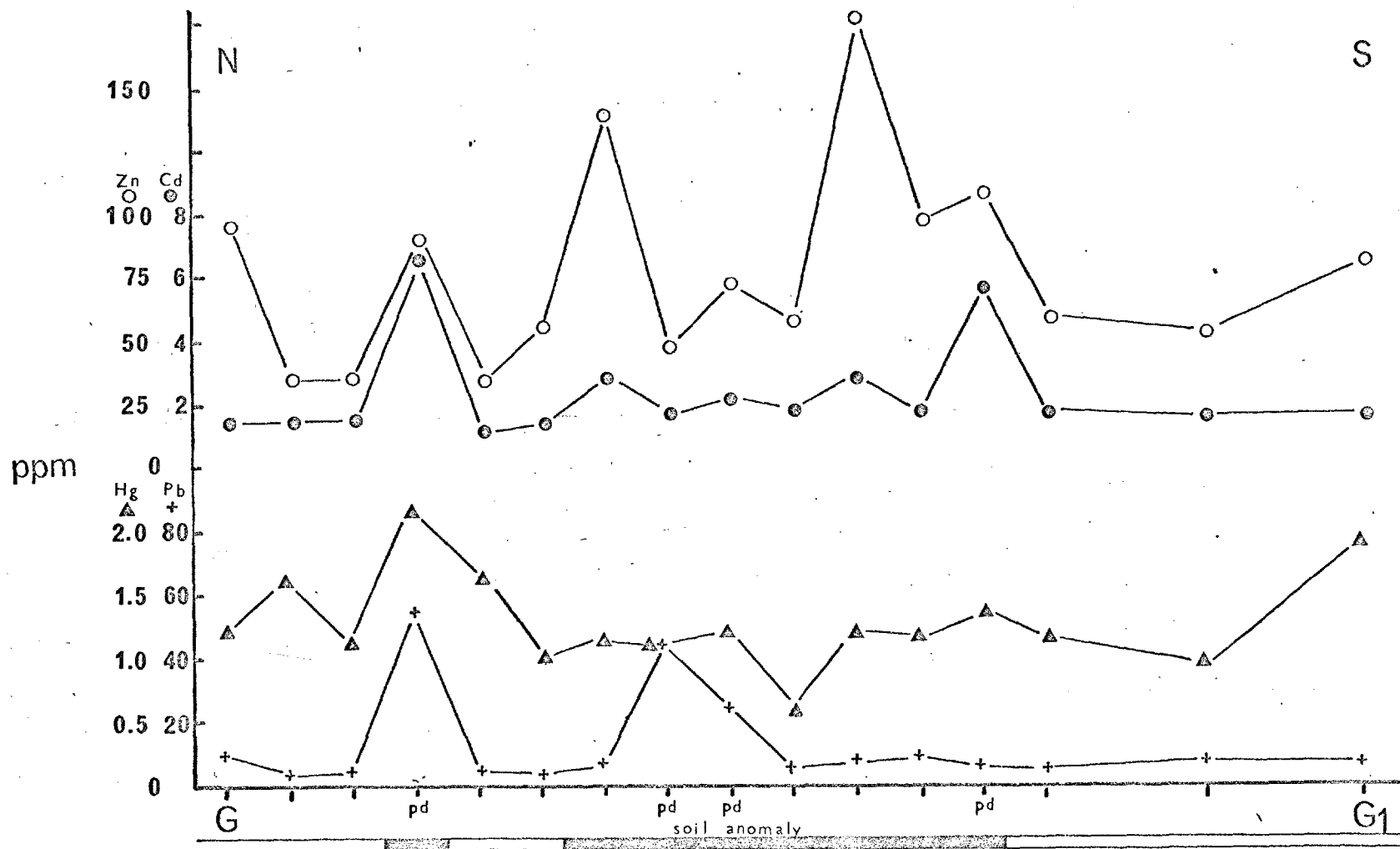


Fig. 30 Selected metals in grass, Keel

pd poorly drained soil  
 † dry weight



Cd for plant uptake.

Mercury exhibits an almost stable level of plant uptake and retention, although soil values range from 300 ppb to 10 ppm. Warren et al. (1966) state "vegetation growing on soil containing less than 1 ppm Hg tend to concentrate the element. Thus, air-dried vegetal matter, which usually varies from 0.1 to 2 ppm Hg, may be considered to have modestly concentrated any mercury present in the associated soil. On the other hand, where soils have a mercury content running to tens or hundreds of ppm, then vegetal matter has less mercury than its related soils." On this account, it would appear that analysis for mercury in plants may be of little, if any use as a mineral exploration aid. The reason for this being that the mercury content of plants may bear little relation to the mercury content of soil.

It is interesting to note that Zn, Pb, and Mn levels are much higher in the March sample collection (essentially previous year growth), while Cd shows little or no change and Hg levels are decidedly lower. The accumulation and retention of Pb in pasture grasses and humus is well known (Vinogradov, 1959), but the significance of stable Cd content and apparent seasonal loss of Hg can only be conjectural owing to the lack of geochemical and biochemical information on these elements and their role in botanical systems. Table 29 summarizes the limited seasonal range and mean data.

Four grass samples have been omitted from previous discussion as they represent special consideration. The sampling stations were those on the small mineralized peat below the Keel shaft site developed over subcropping sphalerite and the Decomposed Zone.

The results of these four samples are unique in that Zn accumulation in grasses is approximately five times that in grasses on mineral soils. As the peat can contain up to 18 per cent Zn (dry weight), grass accumulation of the element is understandable. However,

Table 29. Ranges and means of selected metals in grasses growing on mineral soils, Keel area

| Element | July Collection <sup>1</sup> |                    | March Collection <sup>2</sup> |                    |
|---------|------------------------------|--------------------|-------------------------------|--------------------|
|         | Range<br>ppm                 | Arithmetic<br>Mean | Range<br>ppm                  | Arithmetic<br>Mean |
| Zn      | 35-161                       | 70                 | 76-298                        | 111                |
| Cd      | 1.0-6.6                      | 2.1                | 0.7-6.6                       | 2.4                |
| Hg      | 0.6-2.2                      | 1.4                | 0.5-1.0                       | 0.8                |
| Pb      | <2-53                        | 11                 | 4-102                         | 27                 |
| Mn      | 59-417                       | 162                | 150-1000                      | 436                |

<sup>1</sup> 16 samples

<sup>2</sup> 9 samples

All values dry weight ppm

Cd accumulation in peat grasses relative to grasses growing on mineral soils is not noticeable (although present in hundreds of ppm in dry weight peat) suggesting a "biochemical partitioning" of Cd from Zn. Lead and Mn levels are relatively suppressed in peat grasses while Hg (like Cd) exhibits little change relative to those grasses found growing on inorganic soils. Table 30 shows metal accumulation ratios of peat grasses contrasted to mineral soil grasses.

In summary, a number of points seem noteworthy. Zinc accumulates in Keel pasture grasses in direct response to the level of Zn in mineral soil and peat. This substantiates Cole's finding with hawthorn. Limited results suggest that cadmium is not readily taken up by grasses, reflecting rejection of the element, perhaps related to the element's known toxicity to biochemical systems. Lead accumulation in grass is noted over gleysolic soils with surface accumulations of the element. Mercury appears readily taken up by grass (up to 2.2 ppm), but no clear pattern or relationship with Hg-rich soils has been established. The Mn soil-plant relationship in the Keel area is still unclear, but certainly, peats and their grasses are relatively deficient in the element.

The present application of biogeochemical techniques for prospecting seems somewhat limited in the Keel and Ardagh areas. Supplementary information confirming relative element mobilities has been obtained.

#### 4.10 SUMMARY

Important points deemed from applied geochemical studies on till, soil, peats, stream sediments, water, and pasture grasses from the Keel and Ardagh areas include:

- i) Regional geochemical soil maps show weakly to strongly anomalous levels of Zn, Cd, and Pb flanking the Keel inlier.

Table 30. Selected metals in mineralized peats <sup>1</sup> and associated grasses <sup>2</sup>, Keel area

| Site No.          | Zn ppm |       | Cd ppm |      | Hg ppm |                   | Pb ppm |      | Mn ppm |      |
|-------------------|--------|-------|--------|------|--------|-------------------|--------|------|--------|------|
|                   | Grass  | Peat  | Grass  | Peat | Grass  | Peat <sup>3</sup> | Grass  | Peat | Grass  | Peat |
| P4                | 410    | 22600 | 2.3    | 158  | 1.2    | 1640              | 3      | 250  | 27     | 500  |
| P5                | 570    | 42000 | 1.5    | 350  | 1.0    | 1520              | 3      | 380  | 33     | 90   |
| P6                | 340    | 15700 | 2.6    | 137  | 1.3    | 620               | <2     | 120  | 97     | 140  |
| P7                | 163    | 6800  | 3.8    | 3.4  | 1.2    | 900               | 2      | 100  | 27     | 190  |
| A.R. <sup>4</sup> | 5.3    |       | 1.1    |      | .9     |                   | .27    |      | .35    |      |

<sup>1</sup> Dry weight

<sup>2</sup> Dry weight

<sup>3</sup> Filtered pyrolyzed volatiles

<sup>4</sup> Accumulation Ratio = 
$$\frac{\text{Mean of metal determinations in grasses growing on peat}}{\text{Mean of metal determinations in grasses growing on mineral soils}}$$

Cadmium anomalies correlate well with anomalous levels of Zn. Both elements disperse widely, but strongly anomalous areas appear to be confined by topography to low-lying peaty soils and to soils adjacent to anomalous stream courses.

Mercury levels in soil correlate strongly with those of Pb. Both Pb and Hg exhibit intense residual soil halos, some approximating known faults. The possibility of a lateral, low order dispersion halo of Hg in soils about the Keel deposit should not be overlooked.

ii) Secondary dispersion of ore metals from massive sulphides, disseminated sulphides and the Decomposed Zone in the Keel area follows the mobility sequence  $Zn \geq Cd > Pb$ .

iii) At Keel, metal enrichment of Zn, Cd, Pb, Ag, Ba, Hg, and some other elements is marked over known areas of subcropping metalliferous Decomposed Zone. There appears to be little definition of mineralized faults.

iv) Soil traverses across known soil anomalies in the Ardagh area exhibit much the same distribution and levels of ore and pathfinding elements as found at Keel. Metal sources in the Ardagh area are believed to be known, sub-economic, disseminated mineralization and, perhaps, additional unknown subcropping sulphide occurrences.

v) Lateral hydromorphic dispersion of Zn and Cd play an important part in the regional distribution and patterns of these elements, particularly in the Ardagh area. A mechanism for lateral aqueous dispersion and movement of Zn and Cd and eventual precipitation and/or adsorption has been proposed.

vi) Soil-type (more aptly, soil conditions) is shown to be of some importance in the vertical and areal distribution of ore and pathfinding metals in the Keel and Ardagh areas.

At Keel, metal distribution differs markedly from peats to peaty gleysolics to freely drained Grey-Brown Podzolic soils.

A basin peat has accumulated large amounts of Zn, Cd, and Fe (dry weight material) and significant amounts of Sb, Ni, Ag, Ba, Sr, and Sn in ashed material. Mercury, Pb, and Mn (dry weight) are relatively deficient in mineralized peat.

Anomalous peaty gleysolic soils at Keel are characterized by marked surficial enrichment of Ag, Hg, Pb, Ba, and Cu opposed to their relative depletion at depth. Zinc, Cd, and Mn are relatively depleted in mineralized gleysolic soils, but show sympathetic distribution patterns to the highly enriched suite of metals.

Metal dispersion through an average thickness of till (20 ft.) topped by a freely-drained Modified Grey-Brown Podzolic soil profile is somewhat restricted, perhaps due to the highly compact nature of the overburden.

vii) Analysis of Ca and Mg-rich stream and mine waters from Keel and Ardagh ( $\text{pH} > 7$ ) indicates that Zn and Cd have some migration potential in a carbonate-rich environment. Manganese and Fe are normally restricted to the parts per billion range. Mercury is present in all waters (unfiltered) at about the 0.7 ppb level.

The analysis of stream waters may be a useful mineral exploration aid in the Longford District to supplement stream sediment and soil surveys.

viii) Review of an unpublished report on preliminary biogeochemical investigations at Keel and Ardagh indicates that the Zn content of hawthorn (Crataegus monogyna Jacq) and the Pb content of gorse (Ulex europea L.) may be useful in defining metal-rich soils and perhaps, mineralized faults.

Analysis of pasture grasses by the writer has indicated that anomalous Zn and Pb levels can define metal-rich soils. There is some evidence of Zn/Cd partitioning in grass growing on zinc and cadmium-rich peats. The mercury content of grass shows little, if any,

enrichment over soils containing up to 10 ppm of the element.

Biogeochemistry may be useful as a prospecting aid in the Longford District if applied in areas where drainage and local soil conditions are well known.

ix) Mercury appears to disperse readily in the secondary environment of the Longford District. Its mobility in soils may approach that of Zn. However, mercury has shown a tendency to accumulate in near-surface horizons thereby requiring profile distribution studies during orientation to determine the correct sampling horizon(s). Mercury correlates strongly with Pb and Ag in mineralized soils.

Generally, the use and application of Hg pathfinding seems justifiable in the Keel and Ardagh areas as support for both interpretation of Zn and Pb anomalies and in initial prospecting work.

x) Arsenic and Sb have limited use in the Keel and Ardagh areas as pathfinding elements for sulphide mineralization and/or As-Sb-rich sources. Arsenic mobility seems limited by both ferric iron retention and, in some instances, organic accumulation of the element. Donovan (1965) has suggested the use of As as a "universal" pathfinder for Irish deposits in the Lower Carboniferous, but evidence here does not support his claim.

Antimony does show low order anomalies (particularly with Pb-rich soils), but the application of Sb pathfinding does not present any real advantages.

xi) Barium and Ag would appear to be of some use as pathfinding elements in the Longford District. Both define metal-rich soils at Keel and Drumming Cross Roads with weak to high geochemical relief.

Barium exhibits a somewhat restricted mobility and may have application (like Pb) in approximating metal source areas. However, the element does accumulate quantitatively in peats and peaty horizons

over gleysolic soils, demonstrating some (bio)geochemical mobility.

Silver seems to show a higher mobility than Ba and, in certain instances, it may approximate that of Hg and Zn. Again, Ag accumulates in peats and peaty horizons of gleysolic soils.

Semi-quantitative spectrographic analysis is sufficient for Ag and Ba determinations for present use and application in geochemical prospecting in the Longford District.



## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS - PART A

#### 5.1 GENERAL

Chapter Five contains conclusions and pertinent suggestions on Chapters Two, Three, and Four. Recommendations have been put forward for both mineral exploration application and for further basic research needs.

#### 5.2 CONCLUSIONS

i) The Keel deposit occurs in Lower Carboniferous clastic and carbonate rocks as vein-like orebodies composed primarily of Cd-rich sphalerite and lesser amounts of galena. Tetrahedrite is present as inclusions in both sphalerite and galena and constitutes economically recoverable amounts of Ag (1-3 Troy ozs./ton). Mercury is present (up to 500 ppm) in sphalerite, presumably as proxy for Zn and Cd. The possibility of mercurial tetrahedrite (variety schwartzite) should not be overlooked.

ii) An iron and manganese-rich "capping" (after the definition of Blanchard, op. cit.) has formed at Keel at the expense of the porous, chemically reactive Mixed Beds Group (particularly the Bioclastic Dolomites). Reticulated and boxwork voids (limonitic jasper) have been recognized in drillcore specimens. The name "Decomposed Zone" (coined by Riofinex geologists) has been retained to describe leached and oxidized material as it aptly describes the probable chemical mechanisms of attack and decomposition of calcareous rock by sulphuric acid.

The major source of sulphuric acid to oxidize and leach calcareous-dolomitic sandstones and shales is thought to have been

disseminated sulphides (sphalerite with minor galena) of unknown original grade. Disseminated pyrite is believed to have been important in providing initial sulphuric acid and manganiferous goethite, the latter important in retention of ore and pathfinding metals during leaching processes.

Oxidation has taken place both above the water-table (pre-glacial) and below the water-table (glacial and post-glacial). The relative importance of either environment is difficult to assess, but it is likely that the greater part of leaching occurred prior to glaciation.

The Decomposed Zone is distinctly metalliferous and contains highly anomalous levels of Zn, Cd, Pb, Hg, Fe, and Mn. Sulphide sources are suggested for Zn, Cd, Hg, and Pb while Fe-Mn sources are believed to be acid insoluble residues of calcareous sandstone and shale origin and pyrite. Arsenic, Ag, Sb, Cu, Mo, Ni, and Ba are also relatively enriched (acid insoluble residues and pyritic sources).

Mercury is as highly enriched in leached subcrop as Zn, Cd, and Pb. This suggests a sulphide (sphalerite) origin of Hg. The abnormally high standard deviation from 106 analyses of partially, moderately, and totally oxidized and leached material may reflect localized enrichments of Hg (relative to Zn-Cd). An arithmetic mean of 5.3 ppm has been calculated and indicates a restricted mobility of Hg, like other heavy metals, in an Fe and/or Mn-rich environment.

iii) Regional soil metal patterns in the Keel and Ardagh areas are dominated by widespread dispersion of Zn and Cd. Lateral hydromorphic dispersion about anomalous streams of these two elements has been investigated by total and cold-extractable analyses of the soils effected. Some interesting results have been obtained and a geochemical model for metal movement (Zn, Cd) into a calcareous

environment (basic pH) is presented.

The mobility of Cd in the secondary environment approximates that of Zn. However, in some instances Cd dispersion seems relatively restricted or even independent to that of Zn.

Poorly-drained topographic depressions are favoured sites for Zn-Cd accumulation. Presumably, this involves ground water migration of metals and retention by naturally-occurring humic and fulvic compounds.

Lead and Hg levels correlate well in near-surface soils and both elements exhibit some association with known faulting. Limited data suggests the presence of a widespread secondary dispersion halo of Hg in soil at Keel.

Mineralized soils derived from glacial till within the Keel and Ardagh areas are enriched in ore (Zn-Cd-Pb) and pathfinding (Hg-Ag-Ba-Sb) elements. At Keel, Zn, Cd, Pb, and Hg effectively outline the area of mineral potential. However, the moderately and strongly anomalous classifications reflect the subcrop of the Decomposed Zone rather than the massive sulphide mineralization and associated faults. This feature demonstrates the importance of some knowledge of weathered products of sulphide origin during the investigation of soil anomalies.

Soil anomalies at Keel have been magnified by the presence of the subcropping metal reserves of the Decomposed Zone in direct contact with poorly-drained tills. It is proposed that mixed clay mineral and organo-metallic reactions are responsible for mobilization and eventual accumulation of metals (principally Hg-Pb-Ag) in near-surface humic horizons of peaty, podzolized gleySolic soils. Hydrological considerations, Eh and pH, and perhaps, microbial influences are proposed controls on facilitating metal movement to peats where organo-metallic bonding effectively fix large amounts of Zn and

Cd (dry weight matter) and considerable amounts of Ag, Mo, Sr, Ba, Ni, and Sn (ashed material).

### 5.3 RECOMMENDATIONS

#### 5.3.1 Suggestions for Applied Geochemical Usage

i) Stream sediment surveys ( $\frac{1}{2}$  mile sample intervals) effectively outline potentially favourable areas of near-surface mineralization in the Longford District. This is in accordance with known successfully applied reconnaissance stream sediment surveys elsewhere in Ireland.

ii) Soil surveys in the Longford District are effective and reliable in the approach to mineral exploration and the following guide is presented for prospecting usage.

a) Reconnaissance soil grid sampling (up to 800 ft. line spacings and 400 ft. sample centres) or road-side sampling over areas deemed important by stream sediment surveys or of known and/or of projected mineral potential will adequately define large areas of interest.

b) On definition of promising areas, a survey to examine soil type and profile development, soil conditions, ground water drainage and vegetation should be undertaken. Profile levels of selected metal distributions are necessary as soil conditions may demand different sampling depths at different sites to maximize a true working geochemical relief or to minimize adverse secondary accumulation of heavy metals. Detailed sampling may follow.

c) Small basin peats act as metal accumulators and should be profile sampled at margin and centrally located sites to evaluate potentially favourable areas below and/or flanking bogs which may have contributed metal by ground water (capillary and gravity)

movement. Near-surface sampling of basin peats may be useful during reconnaissance sampling.

d) At present, water analysis and biogeochemistry should be used only in conjunction with soil, peat, or stream sediment work and not as a primary aid for prospecting in the Longford District.

e) Zinc, Cd, Hg, and Pb should be determined on all soils, peats, and stream sediments. Silver, Sb, and Ba determinations may be of some use in certain instances. Arsenic is of limited use as a pathfinding element. Iron analyses should be employed in profile distribution studies on mineral soils and on peats and on any ferric-stained samples or soil horizons as a guard against "scavenged" metals. Secondary Mn oxides may similarly sequester heavy metals and suspected accumulations of the element should be noted and analyzed for Mn and selected elements.

f) The Decomposed Zone is enriched in metals, viz. Hg, Cd, Zn, Pb, Ag, and Ba. These metals have played a major role in the development of soil anomalies at Keel. It is recommended that future studies employing geochemical methods in Ireland should be made aware of the potential influence of the oxidized/leached Fe-rich subcrop. Metal enriched Mn-Fe oxides have been found at Tynagh, Co. Galway (Morrissey and Whitehead, op. cit.) and in Co. Offaly (Y. Maurice, pers. comm.), both revealed by soil sampling; hence, Keel does not represent an isolated incidence as regards the leached, Fe-rich subcrop.

iii) The aspect of Hg and Cd movement and accumulation in a cool, temperate, drift-covered environment may be of direct use to those individuals investigating industrial pollution of these two elements (see Newsweek, July 5, 1971 and The Sunday Times, June 6, 1971 on Cd pollution and Newsweek, April 20 and August 3, 1970, and Environment, Vol. 13, No. 4, 1971 on Hg pollution). Certainly the lateral hydromorphic dispersion characteristics exhibited by naturally-

occurring Cd (and Zn) and surficial accumulation of naturally-derived Hg would seem to be important geochemical parameters when studying movement and distribution of introduced metals.

### 5.3.2 Additional Research Requirements

i) The laterally dispersed soil (Zn-Cd) anomalies about streams in the Keel and Ardagh areas have additional analogue(s) elsewhere in the Longford District (J. Sample, pers. comm.). Further study (both field and experimental chemical work) would seem useful for both mineral exploration and metal pollution research.

ii) The mode of occurrence of Pb-Ag-Hg in the surficial humic horizons of mineralized gleysolic soils and organic accumulating mechanisms of heavy metals in general requires additional fundamental research. Infra-red spectrometry or gas chromatography may be useful techniques in establishing functional groups of humic and/or fulvic acids (partly) responsible for such accumulations. Schnitzer and Skinner (1964) have successfully used infra-red absorption spectra to determine some functional groups in naturally-occurring organic compounds found in soil. Experiments on the mode of occurrence of Hg compounds is currently under investigation at A.G.R.C. (W. T. Meyer and E. Leen) using continuous heating/plasma emission spectrometry analysis and some preliminary results are discussed in Chapter Seven.

iii) Further study on the sulphide-leached outcrop/subcrop-dispersed metal relationship to establish metal movement versus metal retention ratios would seem helpful for modern day mineral exploration.

iv) Biogeochemistry and geobotany require additional study and reserach to critically evaluate their use in drift-covered terrain for application to both regional and detailed mineral exploration.

Also, air-borne "remote-sensing" mineral prospecting techniques will require expert knowledge of plant-soil-metal relation-

ships. Such studies are currently being investigated in the Keel-Ardagh areas using infra-red (false colour) and colour photographic techniques (N. Press, pers. comm.).

v) Multi-element analysis on Fe-Mn accumulations derived from leached subcrop has been successful in both genesis and metal source studies in the Keel area. Analyses for Tl, Ge, In, W, and Te on this (and other) leached and oxidized material of sulphide origin could be rewarding research. Germanium and In are known to be concentrated in some sphalerites while Tl is known to preferentially concentrate in some pyrites. The raised levels of Mo in some oxidized subcrop suggests the possible presence of anomalous W. Although Se was not found in Decomposed Zone material, the Group IVa analogue Te may be found as a residual product after galena and/or tetrahedrite and provide further information on this potentially useful pathfinding element.

vi) Further statistical treatment on class limits for regional soils and cluster analysis for oxidized and leached material may also be of some use.

## CHAPTER 6

### MERCURY AND THE SECONDARY ENVIRONMENT - A REVIEW

#### 6.1 GENERAL

The purpose of Chapter Six is to comment on and to discuss literature sources of information on the present knowledge of Hg dispersion in the secondary environment. Although James (1962) has adequately dealt with the basic chemical and geochemical knowledge of mercury, the writer contends that a further review is required at this time, with particular reference to the biotransformation and interconversion of Hg in the environment and related Hg pollution problems.

The writer has made full use of currently existing review articles (see Chapter One). In addition, another article (Wallace *et al.*, 1970) has been included.

It is hoped that the information here will be of some aid to those wishing to apply Hg analysis to prospecting or requiring to interpret secondary geochemical patterns of Hg. Speculation has been made on the potential influence of environmental Hg pollution as affecting its use as a pathfinder in mineral exploration.

A further reason for discussing current literature sources on Hg (bio)(geo)chemistry is to collate the analytical, chemical, geological and biological findings on mercury which normally may not be referred to in geochemical researches. The writer has found that most articles relating to Hg in the secondary environment are widely scattered in the scientific and trade journals and takes this opportunity to present his library findings.

#### 6.2 GEOCHEMICAL CYCLE OF MERCURY

Attention was first brought to the complex nature of the



geochemical cycle of Hg by Rankama and Sahama (1950). At that time they concluded that the "quantitative cycle" of Hg was inadequately known but did note that the volatility of the element is an important feature in facilitating migration, either in the native state or a soluble  $\text{HgCl}_2$ .

James (op. cit.) has made comment on Rankama and Sahama's cycle and updated the record of Hg occurrences and habit in both the primary and secondary environment as known up to 1962. He concludes the chemical (hence, geochemical) nature of mercury is controlled by its "inert pair" of valency electrons. This has led to predominantly covalent bonding over ionic structures and also to the element's high volatility in the native state.

Boyle (1971) reports on the geochemical cycle of Hg and his "flow diagram" is shown in Figure 31. An interesting feature of Boyle's geochemical cycle is the dependence of soils on the hydrosphere and the biosphere in providing the necessary influences for the volatilization of Hg from soil. Boyle presents a further cycle (probably over-simplified) on Hg reaction and exchange in nature (Fig. 32).

The source of primary Hg for the secondary environment is attributed to diadochy (thought to substitute for  $\text{Ba}^{++}$  and  $\text{Ca}^{++}$ ) in extrusive, intrusive, and metamorphic rock minerals, that released from weathered marine sediments (mainly hydrolyzates), and probably most important, that derived from low temperature differentiate sulphide minerals. Sulphides enriched in Hg include cinnabar, pyrite, sphalerite, tetrahedrite, and the sulpho-salts of As and Sb (Rankama and Sahama, op. cit.). Some juvenile Hg is released from hot-spring exhalations (White, et al., 1970).

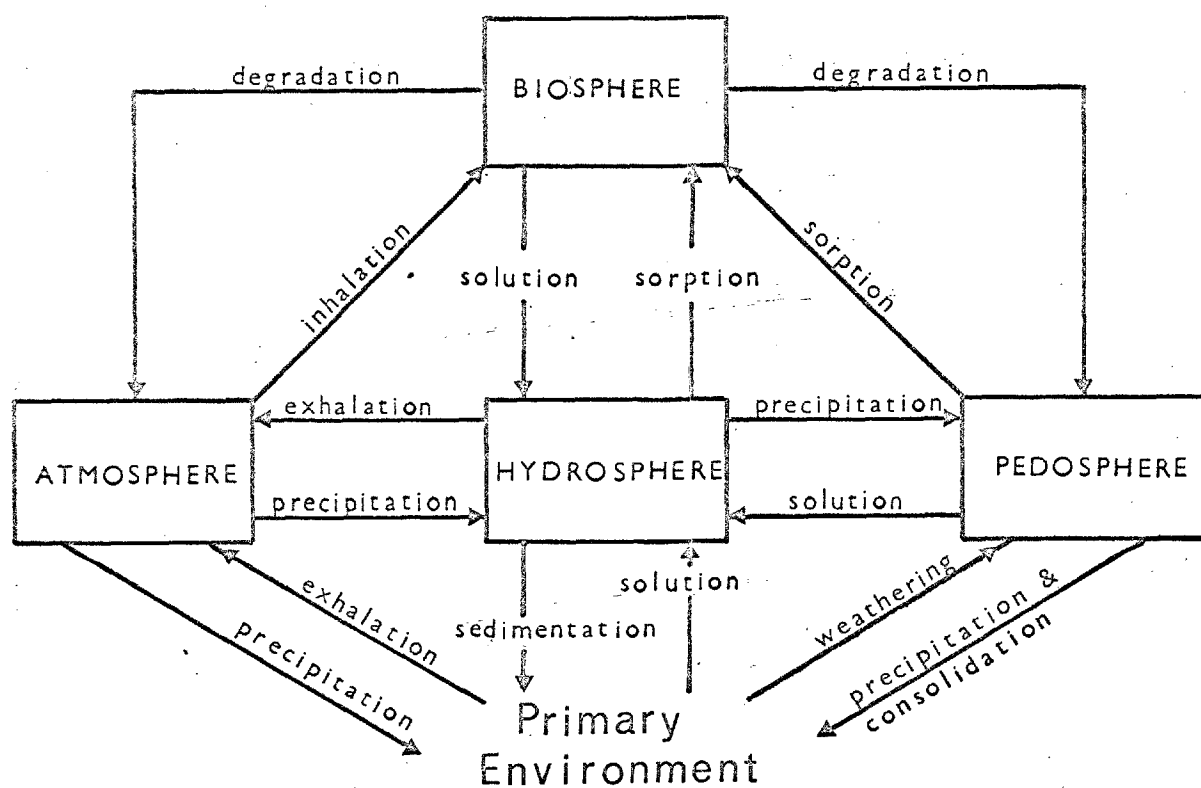


Fig. 31 Generalized geochemical cycle of Hg

after Boyle 1971

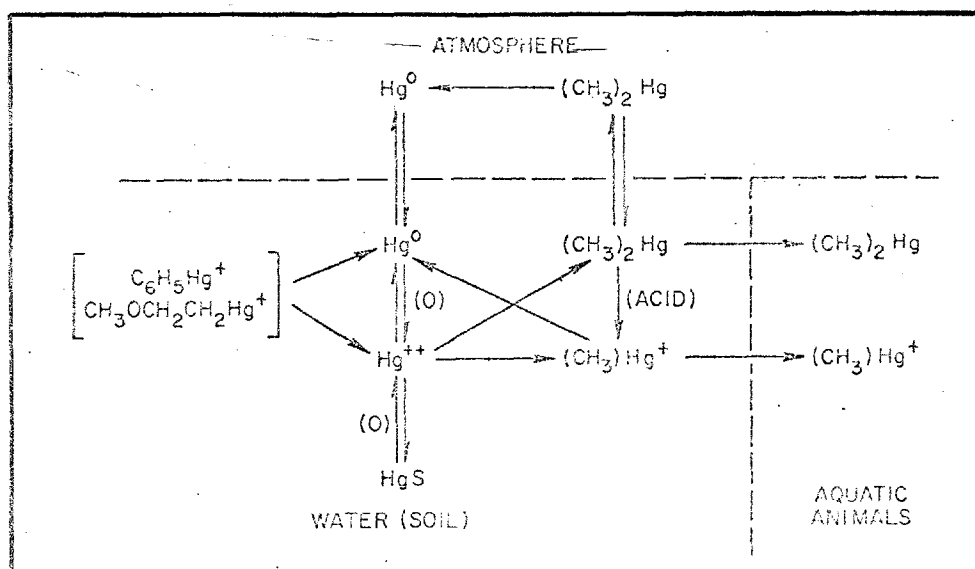


Fig. 34 Known transformation pathways of Hg and its compounds in nature

after Wallace et al 1970

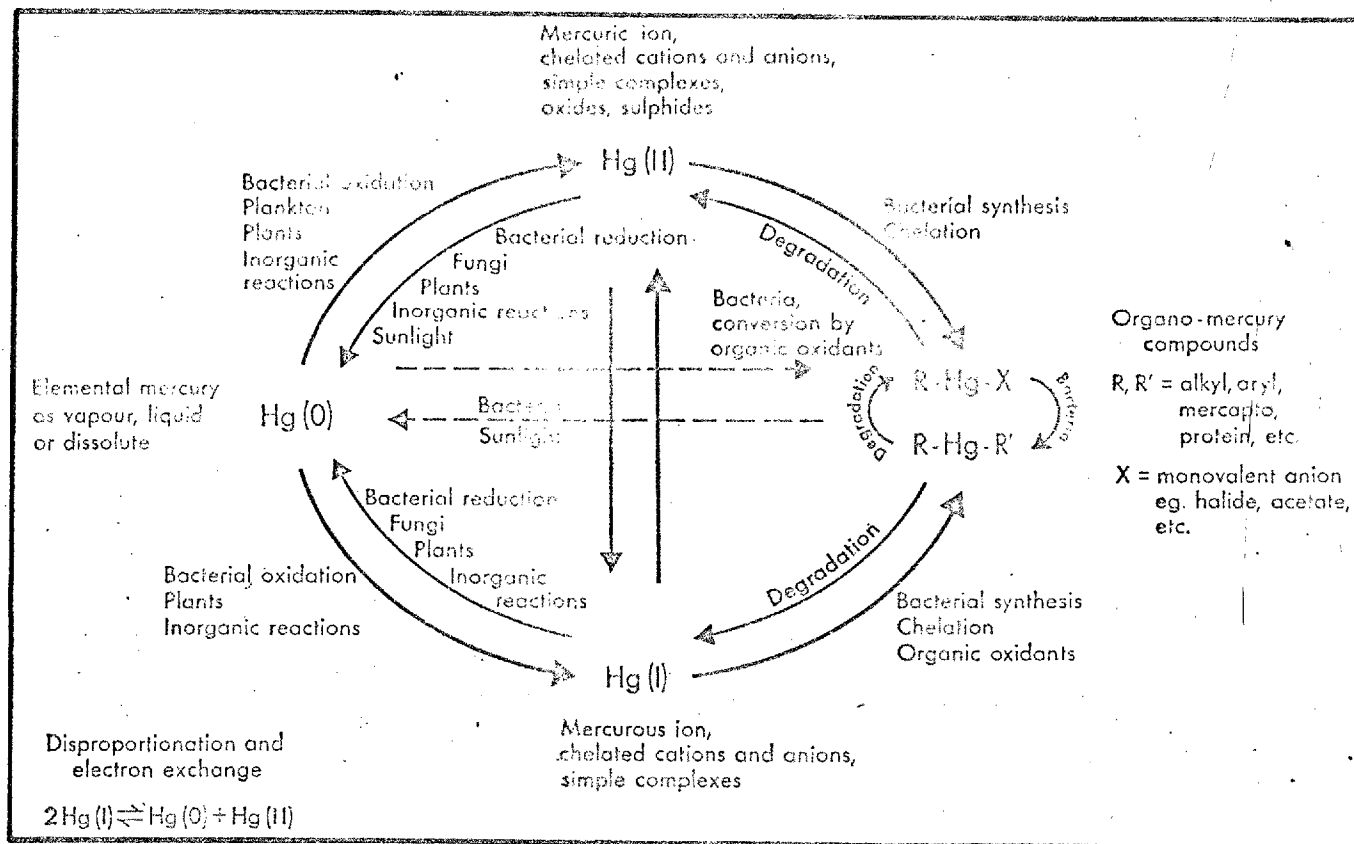


Fig. 32 Mercury interconversions in nature

after Boyle, 1971

### 6.3 MERCURY REACTION AND DISTRIBUTION IN SOILS

In soil (residual or transported), certain conditions may effectively redistribute or modify Hg throughout the profile. The writer considers biological and hydromorphic processes important features in the redistribution of soil Hg. Discussion here reports on those studies in which abundance and profile distribution of Hg were emphasized. Hydromorphic and biological controls and considerations on Hg dispersion are discussed later in this chapter.

Andersson (1967) has studied the distribution and abundance of Hg in Swedish soils and obtains a mean of some 70 ppb for 273 analyses. He concludes that a high humus content is needed for Hg to exceed 150 ppb (assuming no pollution). Apparently the mobility of  $\text{Hg}^{++}$  ions is dependent on pH in an organic matter-water system and between pH 3 and 6 Hg is fixed to organic matter. In the case of the soil mineral-water system, maximum fixation of Hg to solids takes place at pH 7.5-8.0, corresponding to the pH at which  $\text{Hg}^{++}$  is completely converted to  $\text{Hg}(\text{OH})_2$  from  $\text{HgOH}^+$ .

Jonasson (op. cit.) reports that Hg is more easily washed free from mineral soils than humic material suggesting that the binding mechanisms are somewhat different. He relates this to mercury adsorption to sulphur sites on humates. According to Wallace et al. (op. cit.)  $\text{Hg}^{++}$  is in equilibrium with  $\text{HgS}$  in soil (see Fig. 34).

Warren et al. (op. cit.) have investigated mineralized soils in British Columbia and state that when the B and/or C horizons contain appreciably more Hg than do the A horizons it is probable that they reflect underlying sources of mercury. However, where one or more of the A horizons is richest in Hg it is probable that Hg has, in one form or another, been transported and accumulated by vegetal matter.

Warren and Delavault (1969) have studied the mercury content in some British soils and note levels up to 16 ppm. Although not discounting

pollution sources (pesticides here) for the element, they believe most anomalies are related to geological sources, possibly sulphide mineralization.

Shacklette et al. (1971) have determined Hg in 912 samples of soils throughout the conterminous United States. A mean of 112 ppb has been calculated for a range of <10 to 4,600 ppb. The majority of sites greater than 1,000 ppb were either mucks, bog soils, or dark, organic-stained soils.

Aidin'yan et al. (1964) have determined the mercury content of soil profiles from the U.S.S.R. and Viet Nam, and show that mercury is least abundant in the upper humus horizons. High concentrations of mercury are found in eluvial horizons where it has accumulated together with the sesquioxides. The low content of Hg in the humic horizons is ascribed to the evaporation of mercury from the surface where organic matter reduces naturally-occurring compounds to metallic mercury.

#### 6.4 THE PRESENCE AND MOBILITY OF MERCURY IN THE HYDROSPHERE

Recent interest in Hg pollution has stimulated research on mercury solution chemistry, complex formation, and associated investigations into the presence of the element in naturally-occurring waters.

Hem (1970a) has prepared an Eh-pH stability field diagram (Fig. 33) for inorganic aqueous species of mercury. An interesting feature of this figure (within the Eh-pH limits normally found in nature) is the wide range covered by  $\text{Hg}^0_{\text{aq}}$  (an emulsion?). Aqueous  $\text{HgCl}_2$  and  $\text{Hg}^{++}$  also appear to be relatively important phases in any simple ionic dispersion. Although mercury could be contained in this system as high as 25 ppb without loss by chemical precipitation, such levels would seem unlikely for two reasons (Hem, 1970a):

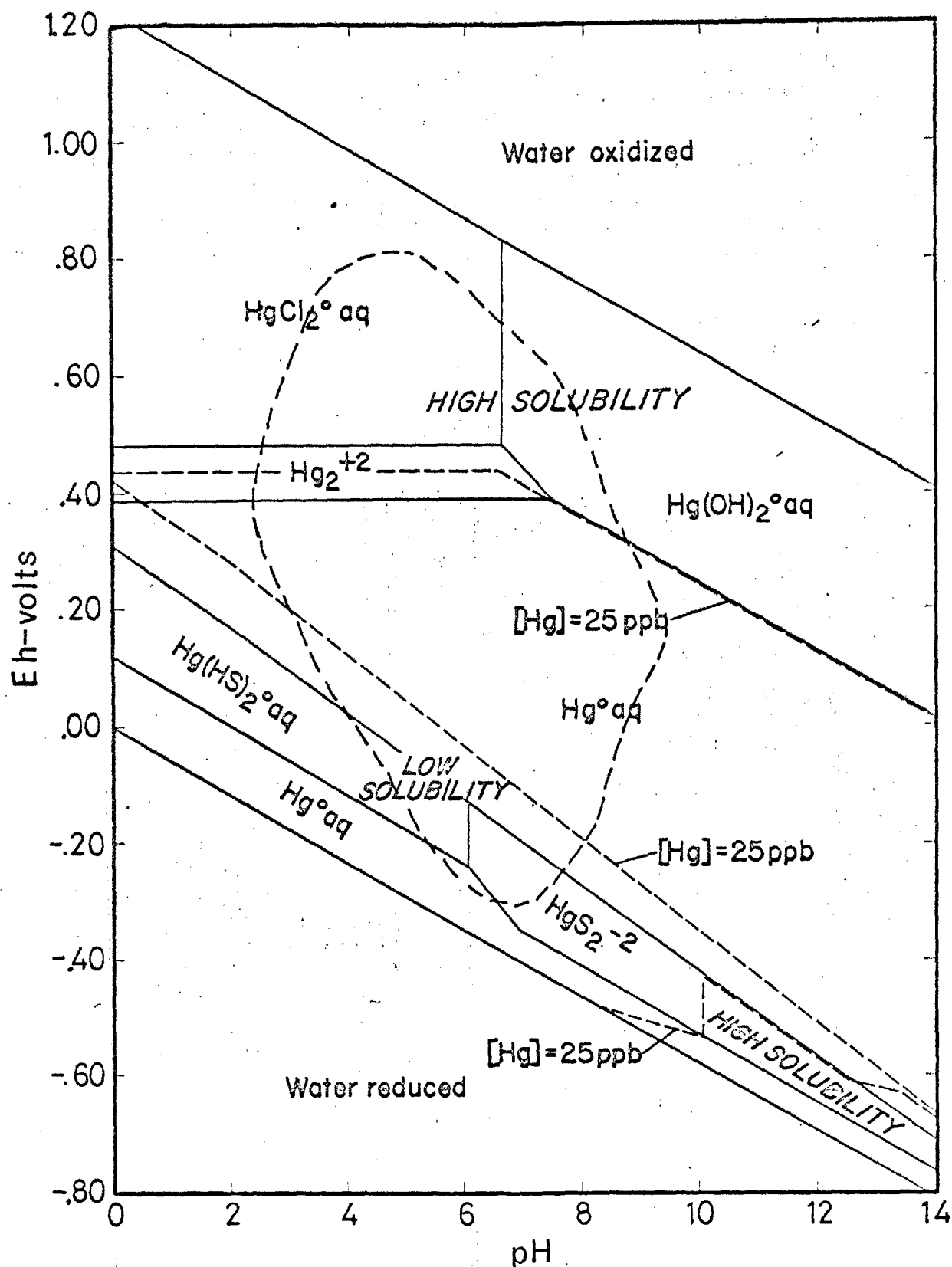
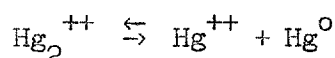


Fig.33 Fields of stability for aqueous species (inorganic) of Hg at 25°C and 1 atmosphere. System includes 36 ppm Cl<sup>-</sup> and 96 ppm S (SO<sub>4</sub>). Dashed line indicates approximate solubility of Hg in this system. after Hem, 1970a

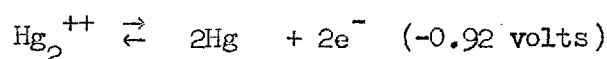
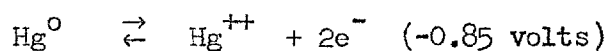
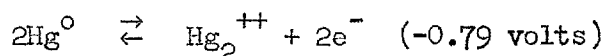
— Eh-pH limits of naturally-occurring environments. after Hansold, 1966

- i) Mercury tends to be volatile and will be lost as vapour from the water surface exposed to the air. This phenomena has been confirmed in laboratory investigations by Toribara et al. (1970).
- ii) Most Hg species are much more soluble in organic solvents than in water. This suggests that organo-metallic complexes (perhaps formed through biochemical reaction mechanisms) may remove Hg from solution.

Mercuric ion, mercurous ion, and metallic mercury are known to chemically transform in solution via electron exchange.



The degree of disproportionation will depend upon the solubility or amount of dissociation of the mercuric compound formed and the extent to which metallic mercury enters or leaves the system. The standard electrode potentials (25°C) of mercury couples are:



These potentials are a measure of susceptibility to oxidation, and the significant feature of the couples is that all the potentials are close in magnitude. Thus, practically any oxidizing agent which is able to oxidize mercury ( $\text{Hg}^0$ ) to mercurous Hg ion ( $\text{Hg}_2^{++}$ ) is also able to oxidize mercury to mercuric Hg ion ( $\text{Hg}^{++}$ ). Conversely, almost any agent that can reduce mercuric to mercurous ion can also reduce either mercuric or mercurous ion to mercury.

Toribara et al. (op. cit.) conclude that the loss of  $\text{Hg}^0$  from a dilute solution containing  $\text{Hg}^{++}$  can be related to the presence of minute amounts of reducing substances and the high oxidation potential of the Hg (II)-Hg (I) system. Any Hg (I) would dispropo-

portionate to  $\text{Hg (II)}$  and  $\text{Hg}^0$ , the latter lost from solution as a gas.

James (1962) is of the opinion that  $\text{HgCl}_2$ , although easily reduced to metallic mercury in the presence of a reducing agent, is a dominant form of Hg in naturally-occurring solutions. However, mercuric chloride may autocomplex in the presence of excess chloride ions to  $\text{HgCl}_3^-$  and  $\text{HgCl}_4^{=}$ . Hem (1970b) indicates that mercury is present in seawater as either  $\text{HgCl}_3^-$  or  $\text{HgCl}_4^{=}$  and states (1970a) that the formation of such complexes proceeds favourably in oxygenated, chloride-containing waters. Karasik *et al.* (1965) have determined mercury in some highly saline waters in the U.S.S.R. and found the Hg content decreases with increasing chloride concentration. They suggest that anionic complexes such as  $\text{HgCl}_4^{=}$  are not so important as transporters of mercury as is  $\text{HgCl}_2$ .

Benes (1969) has studied the state of bivalent mercury at low levels (6 ppb and 600 ppb) in aqueous solution using radioactively labelled metal. Centrifugation, ultrafiltration, dialysis, and electro-migration experiments suggest that from pH 0 to 2 mercury exists in the form of molecular  $\text{HgCl}_2$ . At higher pH values, hydrolysis of mercury occurs so that  $\text{Hg (II)}$  hydroxide or  $\text{HgClOH}$  are the main species in freshly prepared solutions at pH 4 to 13. "Pseudocolloidal" particles of mercury are formed at pH 2 to 7, probably due to the adsorption of Hg on and/or coprecipitation with foreign impurities.

Wiklander (1970) has determined the mercury content of Swedish ground waters (including some sites where Hg disinfected seed has been applied) and reports a range of 20-70 ng/l with an average of 50 ng/l. He attributes the low levels to adsorption of  $\text{Hg}^{++}$ ,  $\text{HgOH}^+$ , and other compounds to organic matter and soil minerals. The adsorbed mercury is apparently held as a relatively non-exchangeable ion.



Kraynov et al. (1966) have investigated the migration of selected metals in carbonate spring waters. They note that levels of mercury were found to increase with increasing bicarbonate concentrations whereas decreases in Cu and Zn concentration were observed under similar conditions. These findings are in some agreement with Hem's stability field diagram, and possibly reflect either  $\text{Hg}(\text{OH})_2^{\text{aq}}$  or  $\text{Hg}^0$  aq forms.

Hosohara (1961) reports that mercury concentrations in sea water increase from surface values of around 0.1 ug/l to 0.15-0.27 ug/l at greater depth. The depletion of Hg in surface waters is attributed to uptake by plankton and accumulation in the marine food cycle.

Aidin'yan (1962) states that it is probably necessary to assume that the greater part of the mercury in sea water solution is in an ion state. Further, he postulates that part of the mercury which is found in the surface layers of the ocean is in the form of a hydroxide which is partially sorbed by colloidal particles and may decay into metallic mercury and evaporate under favourable climatic conditions.

White et al. (1970) have summarized data on the presence of mercury in thermal springs and natural fluids in the United States. Dilute thermal springs normally contain readily detectable Hg. Sediments associated with these springs are sometimes rich in Hg and the element is presumed to have been transported by the spring water. Crude petroleum from the U.S.A. can contain up to 500,000 ppb Hg.

Although Hem's stability field diagram (Fig. 33) indicates that mercury may be readily dissolved in waters, levels of the element and many of its compounds are decidedly low in naturally-occurring solutions. Removal of mercury from waters may occur as chemical precipitation of mercury (particularly as  $\text{HgS}$ ), sorption to particulates with subsequent settling out, and loss to the atmosphere of metallic

Hg through reduction of mercuric and mercurous ions and/or complexes. The depletion of mercury in marine surface waters may also be related to its uptake by plankton.

#### 6.5 MERCURY INTERACTION WITH AND MOVEMENT IN THE BIOSPHERE

The presence of mercury in biological systems has received considerable attention of late. The interest sharpened with the announcement that elevated levels of Hg (as dimethylmercury) were present in some human feedstuffs, particularly marine and freshwater fish. The sources of mercury are believed to be industrial wastes enriched in Hg and residues of Hg-containing fungicides and pesticides. Mercury pollution is discussed in section 6.7.

It is well known that mercury is toxic to humans, but the knowledge that the highly volatile and dangerous dimethyl compound is present in the food cycle has increased monitoring and research investigations, particularly in Sweden, Japan, and the United States.

The biotransformation of mercury to dimethylmercury was first described by Jernelev (1968a) and Jensen and Jernelev (1969). Japanese investigators had also been proceeding along similar lines of research (Tonomura and co-workers) since the ill-fated Minamata Bay incident of the 1950's when 110 people were debilitated or died as a result of eating mercury contaminated fish (Wallace et al., 1970). A model for the bioconversion of inorganic mercury is presented in Figure 34 and shows that complex biogeochemical reaction mechanisms are involved. Although methyl derivatives of mercury are presented in the figure, the writer is of the opinion that other Hg-containing organometallics such as simple ethyl, propyl, and butyl derivatives may also be naturally-occurring through similar conversions.

Jernelev (1969) has reported on experiments attempting to

distinguish differences between the biological effects of "biologically" and "chemically" synthesized dimethylmercury. He concludes that a chemically generated dimethylmercury (or methylmercury compound) breaks down to methylmercuric ion more easily than does biologically generated dimethylmercury (or methylmercury compound). The differences could possibly explain why introduced sources of mercury are more liable to disperse widely as dimethylmercury. More likely, the mercury-dimethylmercury equilibrium is positively stimulated (toward dimethylmercury) with introduced Hg.

The conversion of divalent mercury into methylmercury ( $\text{Hg}^{++} \rightarrow \text{CH}_3\text{Hg}^+ \rightarrow \text{CH}_3\text{HgCH}_3$ ) has been shown to occur in bottom muds (see Fig. 35) and sediments from a large number of lakes have revealed microorganisms capable of methylating mercury (Jernelov, 1968b). The synthesis of methylmercury by extracts of methanogenic bacterium has been described by Wood et al. (1968).

Furukawa et al. (1969) have reported on the action of a mercury resistant strain of Pseudomonas which apparently is capable of decomposing phenylmercuric acetate into metallic mercury, ethylmercuric phosphate into metallic Hg and ethane, and methylmercuric chloride into metallic mercury and methane.

As an initial consideration for mercury biotransformations, the geochemistry of metallic and inorganic Hg also involves numerous interconversions (section 6.4). However, naturally-occurring mercury is generally present either as an inorganic or humic complex or mercuric sulphide (Wallace et al., op. cit.). Into this is now superimposed the biological transformations which are capable of forming methylmercury and dimethylmercury from inorganic mercury, even under anaerobic conditions. The most important, presently-known steps by which inorganic mercury and compounds are interconverted in nature are shown in Figure 34 and the generalizations which

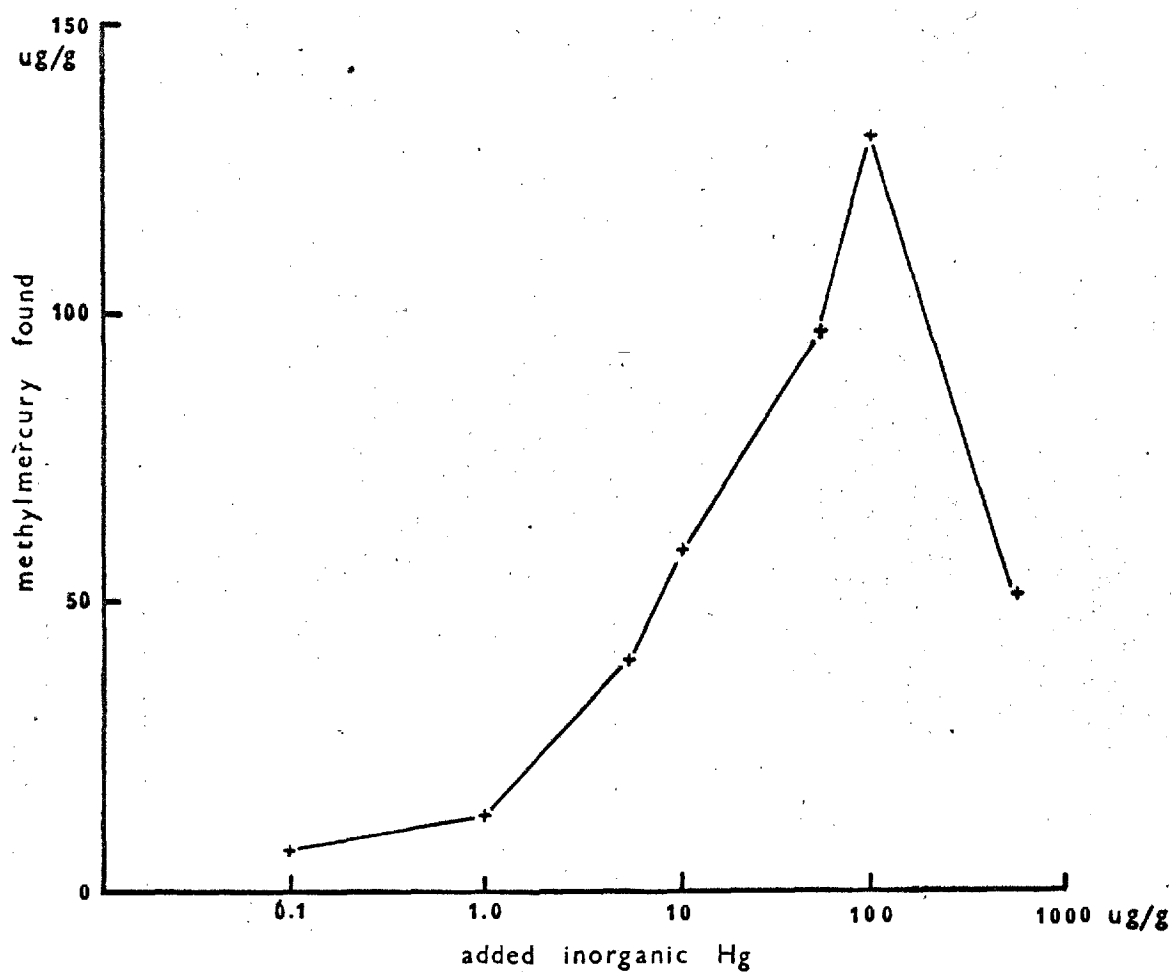


Fig. 35 Concentration of methylmercury in bottom sediment after addition of inorganic Hg followed by incubation for seven days

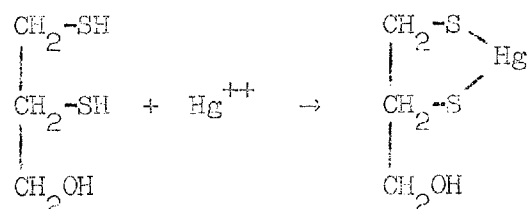
after Jensen & Jernelov 1969

emerge are (Wallace et al., op. cit.):

- i) Mercury, in whatever form, is potentially exchangeable among the air, land, and water phases.
- ii) Mercury, in whatever form and from whatever phase, is potentially capable of being taken up by aquatic animals in the form of methylmercury or dimethylmercury.
- iii) In an aquatic system, methylmercury can be formed directly from inorganic mercury ( $\text{Hg}^{++}$ ) under anaerobic conditions; but
- iv) under permanently anaerobic conditions, mercury will tend to accumulate in bottom sediments either as  $\text{HgS}$  or  $\text{Hg}^0$ , and little methylmercury or dimethylmercury will be formed.
- v) Methylmercury and dimethylmercury can be formed indirectly from either  $\text{HgS}$  or  $\text{Hg}^0$  in the presence of oxygen or under oxidizing conditions.
- vi) Alkaline conditions will tend to promote the release of mercury from aquatic ecosystems via dimethylmercury.

In addition, whatever dimethylmercury is released into the atmosphere is most likely converted into metallic Hg vapour together with methane and ethane (Wallace et al., 1970).

Another important aspect of the organo-interaction of mercury is binding with mercapto groups (sulphydryls), essentially a chelating reaction. Wotjalik (1971) has used the following reaction to demonstrate mercury-sulphur bonding:



The importance of this reaction probably allows mercury retention by plants as sulphydryl groupings carry important protein

functions. Such reactions may also be important in fixing the methyl-mercury radiocle. Mercury-mercapto bonding probably proceeds positively under acid conditions as such bonds are cleaved in the presence of a reducing agent under alkaline conditions (Magos and Cernik, op. cit.). This last mechanism could explain why mercury tends to accumulate in the surface horizons of soils and may not be readily lost to the atmosphere as dimethylmercury.

Booer (1944) says it is necessary to consider the position of mercury with respect to the sulphur cycle in soils. Experiments by Booer using the sulphate-reducing Vibrio (Sporovibrio) desulphuricans in  $\text{HgCl}_2$  solutions suggests that anaerobic conditions probably precipitate Hg in soil as  $\text{HgS}$ .

According to Jonasson (1970), the affinity of mercury for sulphur adsorption sites is reflected by the presence of Hg in humic matter, which contains organic bound sulphur either as chelates or organosulphur complexes.

Shacklette (1970) states that there is little data available upon which to base an actual estimate of the amounts of mercury that are adsorbed by plant roots and translocated to the upper parts of the plant. Apparently, most plants grown in soils that are low in amounts of this element contain very little mercury. The background level of mercury in plants (assumed wet weight) is thought to be less than 500 ppb. Under certain environmental conditions, plants may contain larger amounts of mercury. Shacklette quotes levels of up to 3,500 ppb from selected plant species overlying cinnabar deposits in Alaska. Biogeochemical prospecting employing mercury analysis has been reported by Barakso and Tarnocai (1968) and Warren et al. (1966). The initial results appear to be relatively inconclusive and further research seems both required and warranted.

## 6.6 THE PRESENCE AND DISPERSION OF MERCURY IN THE ATMOSPHERE

The source of mercury in the atmosphere seems almost entirely derived from the continental land masses. Weiss (1970) reports that concentrations found over oceans generally measure less than  $1 \text{ ng/m}^3$ . Williston (1968) has monitored mercury vapour concentrations in the air over Los Altos, California and notes that air brought in from over the Pacific Ocean contains approximately  $1\text{-}2 \text{ ng/m}^3$  while air coming from the southeastern land mass contains about  $2\text{-}4 \text{ ng/m}^3$ . Air from industrial areas give high and erratic readings with peaks over  $20 \text{ ng/m}^3$ . Smog, rain, air temperature, sunlight, and absorption on dust effect levels of mercury in the atmosphere according to Williston.

Table 31 shows maximum mercury concentrations in air measured at scattered mineralized and non-mineralized areas of the Western United States (McCarthy et al., 1970). When compared with data compiled by Sutherland Brown (1966) (Table 32) on anomalous and background soil mercury levels at various mineralized occurrences, much the same order of anomalies are observed. This seems to suggest that the level of mercury in the atmosphere is locally directly dependent on the level of Hg in soil.

In the previous section, it was noted that dimethylmercury is released to the atmosphere through microorganism bioconversion of inorganic mercury. Dimethylmercury apparently degrades to metallic mercury on exposure to sunlight. Barber et al. (in press) have reported on unsuccessful attempts to measure volatile mercury/mercury compounds transpired from Mentha spicata (Mint), a species known to give off several organic compounds, including the terpenes, 1-menthanol, and carvone. Although the results of Barber et al. were negative, other plants may emit volatile compounds containing

Table 31. Maximum mercury concentration in air measured at scattered mineralized and non-mineralized areas of the Western United States <sup>1</sup>

| Sample location                                         | Maximum Hg concentration (ng/m <sup>3</sup> ) <sup>2</sup> |                                        |
|---------------------------------------------------------|------------------------------------------------------------|----------------------------------------|
|                                                         | Ground surface                                             | 400 feet above the ground <sup>3</sup> |
| Mercury mines                                           |                                                            |                                        |
| Ord mine, Mazatzal Mtns., Arizona . . . . .             | 20,000 (50)                                                | 108 (4)                                |
| Silver Cloud mine, Battle Mtn., Nevada . . . . .        | 2,000 (50)                                                 | 24 (8)                                 |
| Dome Rock Mtns., Arizona . . . . .                      | 128 (6)                                                    | 57 (20)                                |
| Base and precious metal mines                           |                                                            |                                        |
| Cerro Colorado Mtns., Arizona . . . . .                 | 1,500 (5)                                                  | 24 (2)                                 |
| Cortez gold mine, Crescent Valley, Nevada . . . . .     | 180 (60)                                                   | 55 (4)                                 |
| Coeur d'Alene mining district, Wallace, Idaho . . . . . | 68 (40)                                                    | -                                      |
| San Xavier, Arizona . . . . .                           | -                                                          | 25 (3)                                 |
| Porphyry copper mines                                   |                                                            |                                        |
| Silver Bell mine, Arizona . . . . .                     | -                                                          | 53 (3)                                 |
| Esperanza mine, Arizona . . . . .                       | -                                                          | 32 (3)                                 |
| Vekol Mtns., Arizona . . . . .                          | -                                                          | 32 (4)                                 |
| Ajo mine, Arizona . . . . .                             | -                                                          | 30 (3)                                 |
| Mission mine, Arizona . . . . .                         | -                                                          | 24 (3)                                 |
| Twin Buttes mine, Arizona . . . . .                     | 20                                                         | 22 (3)                                 |
| Pima mine, Arizona . . . . .                            | -                                                          | 13 (3)                                 |
| Stafford, Arizona . . . . .                             | -                                                          | 7 (2)                                  |
| Unmineralized areas                                     |                                                            |                                        |
| Blythe, California . . . . .                            | -                                                          | 9 (20)                                 |
| Gila Bend, California . . . . .                         | -                                                          | 4 (2)                                  |
| Salton Sea, California . . . . .                        | -                                                          | 3.5 (2)                                |
| Arivaca, Arizona . . . . .                              | -                                                          | 3 (2)                                  |

<sup>1</sup> After McCarthy et al. (1970)

<sup>2</sup> Number of measurements shown in parentheses

<sup>3</sup> Samples taken from single engine aircraft



Table 32. Anomalous and background levels of mercury in soils at deposits of selected metals \*

| Type of deposit | No. deposits | Hg in soil      |      |                 |     |
|-----------------|--------------|-----------------|------|-----------------|-----|
|                 |              | 1               | 2    | 3               | 4   |
|                 |              | ppb             | ppb  | ppb             | ppb |
| Hg              | 7            | 600 -<br>180000 | 9000 | 10 -<br>200     | 45  |
| Au-Ag           | 2            | 1500 -<br>5000  | 3250 | 50<br>100       | 80  |
| Pb-Zn           | 4            | 500 -<br>10000  | 4400 | 25 -<br>1000    | 370 |
| Cu              | 3            | 150 -<br>7000   | 2600 | 25 -<br>1000(?) | 230 |
| Mo              | 5            | 65 -<br>175     | 115  | 10 -<br>45      | 23  |

1. Range of anomalous values
2. Arithmetic mean of anomalous values
3. Total range of background values
4. Geometric mean of each background range; arithmetic mean of the calculated geometric means

\* Data reduced from Sutherland Brown, 1966

mercury. For instance, Rasmussen (1970) has identified isoprene (2-methyl, 1-3 butadiene) as a forest-type emission to the atmosphere while Pertel and Gunning (1959) who report on the photochemical separation of mercury isotopes describe a 1,3 butadiene-water vapour interaction with mercury vapour in an experimental procedure. Although the link here is somewhat tenuous, further research seems warranted to establish the presence of any Hg-containing plant aerosols.

The composition of stream, ground, and sea water has some effect on the presence of Hg in the atmosphere. Magos (1967) reports that the  $\text{Hg}^{++}$ -halide ratio is important in determining the Hg exchange reaction between air and aqueous solution. Turney (1971) ascribes to the claim of Wallace *et al.* (op. cit.) that the raising of pH to alkalinity seems to enhance bacterial conversion of Hg and Hg compounds in water and sediments to the dimethyl form that is normally released from water as a gas. Suzuki *et al.* (1968) have experimented with a mercury-resistant bacterium, *Pseudomonas* K62 strain, which is capable of taking up mercurials to its cells and stimulating the vaporization of metallic mercury. However, uptake of mercury was inhibited by NaCl suggesting that any naturally-occurring exhalation may be restricted to fresh waters only.

## 6.7 MERCURY POLLUTION

Perhaps the most unwanted stimulus for the increased data becoming available on the (bio)(geo)chemistry of mercury has been the realization that Hg pollution has become an environmental and ecological problem in some of the developed countries of the world.

Widespread mercury pollution originates from the previously mentioned Minamata Bay incident and has recently come to light in North America with the closure of at least two of the Great Lakes to sport and commercial fishing, the latter industry now having collapsed

(Bails, in press). An International Conference on Environmental Mercury Contamination was held in Ann Arbor, Michigan, U.S.A. in September-October, 1970 and attracted many concerned individuals. Proceedings of the Conference are currently in press.

Mercury pollution in Lake St. Clair and Lake Erie is believed to originate from chloralkali plants, some of which employ metallic Hg in the electrolysis of NaCl brines to manufacture  $\text{Cl}_2$  and NaOH (Turney, in press). An interesting dispersion train is described by Turney who reports that a stream draining into Lake Michigan contains some 86 ppm Hg in sediment directly below one chloralkali plant that drops to 5 ppm one mile downstream.

D'Itri (in press) discusses the potential and known sources of mercury (both introduced and naturally-occurring) in the environment. Some sources of mercury pollution seem quite obvious. Organomercurials of various kinds are by far the most widely used type of fungicidal dressing for cereal seeds (Bent, 1969). They are used in foliage sprays and dusts to control blights, scabs, smuts, moulds, and rots on almost the whole spectrum of grains, fibres, fruits, nuts, vegetables, root crops, and bulbs (Smart, 1968).

Organomercurials can be chemically divided into three groups: alkylmercury, alkyloxyalkyl-mercury, and arylmercury compounds. Table 33 lists those in use up to 1968.

Phillips et al. (1959) have investigated the volatility of organomercury compounds to assess the hazard arising from the use of sprays and dressings of stored seed in Great Britain. Taking into consideration the English climate, they have speculated the maximum temperature likely to be encountered in British agricultural practice to be  $35^{\circ}\text{C}$  and have made both static and dynamic determinations of the volatility of agricultural mercurials in use prior to 1959. Table 34 lists some of the organomercurials investigated and the

Table 33. Mercury compounds known to be used in world agriculture <sup>1</sup>Alkylmercury compounds

Methylmercury sulphate, acetate, nitrile, propionate, 8-hydroxy-quinolate, 2,3-dihydroxypropyl mercaptide, pentachlorophenolate, p-chlorobenzoate, benzoate, dicyandiamide

N-Methylmercury 1,2,3,6-tetrahydro-3,6-endomethano-3,4,5,6,7,7-hexachlorophthalimide

Ethylmercury silicate, chloride, bromide, phosphate, acetone, urea, oleate, stearate, pentachlorophenolate, hydroxide, thiouronium chloride, p-toluene sulphonamide, 8-hydroxyquinolate

N-Ethylmercury 1,2,3,6-tetrahydro-3,6-endomethano-3,4,5,6,7,7-hexachlorophthalimide

Ethyl phenethynylmercury

Mercury pentanedione

Alkylalkoxyalkylmercury compounds

Methoxyethylmercury chloride, silicate, dicyandiamide, benzoate, lactate, acetate

Ethoxyethylmercury chloride, silicate, hydroxide

1-Carboxy-3-ethoxyethylmercury propandicarboxylate

Chloromethoxypropylmercury acetate

p-(t-Octyl)phenoxyethoxyethyl dimethylmercury benzyl ammonium chloride

Arylmercury compounds

Phenylmercury acetate, dimethyl dithiocarbamate, chloride, dinaphthyl methane sulphonate, urea, nitrate, iodide, benzoate, pyrocatechinolate, triethanol ammonium lactate, 8-hydroxy-quinolate, hydroxide, lactate, oleate, propionate, salicylate, salicylanilide, formamide, naphthenate

<sup>1</sup> after Smart, 1968

Table 34. The volatility of some mercurial fungicides <sup>1</sup>

| Mercury Compound                      | Saturated Vapour Concn. mg/m <sup>3</sup> | Temp. °C | Vapour Pressure - mm Hg <sup>4</sup> |
|---------------------------------------|-------------------------------------------|----------|--------------------------------------|
| Methylmercury chloride                | 293 <sup>2</sup>                          | 35       | 23 x 10 <sup>-3</sup>                |
| Ethoxyethylmercury silicate (tech.)   | 45 <sup>2</sup>                           | 35       | 4.3 x 10 <sup>-3</sup>               |
| Ethylmercury chloride                 | 9.4 <sup>2</sup>                          | 20       | 0.65 x 10 <sup>-3</sup>              |
| Methoxylthyl mercury chloride (tech.) | 15 <sup>2</sup>                           | 35       | 1.0 x 10 <sup>-3</sup>               |
| Methylmercury dicyandiamide           | 1.05 <sup>2</sup>                         | 35       | 6.5 x 10 <sup>-5</sup>               |
| bis-Ethylmercury phosphate            | 0.26 <sup>2</sup>                         | 35       | 1.8 x 10 <sup>-5</sup>               |
| Phenylmercury acetate                 | 0.16 <sup>2</sup>                         | 35       | 9 x 10 <sup>-6</sup>                 |
| Phenylmercury chloride                | 0.06 <sup>2</sup>                         | 35       | 3.6 x 10 <sup>-6</sup>               |
| Phenylmercury nitrate                 | 0.025 <sup>3</sup>                        | 35       | 1.4 x 10 <sup>-6</sup>               |
| Phenylmercury salicylate              | 0.021 <sup>3</sup>                        | 35       | 1.0 x 10 <sup>-6</sup>               |

<sup>1</sup> After Phillips *et al.* (1959)<sup>2</sup> Dynamic measurement<sup>3</sup> Static measurement<sup>4</sup> Vapour pressure of metallic Hg - 4.2 x 10<sup>-3</sup> at 35°C

results of the volatility experiments. Some compounds exhibit relatively high vapour pressures at 35°C and can be considered hazardous when handling. Also, the volatile component of introduced mercurials may provide Hg for atmospheric pollution and/or the (bio)(geo)chemical cycle of the element.

Further, Phillips et al. have found the log. concentration-reciprocal temperature relation to be linear for three temperatures. The partial pressures corresponding to the saturated vapour concentrations have been calculated on the assumption that no dissociations (except ethoxyethylmercury silicate) or association has taken place and that the vapours behave as ideal gases. Hence, the partial pressure ( $P_t$ ) in mm of a mercurial whose molecular weight is M may be derived from the gram-molecular volume, corrected for the experimental temperature ( $T^{\circ}\text{K}$ ).

$$P_t = \frac{W}{M} \times 22.4 \times \frac{T \times 760}{273.2}$$

$$W = \text{gm/l mercurial in air at } T^{\circ}\text{K}$$

However, molecular weight has only a limited function in determining the degree of volatility of organomercurials and other considerations (perhaps stereochemistry) may be equally important.

Not only are some organomercurials readily volatile, but on application to soils degradation can occur; and, according to Kimura et al. (op. cit.), vapours of metallic and organic mercury escape from soil. Apparently, nonvolatile phenylmercuric acetate is degraded to mercury and lost as mercury vapour. The volatile ethylmercuric acetate is also degraded in soil to mercury, but its loss from soil can occur both as mercury vapour and the organomercury vapour. Methylmercury chloride and methylmercury dicyandiamide gave no significant metallic mercury vapour and their loss from soil was due

entirely to the volatility of organomercury compounds. Similar experimental results have been reported by Frear and Dills (1967) and Zimmerman and Crocker (1933).

Organomercurials are not the only mercury-containing compounds to find application in industry/agriculture. Table 35 lists some inorganic mercury compounds, their use in industry, and their solution reaction.

The relative use of mercury compounds in the United States has been analyzed by the "Panel on Mercury", Committee on Technical Aspects of Critical and Strategic Materials (J. Metals, May, 1970). Their projections (Table 36) indicate a slightly changing pattern in the use of mercury compounds in industry, agriculture, and scientific application. The reduction in use of organomercurials for pesticides and fungicides can possibly be related to the introduction and use of "systematic fungicides", compounds which can penetrate and move in plants rather than the normally applied surface sprays and dusts. "Systematic fungicides" are composed of the "organic family" of elements (Bent, op. cit.). However, organomercurials will probably continue in wide usage as they do provide excellent control of fungal diseases.

Quantities of mercury compounds used in or sold to agriculture have been tabulated by Smart (op. cit.) and Table 37 shows the level of usage in selected countries during 1965. Most certainly usage levels and regulatory restrictions have changed or are being changed in response to the potential problems arising from methylmercury and mercury contamination and pollution.

The "social impact" surrounding mercury pollution can be judged by the recent presence of two articles in the internationally syndicated Newsweek magazine (see "The Quicksilver Crisis" and "The Mad Hatter's Legacy", April 20 and August 3, 1970). In addition,

Table 35. Some inorganic mercury chemicals used in industry <sup>1</sup>

| Mercury Compound                                                    | Reaction to Solution                                                 | Use                                                                                     |
|---------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------------------------------------------------------------------|
| $\text{Hg}(\text{CH}_3\text{COO})_2$                                | Sol. $\text{H}_2\text{O}$                                            | Catalyst, manufacture of other mercurials                                               |
| $\text{Hg}_3(\text{AsO}_4)_2$                                       | Insol. $\text{H}_2\text{O}$<br>Sol. $\text{HCl}$ <sup>2</sup>        | Anti-fouling marine paints                                                              |
| $\text{HgCl}_2$ <sup>2</sup>                                        | Sol. $\text{H}_2\text{O}$                                            | Batteries, catalyst, insectide, photography, preservative                               |
| $\text{Hg}(\text{CN})_2$                                            | Sol. $\text{H}_2\text{O}$                                            | Electroplating                                                                          |
| $\text{HgI}_2$                                                      | Sl. sol. $\text{H}_2\text{O}$                                        | Pigment, soaps, antiseptics                                                             |
| $\text{HgO}$ (red)                                                  | Insol. $\text{H}_2\text{O}$<br>Sol. $\text{HCl}$ <sup>2</sup>        | Pigment, anti-fouling marine paint, batteries                                           |
| $\text{HgO}$ (yellow)                                               | Insol. $\text{H}_2\text{O}$<br>Sol. $\text{HCl}$ <sup>2</sup>        | Anti-fouling paint, oxidizing agent, fungicides                                         |
| $\text{HgO} \cdot \text{Hg}(\text{CN})_2 - 4\text{Hg}(\text{CN})_2$ | Sl. sol. $\text{H}_2\text{O}$                                        | Antiseptic                                                                              |
| $\text{HgS}$                                                        | Sol. aqua regia                                                      | Pigment                                                                                 |
| $\text{Hg}(\text{SCN})_2$                                           | Sl. sol. $\text{H}_2\text{O}$                                        | Pyrotechnics                                                                            |
| $\text{HgCl}$                                                       | Insol. $\text{H}_2\text{O}$                                          | Batteries, fungicides, anti-fouling paints, pyrotechnics, ore recovery                  |
| $\text{HgNO}_3$                                                     | Sol. dil. $\text{HNO}_3$                                             | Tanning, metals treatment                                                               |
| $\text{Hg}$ <sup>2</sup>                                            | Insol. $\text{H}_2\text{O}$<br>Sol. dil. $\text{HNO}_3$ <sup>2</sup> | Catalyst, scientific instruments, lamps, manufacture of $\text{NaOH}$ and $\text{Cl}_2$ |

<sup>1</sup> Compiled from "Chemicals for Industry, May and Baker, Dagenham, Essex

<sup>2</sup> Also exhibit partial pressures



Table 36. Estimated trends in consumption of mercury <sup>1</sup>

| Use                                           | Estimated Mercury Consumption, flasks <sup>2</sup> |      |           |      |
|-----------------------------------------------|----------------------------------------------------|------|-----------|------|
|                                               | 1968                                               | %    | 1974-1975 | %    |
| Agriculture                                   | 3,430                                              | 4.6  | 2,650     | 3.2  |
| Amalgams                                      | 259                                                |      | 250       |      |
| Catalysts:                                    |                                                    |      |           |      |
| Urethanes                                     | 800                                                |      | 1,560     |      |
| Vinyl Chloride Monomer                        | 500                                                |      | 250       |      |
| Anthraquinone Derivatives                     | 175                                                |      | 220       |      |
| Miscellaneous                                 | 236                                                |      | 340       |      |
| Dental Applications                           | 3,500                                              | 4.7  | 3,800     | 4.4  |
| Electrical Apparatus                          | 17,200                                             | 22.3 | 22,700    | 27.2 |
| Electrolytic Preparation of Chlorine and Soda | 17,424                                             | 22.4 | 22,864    | 27.4 |
| General Laboratory Use                        | 2,075                                              |      | 2,075     |      |
| Industrial & Control Instruments:             |                                                    |      |           |      |
| Switches and Relays                           | 2,500                                              |      | 2,650     |      |
| Other Instruments                             | 6,400                                              |      | 6,600     |      |
| Paints                                        | 10,566                                             | 14.3 | 10,725    | 12.9 |
| Paper and Pulp                                | 375                                                |      | 250       |      |
| Pharmaceuticals                               | 600                                                |      | 650       |      |
| Others                                        | 7,815                                              |      | 5,960     |      |
| Totals                                        | 73,855                                             |      | 83,544    |      |

<sup>1</sup> "Panel on Mercury" Committee on Technical Aspects of Critical and Strategic Materials, May, 1970.

<sup>2</sup> One flask = 76 lbs.

Table 37. Quantities of mercury compounds used in or sold to agriculture, 1965 <sup>1</sup>

| Country       | Metric Tons of Hg Compounds | Restrictions and Regulations                |
|---------------|-----------------------------|---------------------------------------------|
| U.S.A.        | 400                         | No mercury residue is allowed in foodstuffs |
| Denmark       | 3.5                         | Maximum level of 0.05 ppm Hg in residues    |
| Germany (W.)  | 41                          | Food containing residues banned from sale   |
| Great Britain | 20                          | Residues should not exceed 0.1 ppm Hg       |
| Bulgaria      | 5                           | -                                           |
| Finland       | 1                           | -                                           |
| Italy         | 26                          | -                                           |
| Poland        | 9                           | -                                           |
| Austria       | 4                           | -                                           |
| Norway        | 0.4                         | Alkyl-mercury use is banned                 |
| Portugal      | 0.2                         | -                                           |
| Turkey        | 22.5                        | -                                           |
| Spain         | 7.1                         | -                                           |
| Sweden        | 2                           | Maximum level of 0.05 ppm Hg in residues    |
| Morocco       | 1                           | -                                           |
| Israel        | 0.2                         | Cannot be used on edible crops              |
| New Zealand   | 0.5                         | Maximum level of 0.05 ppm Hg in residues    |
| Japan         | 1,600<br>(approx.)          | No regulations in 1965                      |

<sup>1</sup> Smart, 1968

research articles and progress reports have appeared at regular intervals in trade and academic journals.

Mercury levels have been monitored in emissions from smokestacks (power, incinerator, industrial) in Illinois and Missouri, U.S.A. and up to 5,400 lbs. of Hg are estimated to be emitted from one stack alone during the course of one year. Sources of mercury are believed to be coal, oil, paper, and miscellaneous refuse (Environment, 13, No. 4, pp 24-33).

The real danger of mercury pollution can be seen by the progress of the element through a biological cycle which may terminate at man. The cycle presents a sobering picture as mercury may recycle many times before leaving the system, either as a gas or as a semi-permanently bound organic or inorganic compound. The cycle is as follows:

Introduced and/or naturally-occurring Hg  $\rightarrow$  (di)methyl Hg  $\rightarrow$   
 assimilated by aquatic microorganisms  $\rightarrow$  accumulated in fish  $\rightarrow$   
 eaten by man and/or fish-eating birds.

The biological half-life of methylmercury in man has been calculated to be 70 days, but its persistence in nature is believed to be much longer (Wotjalik, op. cit.). Jernelov (1968b) has estimated that the effects of mercury pollution could last from 10 to 100 years unless proper controls can be instituted.

Wallace et al. (op. cit.) have presented a number of schemes for decontamination of mercury-polluted lakes and water courses. These include dredging, chemical treatments (precipitation, liming), amalgamation, silting over with clays and flocculants, and "biological mining". Unfortunately, each scheme represents a further disruption of the environment.

#### 6.7.1 The Relative Importance of Mercury Pollution on the Use of the Element as a Pathfinder in Mineral Exploration

It is, perhaps, a little early to critically evaluate the subject title of this section and the writer has attempted only some initial speculations on the nature of widespread mercury pollution and its potential effect on the application of Hg pathfinding in mineral exploration.

Tables 33, 35, 36, and 37 show that mercury is being widely used in both industry and agriculture. In addition, Baily and Smith (1964) and the "Panel on Mercury" (1970) are of the opinion that Hg is a necessary requirement of industry and that consumption in the United States will increase with time. That country considers the element a strategic metal and during recent years has provided generous grants for mineral exploration and development of Hg deposits -- up to 75 per cent of the total expenditure ("Panel on Mercury", op. cit.). The U.S.G.S. supplements mercury prospecting through the development of new exploration techniques (mainly geochemical) as part of their commitment to the U.S. Heavy Metals Program initiated in 1966.

As other economically developed countries of the world require mercury for use in industrial practice and/or agricultural application, one may assume that some form of mercury pollution is inherent in some areas of the globe, and is, perhaps, increasing with time. Therefore, Hg pathfinding in mineral exploration may require circumvention of "contamination anomalies". At worst, the technique may conceivably have limited future use, particularly for airborne monitoring systems.

Other than some cursory references to contamination from fulminated mercury blasting caps, Hg anomalies in mineral exploration resulting from industrial and/or agricultural sources have as yet to

be reported in the geological literature. Naturally-derived mercury contamination has been reported by Warren *et al.* (1966) and Warren and Delavault (1969) from base metal and mercury deposits. Mercury contamination from smelting sources seems almost certain owing to the volatility of the element under <sup>such</sup> conditions. D'Itri (*op. cit.*) says that mercury is vaporized and driven off with the evolved sulphur dioxide, some escaping even when the gas is cooled, scrubbed, and filtered. Research at selected smelting sites could provide invaluable data on the atmospheric dispersion of mercury.

In agricultural practice, organomercurials may be applied directly to diseased cereal crops, fruits, and vegetables as either sprays or dusts (Smart, *op. cit.*). Soils exposed to such treatment would undoubtedly contain raised levels of mercury. A soil treated once with mercuric oxide was found to contain 2.6 ppm Hg (Pickard and Grainger, 1962). Smart reports that up to 10,000 gm Hg/ha have been applied to soils in the past, but the dose does not normally exceed 20 gm/ha. The residence time of introduced mercury in soils is still not fully understood. Kimura and Miller (1964), Frear and Dills (*op. cit.*), and Zimmerman and Crocker (*op. cit.*) have all reported the degradation of introduced organomercurials and/or inorganic compounds of Hg and the release of Hg-containing compounds to the air. Certainly, some Hg is lost to the atmosphere, but probably the bulk of the element would be retained in soils for a considerable length of time (years), if not indefinitely. Therefore, soil surveys in mineral exploration where Hg pathfinding is considered must be aware of those areas with a history of mercurial application in agriculture and/or Hg loss by industry.

Mercury has been shown to have a favourable migration habit in oxygenated, carbonate-rich, slightly alkaline waters (Hem, 1970a). This has been substantiated by the presence of anomalous levels of

mercury in Keel mine water (see Table 17). The appropriate analyses of ground and stream water may be required to assess any hydromorphic transport of introduced mercury to or from stream sediments or soils. Anaerobic/reducing conditions may accentuate the accumulation of any introduced Hg as HgS (Wallace *et al.*, op. cit.) or retain the metal through sulphhydryl bonding in naturally-occurring humates.

In the atmosphere, mercury levels have been and will continue to be augmented by the already-mentioned degradation of mercurials introduced during agricultural practices, the smelting of Hg and base metal ores, the burning of coal, peat, and oil, and the continued degradation and release of naturally-occurring  $\text{Hg}^0$  and Hg-containing compounds. Undoubtedly, the industrial atmosphere must be considered to contain more mercury than non-industrial or oceanic atmospheres. If one selects to employ mercury in soil gas/atmospheric air for prospecting purposes, potentially polluting sources require definition for a meaningful interpretation of Hg degassing from sulphide occurrences. Spheres of pollution influence (known, probable, possible) may be required. Seasonal and meteorological information may also be critical aspects of interpreting polluting influences.

#### 6.8 ANALYTICAL METHODS AND TECHNIQUES FOR MERCURY ANALYSES

The increased interest in the (bio)(geo)chemistry of mercury has provided stimulus for the development of new analytical methods and techniques and it is appropriate here to discuss briefly current trends in the analysis of naturally-occurring material for Hg and the identification of mercury compounds.

Classical and/or recommended methods for determining submicrogram and microgram quantities of mercury normally rely on modifications of the dithizone method. The American Conference of Governmental Industrial Hygienists (1958) recommend extraction of divalent mercury

from dilute acid solutions using dithizone in chloroform to form the characteristic orange-yellow keto complex. The method is applicable to air and biological material.

The Analytical Methods Committee of The Society for Analytical Chemistry (1965) describe a preferred method for the determination of mercury in organic matter. The sample is oxidized in a mixture of nitric and sulphuric acids coupled with lengthy refluxing in a Bethge apparatus. A suitable aliquot is buffered for determination with dithizone.

The writer's method of analysis for mercury (flameless atomic absorption) is discussed in Appendix Two. Further reference to this method and the application of Tin (II) reduction techniques for the analysis of Hg-containing solutions has been adequately covered in a recently published article entitled "Non-flame methods for mercury determination by atomic absorption, a review" (Manning, 1970).

Flameless atomic absorption has been successfully applied by an increasing number of investigators to determine mercury in a wide range of materials. Recently, a similar approach has been adopted for the determination of As and Se in solutions. Simply,  $AsH_3$  and  $SeH_2$  are generated using "Gutzeit" evolution and the metal-containing vapours are swept by a flow of argon into an argon-hydrogen entrained flame of an atomic absorption spectrophotometer. Interferences are minimized and detection limits of 0.02 ug As and 0.03 ug Se are obtainable (Fernandez and Manning, 1971).

Neutron activation analysis is considered an extremely precise and accurate method of determining mercury. Morris and Killick (1964) report the high precision determination of mercury in G-1 and W-1. Kosta and Byrne (1969) have determined nanogram quantities of mercury in biological samples using an interesting scheme of separations. The material is pre-irradiated, volatilized in a sealed, oxygenated

chamber, the gases swept over a heated Pt gauze to complete ignition, interferring elements (halogens, As, Se) removed using heated silver wool and Hg quantitatively retained by a SeS pad for counting.

Ruzicka et al. (1969) have used an automated (auto analyzer) method to determine traces of mercury in biological material using substoichiometric radioisotope dilution. Their determinations on international biological standards agree with values attained by activation analyses.

Sjostrand et al. (1971) describe a neutron activation method to determine mercury in a wide range of naturally-occurring materials. Samples are pre-irradiated,  $\text{Hg}^{++}$  carrier introduced, and followed by hot acid oxidation in a suitable refluxing apparatus. Mercury is distilled from solution onto Au foil (weighed for recovery) and the amount of  $^{197}\text{Hg}$  relative to the standard is determined by spectrometry of the combined 68 to 77 KeV X-ray and  $\gamma$ -ray peaks.

The method most often referred to and/or employed in investigations requiring the determination and identification of organomercurials is chromatography. Fishbein (1970) has published a review article on the chromatographic and biological aspects of organomercurials.

In a series of papers, Westoo (1966, 1967, 1968) describes the determination of methylmercury in food and various kinds of biological materials utilizing both thin layer chromatography (TLC) and gas liquid chromatography (GLC). TLC separation of mercuric, methylmercuric, and phenylmercuric dithizonates has been attained using an aluminum oxide adsorbent. The limit of detection is 0.2 ug Hg. Methylmercuric cyanide, MM chloride, MM bromide, MM iodide, and phenylmercuric chloride are separated on silica gel and identified with an ethanolic solution of Nichler's thicketone. Westoo has used GLC to separate and identify methylmercury, ethylmercury, and methoxyethylmercury.



Tanaka et al. (1968) have combined radioisotope dilution with paper chromatography to determine organic and inorganic mercury. The technique has been successfully applied using a penicilliamine chelate to determine one ug of either phenylmercuric chloride or mercuric chloride.

Kurayuki and Kusamoto (1967) describe the chromatographic separation of inorganic and organic mercury compounds on anion-exchange paper using dithizone in chloroform for detection. The  $R_f$  values were: for alkylmercury compounds, 0.19-0.33; inorganic mercury compounds, 0.09-0.11; and phenylmercury compounds, 0.01-0.03. A detection limit of 0.2 ug is obtainable.

Kitamura et al. (1966) have reported on the GLC behaviour of a number of organomercurials using flame ionization and electron capture (tritium) detection devices. Methyl-, ethyl-, propyl-, and methoxyethylmercuric chlorides were successfully separated and determined. When using the electron capture device a detection limit of 0.5 ng methylmercury chloride was easily obtainable. Beauford (pers. comm.) confirms this last detection limit.

Fujita et al. (1968) have developed an interesting oxidation technique to extract mercury from biological matter. Samples are placed in a Pt dish, wetted with 1N  $\text{HNO}_3$ , and placed in a pressure bomb. Oxygen is passed into the bomb until a pressure of 25 kg/cm<sup>2</sup> is attained and the sample then ignited by a small AC current. The bomb is cooled, gases released, and mercury determined by a colorimetric procedure. Recoveries of Hg range from 91 to 96 per cent.

Goulden and Afghan (1970) report water samples from rivers in Saskatchewan, Canada that have been pre-irradiated with a UV source for two hours release more mercury (via the  $\text{SnCl}_2$ -flameless atomic absorption technique) for detection than do samples not irradiated.

Table 38. Ultra-violet reduction of some organomercurials in solution <sup>1</sup> to mercuric ion

|                                     | Apparent Mercury Level - % of Total |    |    |     |     |     |
|-------------------------------------|-------------------------------------|----|----|-----|-----|-----|
| Irradiation <sup>2</sup> Time-Mins. | 0                                   | 10 | 20 | 30  | 40  | 60  |
| Compound                            |                                     |    |    |     |     |     |
| Phenyl. Mercuric Acetate            | 5                                   | 60 | 75 | 90  | 95  | 100 |
| Methyl Mercuric Bromide             | 0                                   | 70 | 85 | 95  | 100 | -   |
| Di-Methyl Mercury                   | 5                                   | 70 | 90 | 100 | -   | -   |
| Ethyl Mercuric Chloride             | 50                                  | 80 | 95 | 100 | -   | -   |
| Di-Ethyl Mercury                    | 40                                  | 70 | 90 | 100 | -   | -   |

<sup>1</sup> about 10 ug/l

<sup>2</sup> 550 Watt Hg arc lamp

(after Goulden, 1970)

The results of control experiments on selected organomercurials in solution are shown in Table 38 and indicate that naturally-occurring water samples require pre-treatment for a more absolute value of the total Hg present.

## CHAPTER 7

### MERCURY IN SOIL GAS AT KEEL

#### 7.1 GENERAL

##### 7.1.1 Introduction

Primary and secondary halos of mercury around ore deposits are believed to reflect (to some extent) the gaseous migration of Hg vapour through rock and unconsolidated overburden.

James (1962) has stated that gaseous halos of Hg may be thought of as consisting of two components:

- i) Residual gas from the time of ore formation
- ii) That given off during weathering

The first component is, of course, the emplacement of the primary halo known to be present about both mercury and polymetallic deposits (Ozerova, op. cit.). The second migration of mercury is all that Hg vapour (or volatile compounds containing Hg) released after completion of epigenetic (hydrothermal) or syngenetic emplacement of sulphide mineralization. This includes oxidation and release of mercury from sulphide minerals and hydrothermally altered products and subsequent processes enhancing or depressing gas evolution in soil and unconsolidated overburden.

##### 7.1.2 Gaseous Aspect of Primary Halos of Mercury

Although the subject of this chapter reports on the gaseous dispersion of mercury in the secondary environment, primary halo emplacement is briefly commented on for a comparison with the known secondary mobilization processes of volatile Hg/Hg compounds.

James (op. cit.) states "As a result of the high vapour pressure of mercury, the element may be expected to penetrate the wall rocks

in the form of vapour. Even in dense rocks, an aureole could be produced in this manner by the vapour following interstitial spaces in the rock. Such a pattern may extend for many hundreds of feet." Further, James theorizes that the greatly increased vapour pressure of Hg at mesothermal and hypothermal temperature ranges would aid the formation of well-developed primary halos and/or continued hydrothermal transport (gaseous aspect?) for eventual epithermal deposition.

The contribution of aqueous hydrothermal movement of Hg along faults, fissures and interstitial spaces should not be overlooked as an accompanying facet of gaseous primary halo emplacement. Ozerova (op. cit.) reports that primary halos of Hg form by both gaseous and hydrothermal mechanisms of metal transport and deposition.

A suggestion that thermal dissociation of HgS may put significant quantities of Hg into hydrothermal solution at elevated temperatures (about 0.3 ug/ml at 250°C) has been proposed by Dickson (1968). Further, he adds that certain species of sulphur ( $S_{(n)}^{=}$ ,  $S_2O_3^{=}$ ,  $S_{(n)}O_6^{=}$ ,  $H_2S$ ,  $SO_4^{=}$ ) have the ability to solvate mercury and could introduce even more of the element into alkaline solutions as  $HgS_2^{=}$ . The hydrothermal transport of mercury is then possible and could explain the presence of Hg vapour accompanying exhalations from thermal springs (White, 1967).

### 7.1.3 Gaseous Movement of Mercury from Mineralized Occurrences

Reported information on the mode of gaseous dispersion of mercury from weathering sulphides is extremely limited. Most applied investigators refer to the comparative ease of reduction of some mercury compounds and minerals to metallic Hg, coupled with the high vapour pressure of the element as leading to soil air or atmospheric air halos.

Hawkes and Williston (1962) have elaborated on the stages of mercury vapour migration from oxidizing sulphides. They conclude that native Hg is released by the oxidation of primary sulphide minerals

and the element moves upward to form secondary dispersion halos. Migration of Hg vapour is said to proceed via Hg complexes (inorganic and organic?) and sorbed Hg vapour on clay minerals, the gas eventually being released to the atmosphere.

Laboratory experiments have been conducted to demonstrate the formation of mercury vapour over cinnabar (Karasik et al., 1967). Measurements at 20 to 227°C suggest that Hg vapour is forming continuously, at depth as well as in the oxidized zone.

Trost and Bisque (1970) claim to be able to differentiate between ionic and vaporous mercury in soils from both experimental information and results from field studies on two mineralized occurrences in the United States. The experimental results are enlightening, but the writers assume mercury vapour is being generated at depth and is being actively dispersed as a gas along mineralized faults. In addition, they neglect to mention if any equilibria may exist between saline and gaseous forms of naturally-occurring Hg compounds in soils.

## 7.2 SOME CASE HISTORY APPLICATIONS OF GASEOUS DISPERSION IN MINERAL EXPLORATION

### 7.2.1 Mercury

The first known reference on the determination of mercury vapour dispersing from oxidizing sulphides is that by Sergeev (1961). Figure 36 shows the soil gas anomaly (but no measurable atmospheric anomaly) detected by Sergeev over an unnamed Hg deposit in the Karatan Range, U.S.S.R. Soil air was collected by means of pumping through shallow bore holes in friable material.

Williston (1964) has detected an atmospheric air mercury anomaly over a Hg prospect in California. He appears to be the first to mention that the mercury content of air can vary with temperature, wind direction, and precipitation and that the application of the technique to mineral

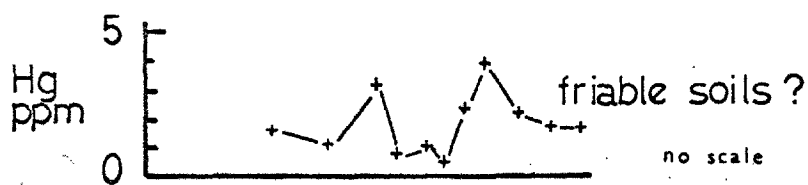


Fig. 36 Hg in soil air and atmospheric air over an unnamed deposit in the USSR (after Sergeev, 1961)

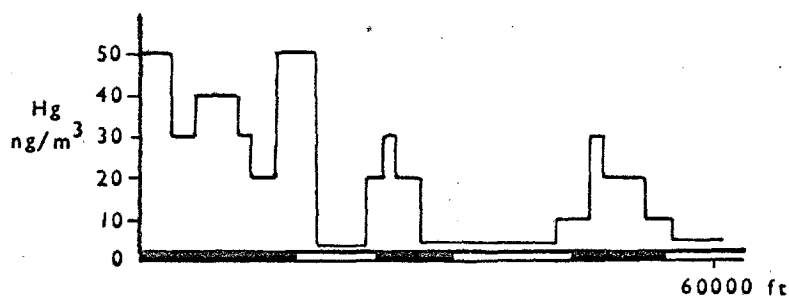


Fig. 37 Hg in air at 200 ft. altitude, Bruce Peninsula, Ont., Canada (after Motycka, 1970)

Zn soil anomaly

exploration seemed to hold most promise for warm, dry areas.

A significant contribution to the application of Hg in soil gas and air for mineral exploration has been the examination of mercury vapour anomalies at Cortez, Nevada, U.S.A. by McCarthy *et al.* (1969). Mercury traps (plastic tents containing noble metal foil to amalgamate escaping Hg vapour) were placed over gravels covering a Au deposit with a known mercury soil anomaly. Results of these experiments (see Fig. 38) revealed that anomalous Hg soil gas levels complemented the outline of the deposit as well, if not better than the soil anomaly. Atmospheric air immediately above the deposit also contained anomalous levels of Hg. Further experiments using aircraft collecting procedures were also successful in detecting airborne anomalies. Mercury in air anomalies were also found associated with porphyry Cu deposits and Hg (cinnabar) occurrences.

Barringer Research Ltd. of Toronto, Canada has recorded anomalous mercury concentrations in atmospheric air over Zn soil anomalies in the Bruce Peninsula, Canada (Motycka, 1970). Also, anomalous atmospheric readings have been recorded over the well-mineralized Cobalt area, Ontario (A. R. Barringer, pers. comm.).

Crosby reports that mercury soil gas anomalies have been found overlying subcrop of major faults related to mineralization in Idaho, U.S.A. (a pers. comm. *in* Crosby, 1968). He also states that the mercury soil content is not sufficient to account for the magnitude of the soil gas anomaly suggesting that there may be a continuous release of Hg vapour at depth and subsequent migration of the element through soil cover.

#### 7.2.2 Radon Gas in Uranium Prospecting

Mercury is not the only gas to find application in mineral exploration. Radon gas is now an accepted method of prospecting for



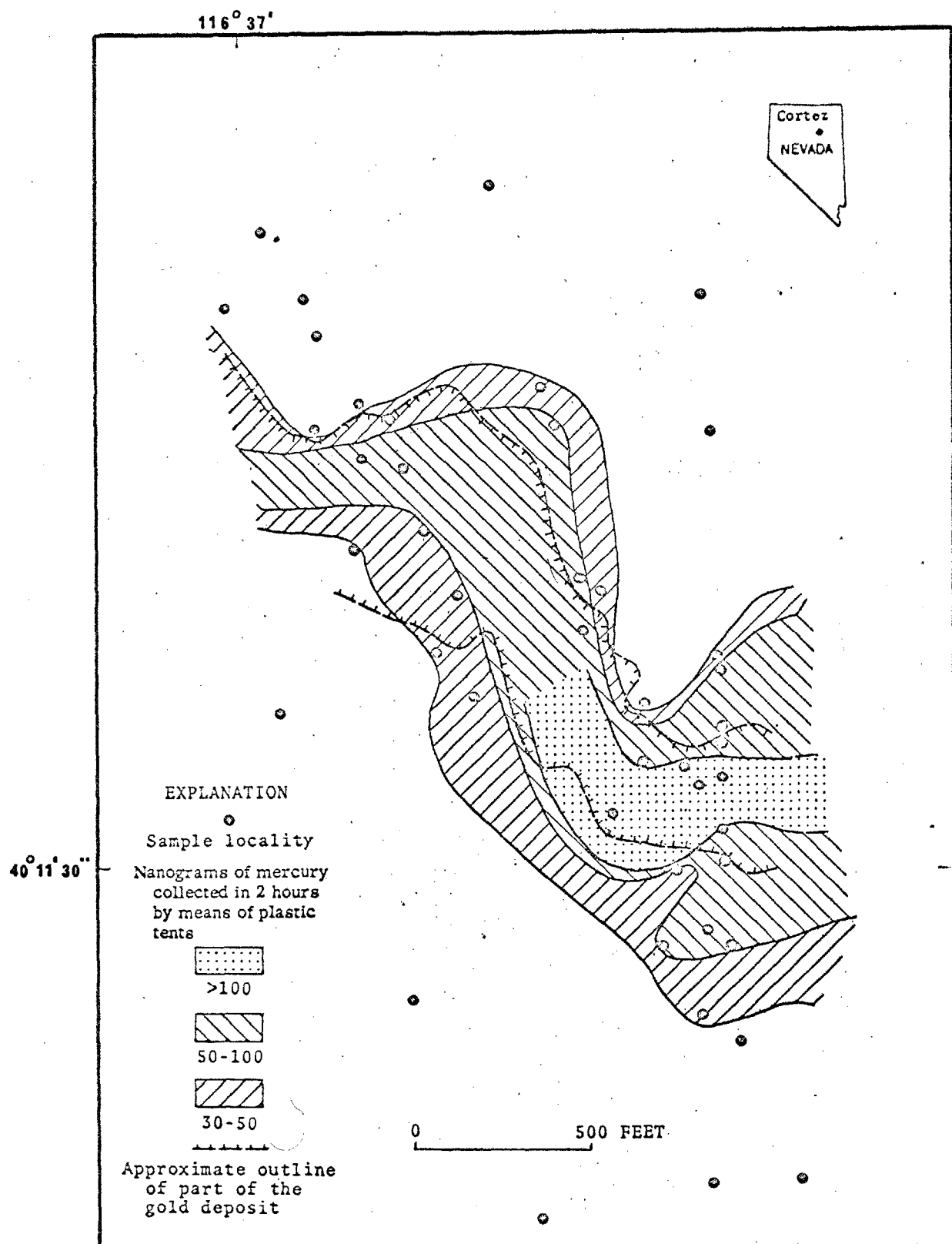


Fig.38 Mercury content in soil gas  
at Cortez, Nevada, USA

after McCarthy et al, 1969

U/Th and the writer takes this opportunity to briefly elaborate on analytical methods and sampling techniques employed to monitor Rn.

Saum and Caneer (1969) have made on-site measurements of Radon-222 gas emanating from soils on the Colorado Plateau, U.S.A. They employ a vehicle-mounted power auger to drill a three-inch diameter hole to a depth of three feet into which they insert a sampling probe. A hand-operated pump is used to extract the soil gas into a counting chamber which is coated with a phosphor sensitive to alpha particle bombardment. The radiation emitted by the phosphor is amplified for measurement by a photomultiplier and a detection limit of  $3.5 \times 10^{-18}$  grams Rn-222 in 30 cc of soil gas is claimed. Actinon (Rn-219) and thoron (Rn-220) are potentially interfering gases.

Peacock and Williamson (1961) describe equipment to measure radon in soil gas pumped (by hand) from a shallow auger hole. Further, they employ a metal cone to collect radon gas when the water-table is near the surface. Apparently, any radon present builds up to equilibrium and the gas is then drawn through the scintillation chamber and the alpha activity measured.

Dyck (1969a) describes radon determination apparatus for geochemical prospecting as developed by the Geological Survey of Canada. The method is applicable to water (Rn is degassed from the sample before alpha measurement) and soil air. Dyck claims to be able to distinguish radon from thoron by observation of decay curves. Further, Dyck (1969b) describes successful prospecting application employing traverse sampling stations over uranium mineralization at Elliot Lake, Ontario and in the Gatineau Hills, Quebec.

Apparatus to determine radon is commercially available from at least one Canadian firm (McPhar Geophysics Ltd., Don Mills, Ontario) for Rn measurement in ground or stream water. It would seem possible in the light of the previously discussed methods that the apparatus

could be adapted for soil gas work.

### 7.2.3 Other Gases in Mineral Exploration

Boyle and Garrett (1970) describe the use of volatile elements and compounds in searching for mineral deposits as "Atmogeochemical" prospecting. Besides Hg and Rn, they note future use may be made of iodine, As, Sb, and sulphur-containing gases.

Barringer (1969) states that iodine may be a useful pathfinder in mineral exploration owing to the knowledge that halide-rich brines play an important part in the formation of some epigenetic orebodies. Also, actual occurrences of iodine minerals have been reported in a number of mineral deposits. A. R. Barringer (pers. comm.) has indicated that potential application may exist for I pathfinding in searching for porphyry Cu-Mo mineralization in arid environments.

R. Peters (pers. comm.) at A.G.R.G. is currently investigating sulphur dioxide and other sulphur-containing gas emanations from base and noble metal deposits in Newfoundland, Canada. A. R. Barringer (pers. comm.) reports measuring sulphur dioxide dispersion from sulphide occurrences using a direct-reading correlation spectrometer.

There would appear to be a considerable range of potentially useful gaseous compounds in mineral exploration if one considers organo-metallics. Compounds analagous to the biologically generated and highly volatile  $(CH_4)_2Hg$  such as Cd, Zn, Pb, and Bi derivatives all have low boiling points (see Table 39) and could form secondary gas halos through appropriate biochemical reaction mechanisms. Tellurium may also have potential application as a gas pathfinder owing to some relatively low boiling point organic and inorganic compounds.

Although not a directly related subject, W. T. Meyer at A.G.R.G. is currently investigating "readily-volatile" metals in soils and weathered material as potential guides for mineralization.

Table 39. Physical constants<sup>1</sup> of some potentially useful organo-metallic compounds for mineral exploration

| Organo-metallic compound          | Melting point (°C) | Boiling point (°C) |
|-----------------------------------|--------------------|--------------------|
| $(\text{CH}_3)_2\text{Hg}$ liquid | -                  | 95                 |
| $(\text{CH}_3)_2\text{Cd}$ oil    | -4.5               | 105                |
| $(\text{CH}_3)_2\text{Zn}$ liquid | -42.2              | 46                 |
| $(\text{CH}_3)_3\text{Sb}$ liquid | -                  | 80.6               |
| $(\text{CH}_3)_3\text{As}$ liquid | -                  | 70                 |
| $(\text{CH}_3)_3\text{Bi}$ liquid | -                  | 110                |
| $(\text{CH}_3)_2\text{Te}$ oil    | -                  | 82.9               |
| $(\text{CH}_3)_4\text{Pb}$ liquid | -27.5              | 110                |

<sup>1</sup> from Handbook of Chemistry and Physics, 51st Edition, 1970-1971, The Chemical Rubber Co., U.S.A.

### 7.3 EXPERIMENTS TO DETERMINE MERCURY VAPOUR IN LABORATORY AIR

#### 7.3.1 Introduction

It was apparent after an investigation of literature sources that the most suitable method of determining mercury in soil and atmospheric air was to emulate the technique of McCarthy *et al.* (op. cit.). Direct-reading of Hg vapour in soil gas and atmospheric air using the James-Webb (1964) spectrophotometer required several orders of magnitude of improvement and/or amplification of instrument sensitivity as well as a special power supply for field use. Pre-concentrating of mercury vapour/volatile Hg compounds on a suitable collector(s) was required.

#### 7.3.2 Collectors for Mercury Vapour and/or Volatile Mercury Compounds

Collectors for mercury vapour can be essentially divided into two types:

- i) Absorbing solutions containing organic and/or inorganic complexing agents.
- ii) Solid collectors, including metal amalgamation or selective sorption substances.

Absorbing solutions have been successfully used by a number of investigators. Sergeev (op. cit.) used a mixture of KI solution and vapours of bromine to trap mercury vapour in his soil gas experiments. Linch *et al.* (1958) have employed 0.1N iodine monochloride in 0.5N hydrochloric acid to absorb dimethyl and diethyl mercury, monomethyl and monoethyl mercuric chlorides, mercury vapour, and mercurial-bearing dusts.

The separation of metallic mercury from some organic Hg vapours has been accomplished by the passage of mixed vapours through a solution of sodium carbonate and dibasic sodium phosphate and then through a  $\text{H}_2\text{SO}_4$ /permanganate absorber. Vapours of ethyl and methylmercury chloride (100 to 1000 ug range) are retained in the carbonate-phosphate

absorber and the Hg vapour is captured by the acid permanganate (Kimura and Miller, 1960).

The writer has not attempted application of absorbing solutions mainly on three accounts.

- i) Difficulty in obtaining mercury-free chemicals (solutions containing less than 0.005 ug/l Hg would seem desirable for good quality control).
- ii) The absorbing solution may be required to collect both Hg vapour and any naturally-occurring organo-mercurials with suitable efficiency. A lengthy laboratory investigation was envisaged with little or no guarantee of finding the needed reagent.
- iii) Most important, some difficulties were foreseen for field application. Fragile glassware was required for sintered glass bubblers, and the transport of mercury-bearing solutions adds the problem of element sorption to glass and polyethylene containers (i.e. see Benes and Rajman, 1968 and Benes, 1969).

Solid collectors have been successfully employed by a number of investigators. Christie *et al.* (1967) have collected mercury vapour and organo-mercurials with CdS-impregnated fibre glass filter pads and on fluidized beds of active carbon. Preliminary tests by the writer revealed that prepared CdS pads contained high and erratic amounts of Hg (5 - 50 ng) that could be purged only on heating to temperatures that destroyed the usefulness of the filter. However, Barber *et al.* (in press) report a successful application of CdS pads in collecting nanogram levels of mercury in radio-tracer studies.

"Hopcalite" (a preparation containing 60%  $\text{MnO}_2$  and 40%  $\text{CuO}$  manufactured by Hopkin and Williams Ltd., Chadwell Heath, Essex) has been employed by Magos (1966) to absorb radioactive mercury vapour in the range 200 to 1200 ng/l. A further investigation by the writer

confirmed the scavenging qualities of hopcalite for mercury vapour, but the preparation contains erratic amounts of contamination. In addition, loss of chemical activity on heating of hopcalite above  $350^{\circ}\text{C}$  has been reported by D. J. B. Cox (written comm.).

Iodized active carbon collects all forms of mercury in air at concentrations approximating  $100\text{ ug/m}^3$  (Sergeant *et al.*, 1957). Experiments by the writer have indicated that a small bed of the substance readily absorbs mercury vapour down to levels much less than  $100\text{ ug/m}^3$  and the mixture has now replaced  $\text{PdCl}_2$ -impregnated glass wool as a de-mercurifying agent for use in the James-Webb spectrophotometer (see Appendix Two). Unfortunately, the material ignites on heating and was not suitable for collecting and desorbing of mercury-bearing compounds.

Fibre-glass filter pads have been used by Barringer Research Ltd., Canada to collect mercury vapour (A. R. Barringer, pers. comm.). Similar tests by the writer indicated that newly purchased pads not only contained erratic levels of contamination, but also exhibited a low collecting efficiency for mercury vapour. The pads seem best suited for collecting mercury-bearing dusts.

Mercury amalgamates with most metals, iron being the most notable exception (Bratt, 1967). For centuries, both Ag and Au have been recovered from their ores using mercury alloying and amalgamation. The analytical use of noble metal capture of mercury has been reported by Holmes and Lauder (1965), Azzaria (1966), and Williston (1968). Thilliez (1968) has used Pt for collecting mercury vapour. McCarthy *et al.*, (op. cit.) have used both Ag and Au foil in their investigations at Cortez, Nevada.

The writer decided to employ noble metal amalgamation to collect mercury vapour as the technique appears to be reasonably efficient. In addition, noble metals presented little problem for purging and were easily adaptable to the facilities available.

A dynamic sampling system was developed based on the pumping of soil air through a series of Ag gauze filters to replace the static technique of McCarthy *et al.* (1969) which depends on soil respiration of mercury vapour.

### 7.3.3 Apparatus and Materials

The basis for mercury determination in this investigation is the James-Webb (1964) double-cell, flameless atomic absorption spectrophotometer. Discussion here on analysis will be limited to instrument calibration using mercury vapour and determination of Hg vapour released from heated Ag gauze. Further details on procedural information and mercury analysis for soils, etc. can be found in Appendix Two.

Normally, the spectrophotometer is calibrated by injecting known amounts of mercury vapour into the instrument and noting the voltmeter readings over the range 0 to 7000 mV (0 to 600 ng). Although representing adequate sensitivity for soils, discrimination below 100 mV (about 5 ng Hg) is poor and a new calibration procedure was required.

A modified version of the James-Webb (1964) instrument had been acquired and was extremely stable on the 300 mV scale (0 to 15 ng Hg). By using a gas syringe (Hamilton-2500 ul), a suitable working curve over the range 0 to 20 ng was possible (see Fig. 39). Now a detection limit of 0.5 ng Hg was easily obtainable with good discrimination for increasing 0.5 ng amounts (when required).

Silver gauze (60 mesh) was purchased from commercially available sources and cut into one inch diameter circles (to fit filter holders). For analysis, gauze was heated (singly) using the existing Radio Frequency heating unit (Appendix Two) to release amalgamated mercury. Simply, an exposed Ag gauze was placed in the sealed glass tube, heated to redness by RF, and the released volatiles quickly swept to the reference and measuring cells of the spectrophotometer for mercury determination.



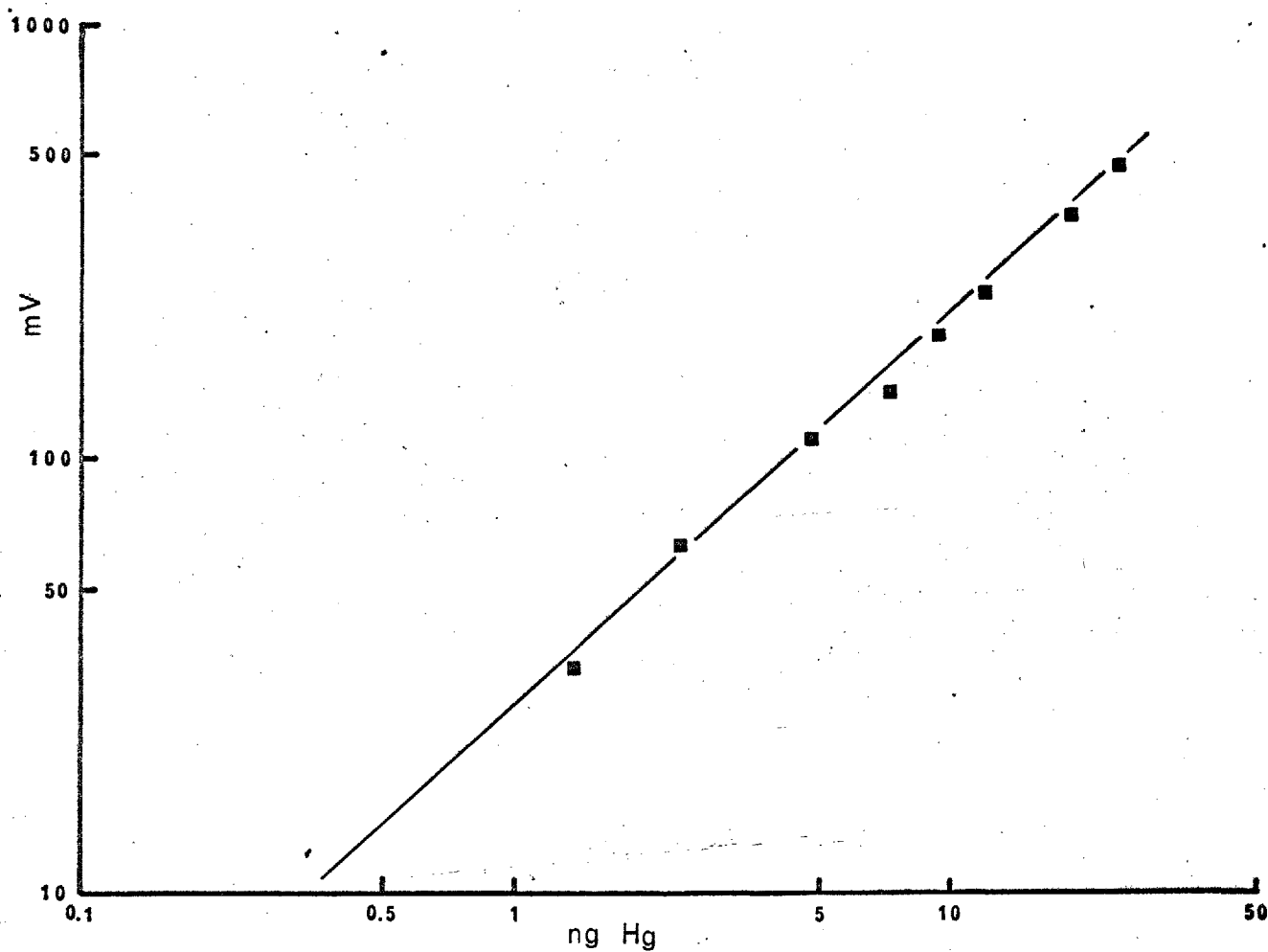


Fig. 39 High sensitivity calibration<sup>1</sup> graph for the mercury vapour spectrophotometer

<sup>1</sup> using a 2500  $\mu$ l gas syringe

Purging of the gauze by heating to 700°C in a muffle furnace for at least 36 hours was a required procedure to clean (degrease) and decontaminate the silver. In most instances, a background of 1 ng/gauze was maintained, but on occasion this could rise to 3 or 4 ng/gauze for no apparent reason. Over a period of three to four weeks, gauze confined from laboratory air and other sources of contamination usually showed levels of 2 to 3 ng Hg/gauze. All laboratory test experiments were performed on gauze with background levels  $\leq 0.5$  ng Hg/gauze. A trend for gauze to become susceptible to increased levels of contamination with usage has been noted.

Table 40 lists the apparatus and materials used to implement a sampling system for the collection of mercury vapour from laboratory air. The apparatus was assembled into a dynamic air sampling system as follows:

Filter holders → Rotameter → Limiting orifice →

Air sump → Vacuum pump

The above system provided a working unit to study mercury amalgamation with Ag gauze using both introduced and laboratory (Hg-containing) atmospheres. The system was later adapted for field studies using a 12 V DC battery-operated pump and suitable attachments for obtaining soil gas.

In addition, a small, battery-operated air sampling unit (C. F. Casella and Co. Ltd., London N. 1) was used for both laboratory air sampling studies and for atmospheric air sampling in the field.

#### 7.3.4 Results of Laboratory Experiments

The correct flow rate for suitable collection efficiency was required for the system. Limiting orifices of 14, 5, and 2 l/m were selected and a series of five Ag gauze contained in "in-line" filter holders exposed to laboratory air. Figure 40 shows the results and it is easily seen that a low air flow rate is required for controlled

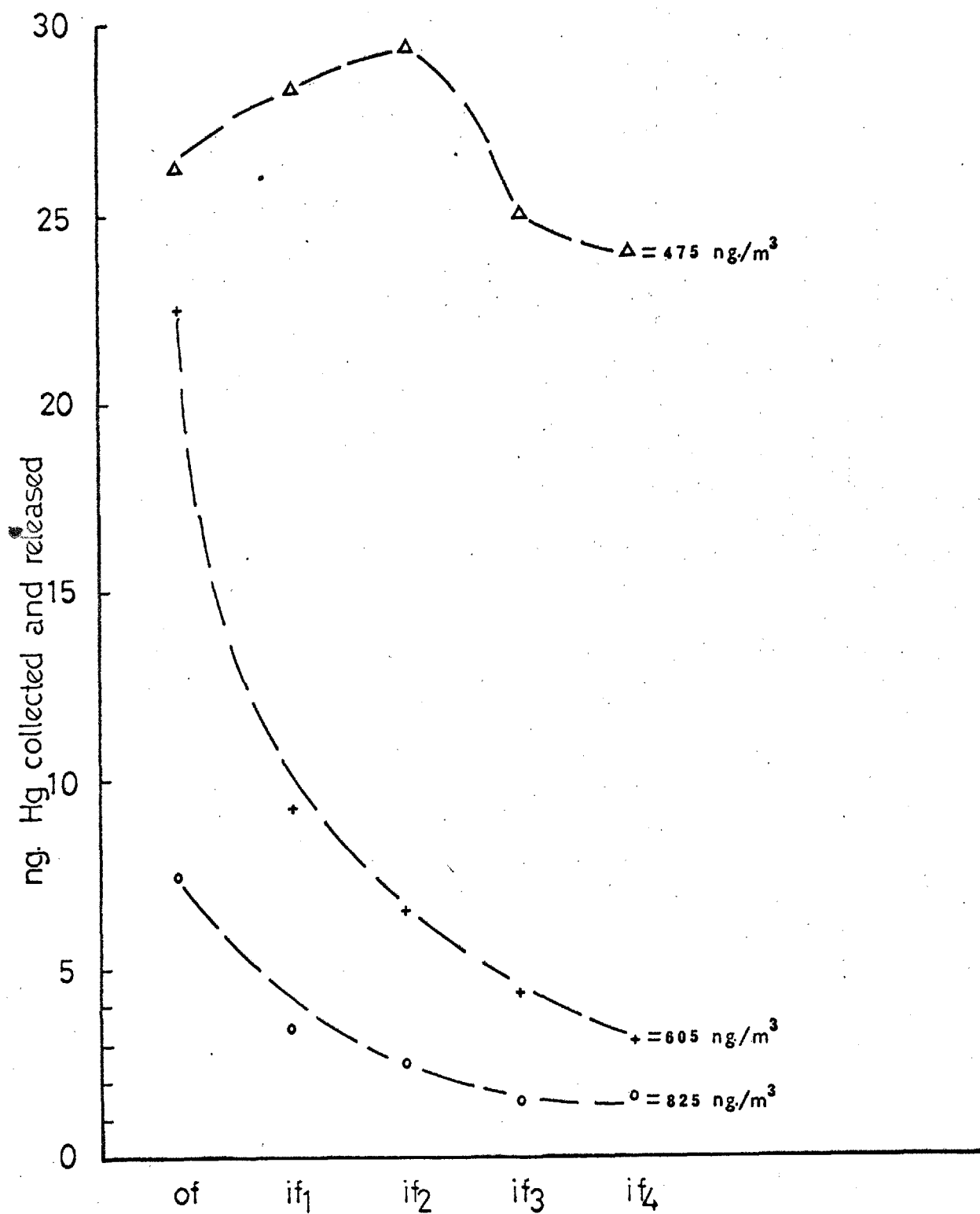


Fig. 40 The effect of air flow rate on the amalgamation of Hg vapour with 60 mesh Ag gauze

Δ 14 l/m  
 + 5 l/m  
 ° 2 l/m  
 of-open filter  
 if2-inline filter and no.

Table 40. Apparatus and materials employed in laboratory air experiments and in soil gas investigations

| Number      | Description                                          | Purpose                                                          | Notes                                                                                                                                        |
|-------------|------------------------------------------------------|------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| One         | 1 inch "open" filter holder                          | To hold one to five 60 mesh Ag gauze circles                     | Manufactured by Gelman Instrument Co., U.S.A. Filter holders made of an acetal plastic "DELRIN". Limiting orifice(s) made of stainless-steel |
| Two or more | 1 inch "in-line" filter holders                      |                                                                  |                                                                                                                                              |
| One         | Limiting orifice                                     | Provides accurate air flow rate at given conditions <sup>1</sup> |                                                                                                                                              |
| One         | Five 1 bell jar (air sump)                           | Vacuum reservoir to reduce "hunting" of pump                     | Not normally used in field work                                                                                                              |
| Two         | Rotameters (1-10 l/m)                                | Visual control that limiting orifice is functioning              | Two columns used during soil gas experiments                                                                                                 |
| Two         | Vacuum air pump                                      | Vacuum source <sup>2</sup>                                       | Must have a capacity greater than limiting orifice                                                                                           |
| -           | PVC tubing, jubilee clips, glass tubing, rubber bung | Linkage for filter holders, sump, and pump                       | All joins must be air-tight                                                                                                                  |

<sup>1</sup> For a given set of upstream conditions, the discharge of gas through an orifice will theoretically increase for an increase in the value of  $P_1/P_2$  ( $P_1$  = upstream pressure,  $P_2$  = downstream pressure) until the linear velocity in the throat reaches the velocity of sound in the gas at that point. For air, this condition exists when  $P_2 = 0.53 P_1$ . The critical or limiting air flow of an orifice occurs when the pressure on the downstream side of the orifice is 53% of the pressure on the upstream side. When using a limiting orifice with a filter sufficient vacuum must be maintained at the pump to compensate for any pressure drop developed across the filter, in order to maintain a constant flow rate.

<sup>2</sup> 12 V DC pump for field use, 240 AC pump for laboratory experiments.

efficiency when using 60 mesh Ag gauze to collect Hg vapour. Also, Figure 40 would suggest that the relative efficiency of the system is such that lower flow rates (less than 2 l/m) may be required when Hg vapour levels drop to naturally-occurring levels (thought to be less than  $1 \text{ ng/m}^3$  in atmospheric air).

Kalb (1970) reports that a flow rate of 1.88 l/m gives the greatest reproducible sensitivity in an analytical technique using eight gm of Ag chips to amalgamate Hg vapour. Lower flow rates have been attempted by the writer in both field and laboratory work, but were discontinued as the vacuum pump(s) tended to overheat.

That mercury vapour is collected and determined with little interference is shown by Figure 41. Ninety-two ng of Hg vapour were injected into a series of "in-line" Ag gauze filters whose air was pre-cleaned with iodized active carbon. Seventy-five ng Hg were recovered representing an efficiency of 82 per cent. A reference series of determinations is also presented to show the efficiency of the active carbon.

Some analyses on laboratory air are shown in Table 41. In these experiments, three Ag gauzes were employed, but it is apparent that more filters are required to obtain a more absolute value of mercury vapour present. The efficiency of a three gauze system appears to be about 50 per cent. The differences in the estimated content of mercury in laboratory air may reflect actual changes in the level of Hg vapour/volatile Hg compounds as the air was constantly being circulated by fume cupboard fans. Also, a single heating to redness of Ag gauze is shown to volatilize almost all amalgamated Hg.

Mercury could not be determined in London air as the Ag gauze quickly reacted (darkened) when exposed and any amalgamation was effectively curtailed. Atmospheric sulphur compounds (probably  $\text{H}_2\text{S}$ ) are thought to be responsible. This feature has some bearing on soil gas

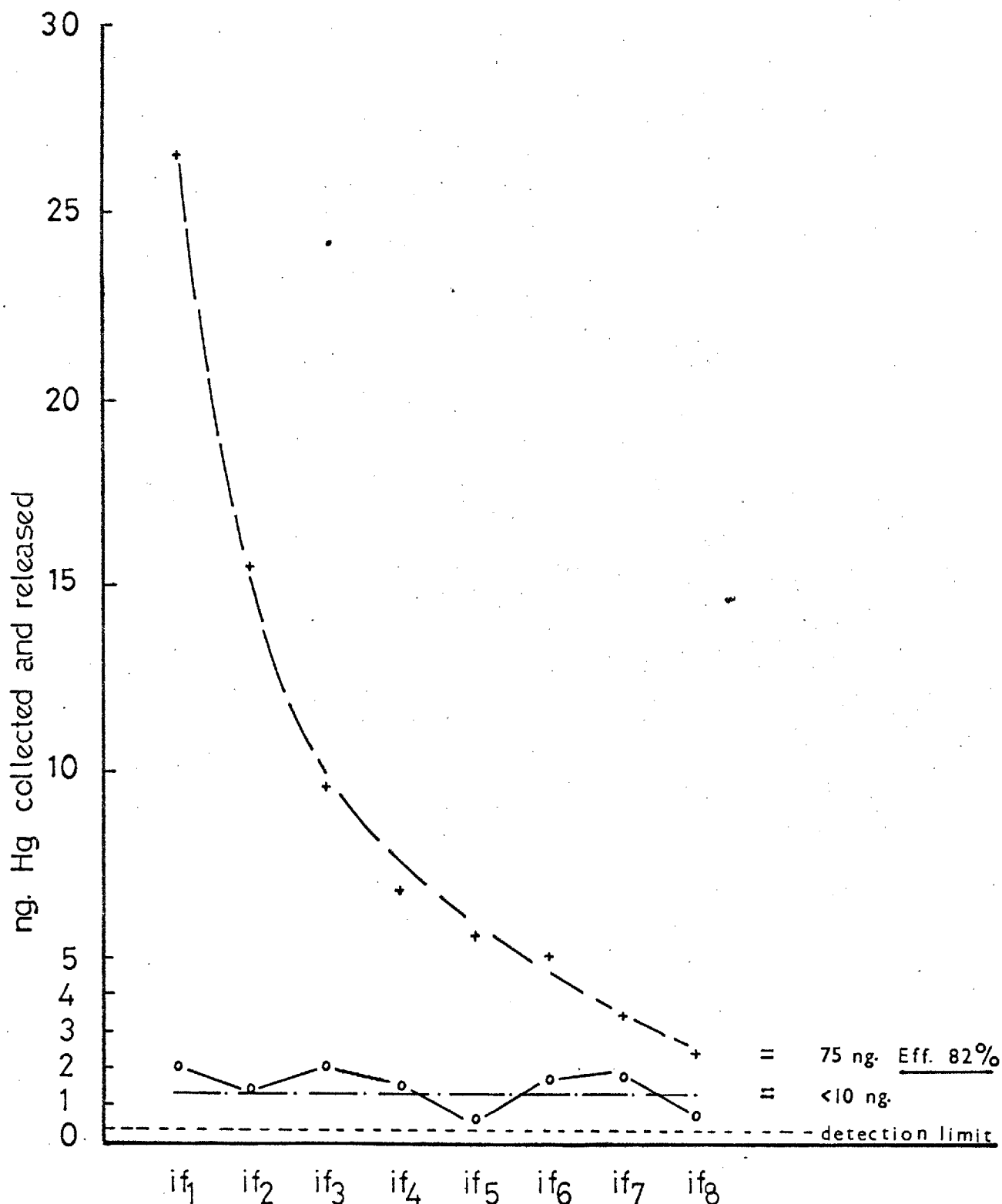


Fig. 41 Efficiency of a series of 60-mesh Ag gauze for collecting Hg vapour<sup>3</sup>

+--experimental series, Hg vapour introduced<sup>1</sup>  
 o--control series, Hg vapour removed<sup>1,2</sup>

if<sub>2</sub>-inline filter and no.

- 1 92 ng.
- 2 iodized active carbon
- 3 5 l/m

Table 41. Results of dynamic sampling experiments for the determination of mercury vapour in laboratory air

|                                | Sample No. | Litres of air sampled <sup>1</sup> | Nanograms of Hg released, first heating <sup>2</sup> | Nanograms Hg released, second heating <sup>2</sup> | Total Hg released (ppb) | Estimated Hg content of laboratory atmosphere <sup>3</sup><br>ng/m <sup>3</sup> | Efficiency <sup>4</sup><br>% |
|--------------------------------|------------|------------------------------------|------------------------------------------------------|----------------------------------------------------|-------------------------|---------------------------------------------------------------------------------|------------------------------|
| D<br>A<br>Y<br><br>O<br>N<br>E | 2817       | 60                                 | 33.0<br>19.0<br>11.5                                 | 1.8<br>0.8<br>< 0.3                                | 66.1                    | 1250                                                                            | 47                           |
|                                | 2847       | 60                                 | 18.0<br>11.5<br>8.4                                  | 1.5<br>< 0.3<br>< 0.3                              | 39.4                    | 800                                                                             | 41                           |
|                                | 2877       | 62                                 | 24.0<br>15.0<br>9.8                                  | 2.2<br>1.1<br>-                                    | 52.1                    | 985                                                                             | 46                           |
| D<br>A<br>Y<br><br>T<br>W<br>O | 2908       | 40                                 | 12.5<br>6.8<br>3.8                                   | 0.8<br>< 0.3<br>< 0.3                              | 23.9                    | 695                                                                             | 48                           |
|                                | 3157       | 28                                 | 10.5<br>3.4<br>1.8                                   | < 0.3<br>< 0.3<br>< 0.3                            | 15.7                    | 595                                                                             | 63                           |
|                                | 3143       | 28                                 | 10.8<br>2.7<br>1.5                                   | < 0.3<br>< 0.3<br>< 0.3                            | 15.0                    | 675                                                                             | 57                           |
|                                | 3125       | 36                                 | 15.0<br>5.7<br>3.6                                   | 1.5<br>< 0.3<br>< 0.3                              | 25.8                    | 815                                                                             | 56                           |

<sup>1</sup> Two 1/m

<sup>2</sup> Radio Frequency heating (700°C) of three separate 60 mesh silver gauze

<sup>3</sup> Projected curve estimations

<sup>4</sup>  $\frac{\text{Total Hg released}}{\text{Estimated Hg content of laboratory atmosphere}}$

investigations as sulphur-bearing volatiles may be emitted from oxidizing sulphides (Blanchard, op. cit.). However, this problem seems not to have arisen during soil gas sampling at Keel.

Limited experiments have also been performed to show that Ag gauze collects some volatile mercury-bearing compounds. Diethylmercury ( $\text{Hg}(\text{C}_2\text{H}_5)_2$ ) vapour is collected by Ag gauze when atmospheres of the compound are injected into a series of "in-line" filters. Limited data indicates that the compound is readily taken up (or catalytically reduced to Hg vapour and amalgamated), but efficiency controls have not been investigated. Dimethylmercury was not investigated (although such information would seem desirable) as adequate facilities to vent this highly volatile (about 50 times that of Hg vapour) and toxic compound were not readily available.

#### 7.3.5 Transport of Hg-free and Exposed Ag Gauze to and from the Field Area

Any contamination of the Ag gauze in the laboratory from introduced sources (thought to be Hg-containing chemicals and a polarograph) could be circumvented by purging gauze in a muffle furnace or the RF heater immediately before laboratory experiments. Silver gauze circles taken to the field for exposure required special consideration and the following packaging procedure was adopted.

Cleaned gauze were placed (singly or doubly) in unused self-sealing polyethylene bags ( $2\frac{1}{4} \times 2\frac{1}{4}$  in.), the bag folded and placed with other bags in a wide-mouth jar ( $2\frac{1}{4} \times 1\frac{1}{2}$  in.) capped with a bakelite screw top lined with a soft plastic sealer. A loose gauze was placed in the capped jar to mop up any introduced mercury vapour. Overall, the jars proved satisfactory, but some contamination was encountered from time to time. Exposed gauze were placed (singly) in numbered polyethylene bags, returned to the bottles, and only opened for analysis at the laboratory. "Blank" levels were determined on both



batch and individually packaged gauze to maintain quality control. All field results reported here have been corrected for "background" contamination levels of mercury.

#### 7.4 SOIL GAS COLLECTION PROCEDURES

##### 7.4.1 Introduction

The collection of mercury vapour/volatile mercury compounds from soil gas involved the testing and application of apparatus with little history of use.

The only known collection of mercury from soil gas for geochemical purposes was reported by Sergeev (op. cit.) who pumped air out of shallow bore holes. No details were supplied on the apparatus employed. McCarthy et al. (1969) used plastic tents to funnel soil gas into a noble metal trap. This technique depends somewhat on the stimulation of natural soil respiration processes through air pressure changes and slightly elevated temperatures. Other than the specialized chambers and hoods required for trapping Rn emanations and the "soil respirometers" used by soil scientists to monitor oxygen and carbon dioxide in soils, little else seems reported on soil gas equipment and application.

The vacuum apparatus described and used in the laboratory experiments has been adapted for field use. A 12 V DC battery-operated pump (Capex Mark I, Charles Auston Pumps Ltd., Byfleet, Surrey) replaces the mains-operated vacuum source while "perspex" and stainless steel "hoods" (see Fig. 42 and Fig. 43) have been devised and/or modified to extract soil gas from soils.

##### 7.4.2 Previous Work at Keel (Soil gas respiration experiments)

Initial attempts to measure mercury vapour in soil air and atmospheric air at Keel have been made by the writer and M. D. Leggo using a technique similar to that described by McCarthy et al. (1969).

Data and results have been reported by Leggo (1970). These findings were inconclusive as contamination of the plastic "tents" (here nine litre polyethylene bottles) is believed to have caused spurious readings. Corrected results showed little, if any, readily volatile Hg/Hg compounds degassing from mineralized soils. It should be noted that less than optimum sampling sites were used during these investigations.

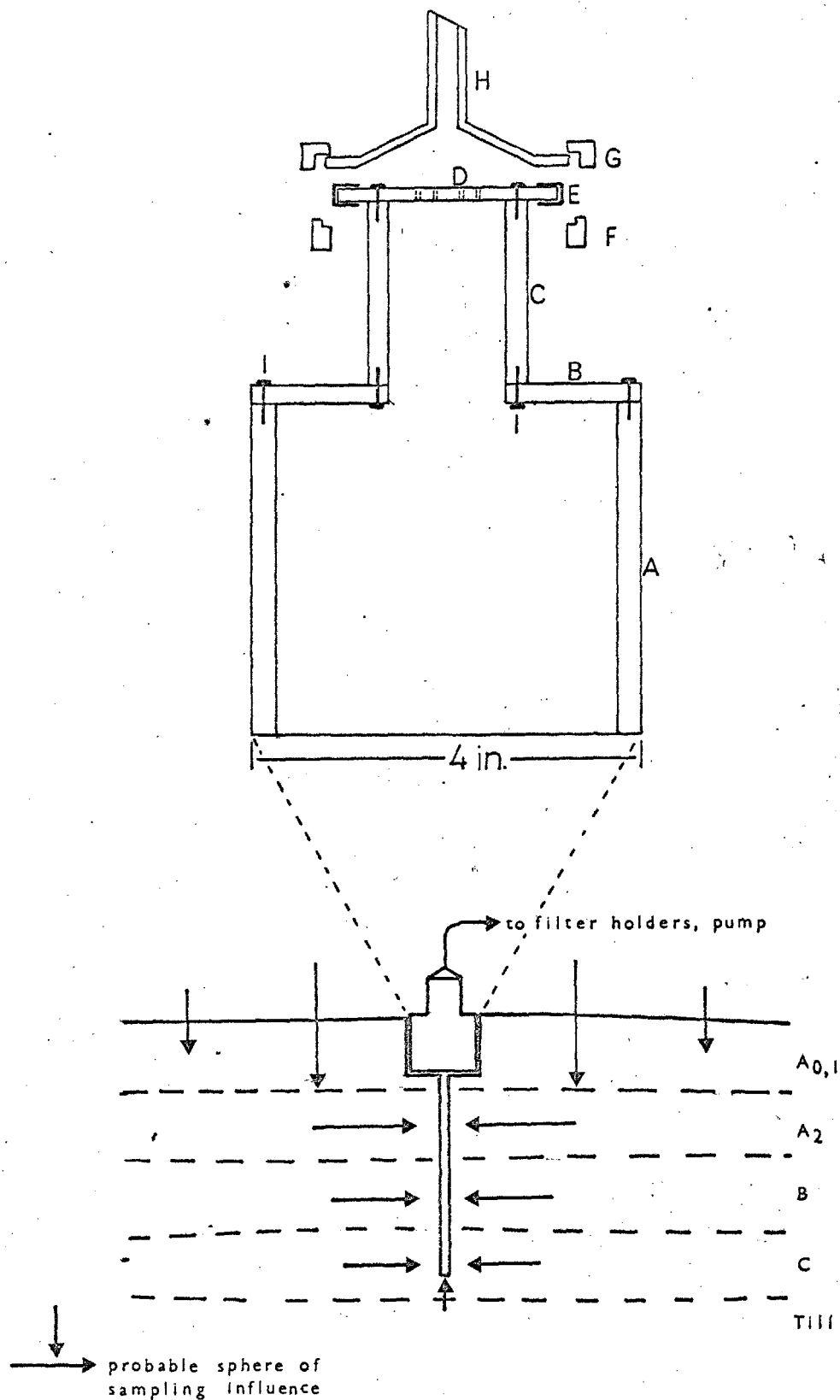
Leggo (op. cit.) discusses in detail cleaning procedures adopted for Ag gauze and has made valuable comment on analytical problems in Hg analysis.

#### 7.4.3 Soil Gas from Depth (Induced mass flow by pumping)

The techniques employed to gain access to soil air at depth and extract gases are essentially those used by Sergeev (op. cit.) modified for use with the apparatus at hand.

A four inch diameter "collar" in soil is removed to a depth of three or four inches with a post hole borer (City Timber Ltd., Brasted, Kent). Inside this collar, a vertical hole (one inch in diameter) is fashioned using the conventional soil auger to a depth of 24 inches (or deeper). The perspex hood (Fig. 42) is then positioned in the collar and pressure gently applied to produce a seal with the soil. The walls of the collar are flattened against the sides of the hood to limit atmospheric dilution of soil gas. Once in position, pumping is commenced through a closed system of Ag gauzes as described in the laboratory experiments.

The "tightness" of seal is thought to be adequate. During pumping on poorly-drained sites, ground water was occasionally observed to be "boiling" in the hood. Once, ground water was brought through the entire system and, needless to say, the apparatus had to be completely dismantled and cleaned.



| Key | Description    | Material        |
|-----|----------------|-----------------|
| ABC | Housing unit   | Perspex         |
| D   | Grid plate     |                 |
| E   | Sealing ring   | Silicone        |
| F   | Retaining ring | Stainless Steel |
| G   | Retaining ring |                 |
| H   | Funnel         |                 |
| I   | Screw          |                 |
|     |                |                 |

Fig. 42  
Sampling hood  
and field  
arrangement to  
obtain from depth  
soil gas

#### 7.4.4 Soil Gas in Near-surface Horizons (Induced mass flow by pumping)

To obtain "near-surface" soil gas, a stainless steel hood (modified from an original use as a buchner funnel) is employed (Fig. 43). The funnel bowl is placed on the ground and pressed firmly into the grass. The impression made by the rim in the turf is incisioned using a stainless steel hand trowel and the hood then forced into the soil. Soil vapours are pumped off as described above. This technique was introduced primarily to investigate volatile Hg/Hg compounds as found in the near-surface, organic-rich horizons with little disruption of soil structure or fabric. Plate 9 shows simultaneous "from depth" and "near-surface" soil gas sampling in operation.

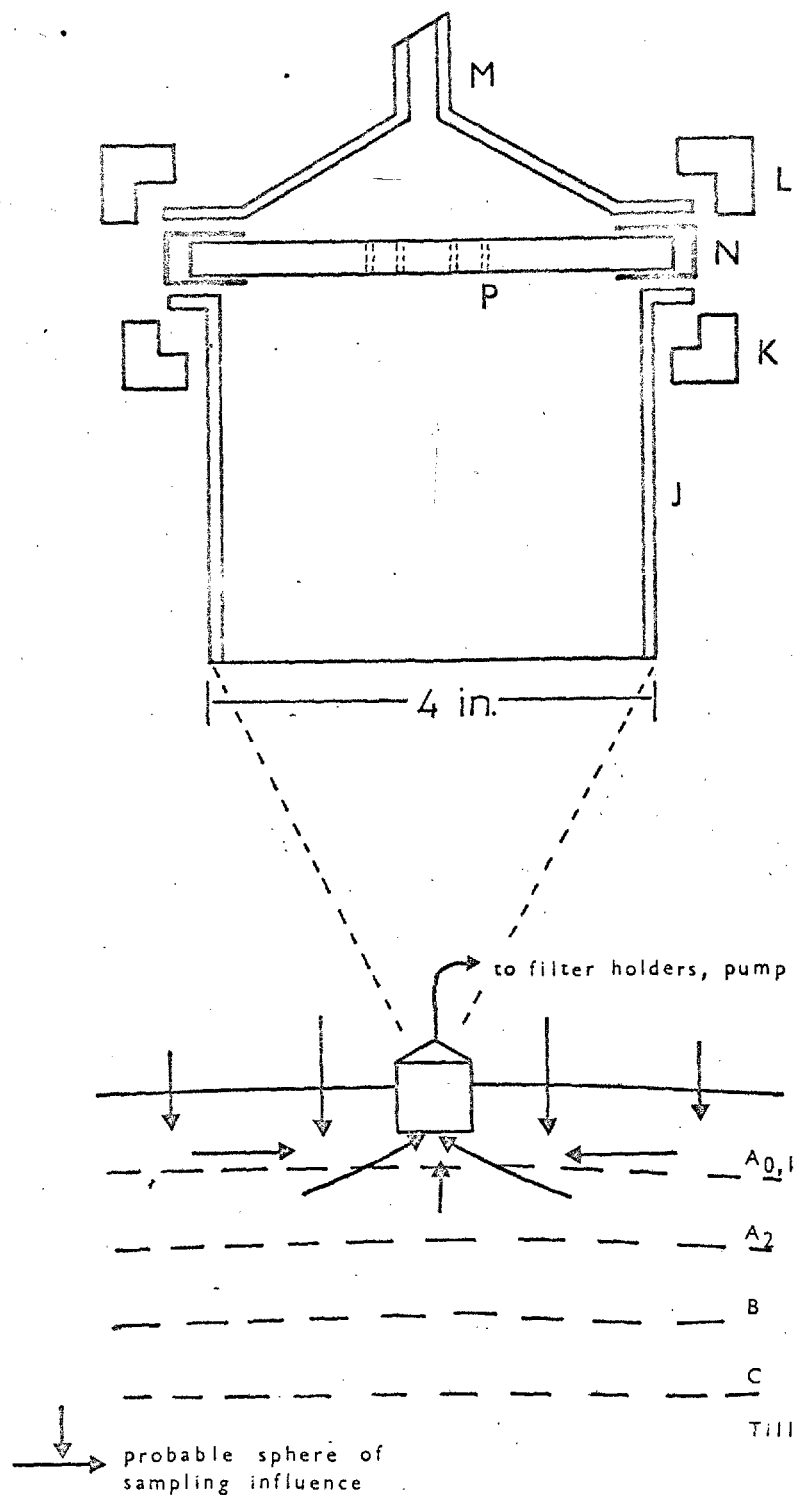
### 7.5 RESULTS AND DISCUSSION OF FIELD TESTS

#### 7.5.1 Introduction

Attempts to measure volatile Hg/Hg compounds in soil gas at Keel were made during four separate field trips (March-April, 1970; July-August, 1970; September-October, 1970; and May, 1971). The reader will appreciate that the techniques employed here were subject to modification and improvement as refinements became known or required. However, the ultimate aim of the investigation did not change, which was to determine the presence of volatile Hg/Hg compounds in soil gas in mineralized soils at Keel (see Chapter Four for soil data).

All soil gas results have been reported in  $\text{ng/m}^3$ , as is the convention with trace constituents in atmospheres. Sample collection times range from 45 to 120 minutes (normally 60 minutes) and flow rates of 2.0 and 2.5 l/m were used in all instances as laboratory work had indicated suitable collecting efficiencies were obtainable when using 60 mesh Ag gauze.

Emphasis has been placed on the measurement of soil gas as a supplemental aid to the interpretation of soil anomaly formation at



| Key | Description    | Material        |
|-----|----------------|-----------------|
| J   | Bowl           | Stainless Steel |
| K   | Retaining ring |                 |
| L   | Retaining ring |                 |
| M   | Funnel         | Silicone        |
| N   | Sealing ring   |                 |
| P   | Grid plate     |                 |
|     |                |                 |

Fig. 43  
Sampling hood  
and field  
arrangement to  
obtain near-surface  
soil gas



Plate 9 Dynamic sampling apparatus in position to obtain "near-surface" (L) and "from depth" (R) soil gas. The small unit to the left of the storage battery is an atmospheric air sampler. Scale 1:10

Keel, the possible relationship between solid, ionic, and gaseous forms of mercury in soils, and finally, on the evaluation of soil gas as a prospective mineral exploration aid in the Irish environment.

#### 7.5.2 Presentation of Soil Gas Results

Figure 44 is a mercury in soil gas and in soil traverse across the Decomposed Zone and sulphide-bearing faults at Keel collected during March, 1970. Soil gas levels of mercury (from depth only) reflect both the general soil anomaly and the accompanying Hg in soil anomaly.

Further collecting of soil gas (now using both near-surface and from depth soil gas sampling procedures) was accomplished during July-August and Sept.-Oct., 1970. These experiments centered on the moderately and strongly anomalous soil classifications (see Fig. 45) to add confirmatory results to the March results and, if possible, to observe any seasonal fluctuation of mercury in soil gas. Figure 46 and Table 42 summarize data from all 1970 soil gas samplings. Soil gas collections during May, 1971 were confined mainly to selected experiments (see section 7.5.3).

The level of mercury in soil gas (as collected by 60 mesh Ag gauze) may exhibit some seasonal variation (Fig. 46). The Sept.-Oct. levels of mercury in soil gas are much lower than the March-April and July-August levels. This is substantiated by data from Table 42 which shows that similar range and mean levels of mercury in soil were encountered in the July-August and in the Sept.-Oct. samplings. The differences in soil gas levels may well represent a seasonal influence on mercury outgassing from soils.

Results from Table 42 also suggest the levels of Hg in "from depth" soil gas are slightly higher than Hg in soil gas from "near-surface". This is in some conflict with the previously discussed soil profile investigations (Chapter Four) as mercury is known to

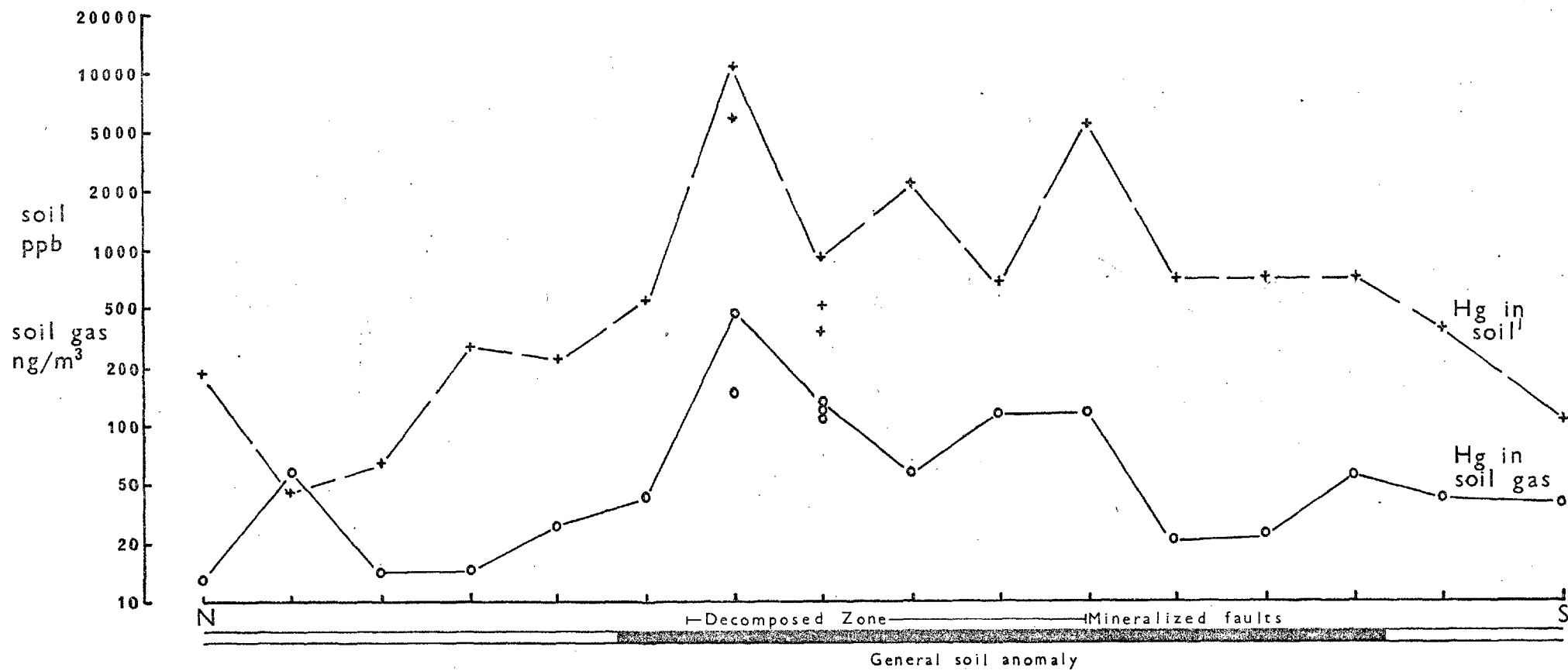
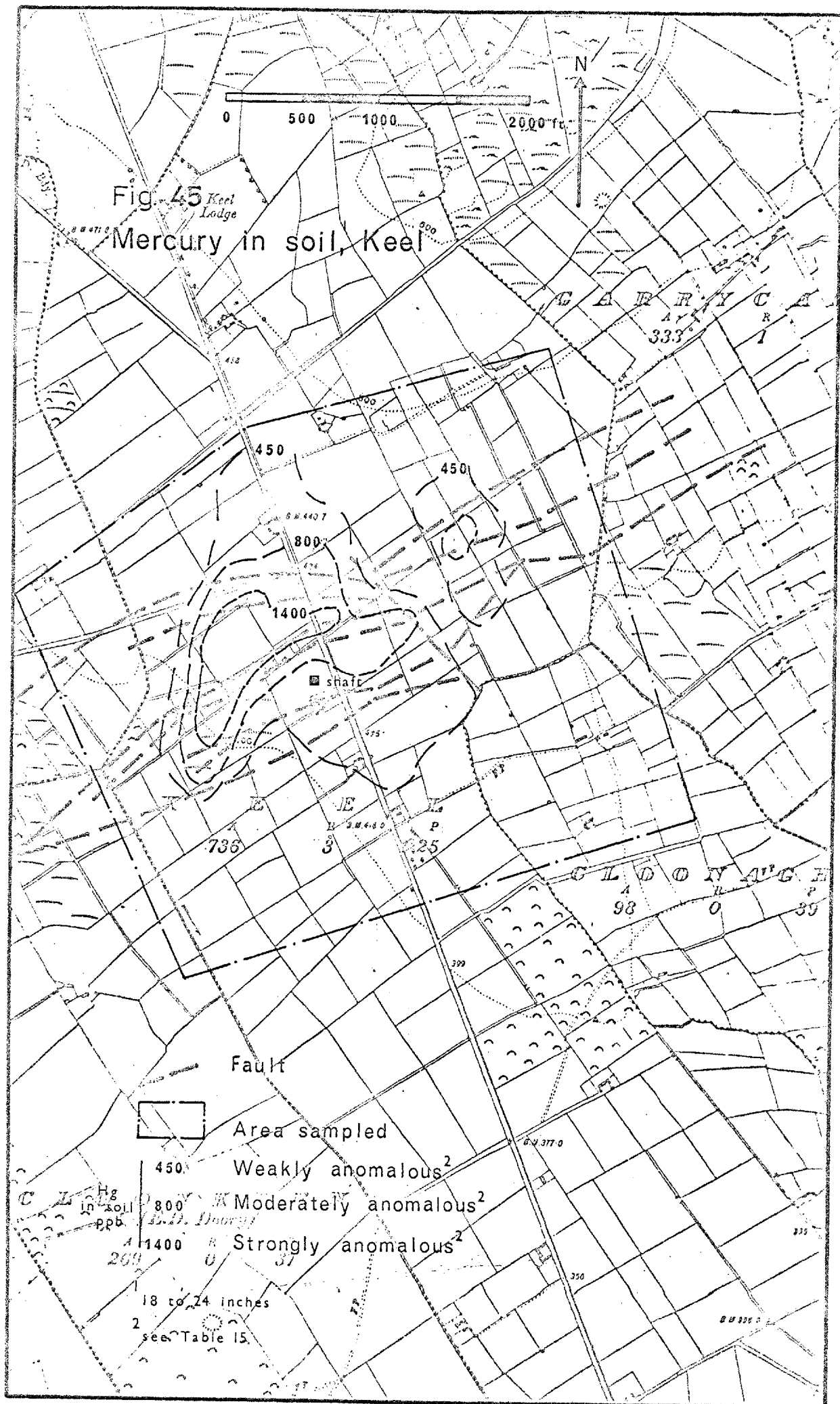


Fig. 44 Mercury in soil gas  
at Keel, March, 1970

<sup>1</sup> 18 to 24 in.





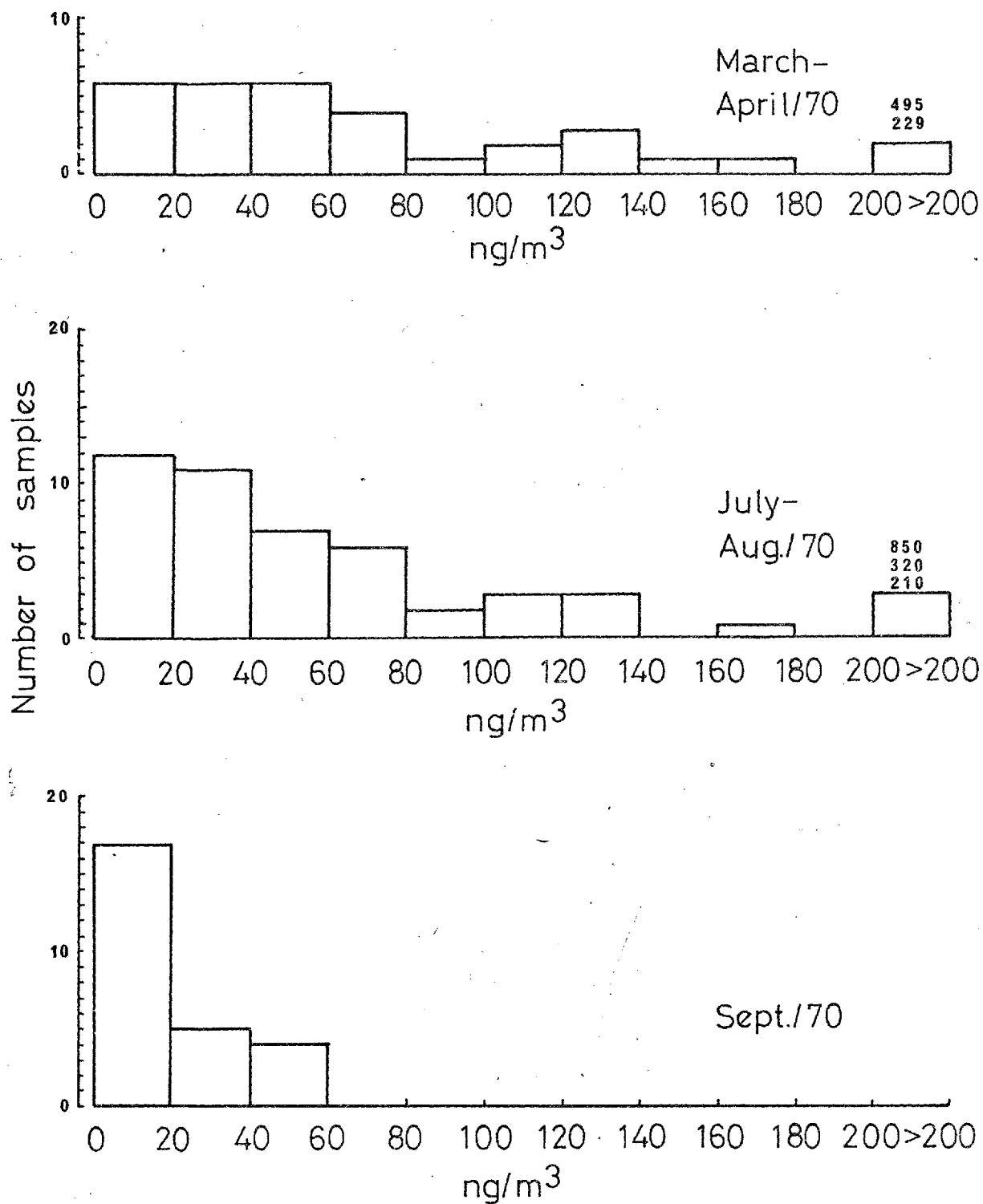


Fig.46 Mercury in soil gas at Keel, all results, 1970

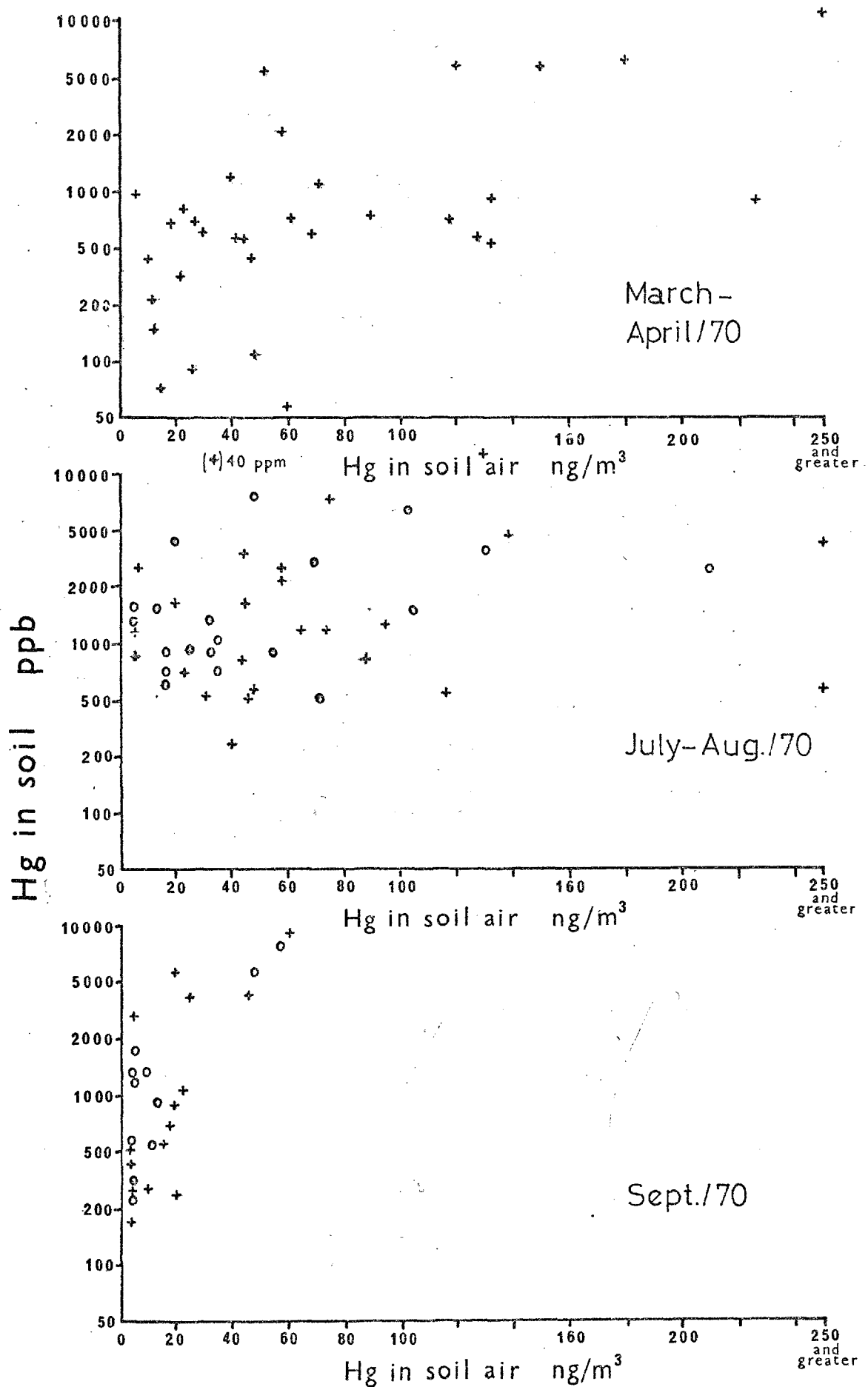


Fig. 47 Relationship between mercury in soil air and mercury in soil at Keel

+ From depth soil air, soil at 18 to 24 in.

o Near-surface soil air, soil at 4 in.

Table 42. Summarized results on mercury in soil and soil gas, 1970 investigations

| Date of Field Trip |                        | Mercury in soil gas <sup>1</sup><br>(ng/m <sup>3</sup> ) |            | Mercury in soil <sup>2</sup><br>(ppb) |                        |
|--------------------|------------------------|----------------------------------------------------------|------------|---------------------------------------|------------------------|
|                    |                        | Near-surface                                             | From depth | 4 inches                              | 18-24 inches           |
| March-April, 1970  | No. of Samples         | -                                                        | 30         | 30                                    | 30                     |
|                    | Range                  | -                                                        | <10-180    | 130-6850                              | 46-11000               |
|                    | Mean                   | -                                                        | 62         | 1110                                  | 1355                   |
|                    | Threshold <sup>3</sup> | -                                                        | 124        | N.C. <sup>4</sup>                     | N.C.                   |
| July-August, 1970  | No. of Samples         | 19                                                       | 26         | 24                                    | 23                     |
|                    | Range                  | <10-130                                                  | <10-175    | 500-7320                              | 236-12200 <sup>5</sup> |
|                    | Mean                   | 44                                                       | 58         | 2100                                  | 2190                   |
|                    | Threshold              | 88                                                       | 116        | N.C.                                  | N.C.                   |
| Sept.-Oct., 1970   | No. of Samples         | 11                                                       | 15         | 12                                    | 18                     |
|                    | Range                  | <5-57                                                    | <5-60      | 290-7800                              | 260-8800               |
|                    | Mean                   | 14                                                       | 18         | 2013                                  | 1937                   |
|                    | Threshold              | 28                                                       | 36         | N.C.                                  | N.C.                   |

<sup>1</sup> Soil gas measurements > 200 ng/m<sup>3</sup> omitted

<sup>2</sup> Includes all soil determinations

<sup>3</sup> Anomaly threshold = 2 x arithmetic mean of soil gas measurements ≤ 200 ng/m<sup>3</sup>

<sup>4</sup> Thresholds Not Calculated, class limits defined otherwise (see Fig. 45)

<sup>5</sup> One determination (40 ppm) not included

accumulate in the  $A_0$  and  $A_1$  horizons, particularly in poorly-drained areas. Discussion on the possible generation mechanisms of mercury vapour and volatile Hg-containing compounds in the soil profile at Keel is commented on later in this chapter.

Table 43 summarizes data on the anomalous soil gas sites and corresponding levels of mercury found in soil at two depths. A provisional threshold for anomalous mercury in soil gas was arbitrarily established as two times the arithmetic mean of all results except those highly anomalous values (greater than  $200 \text{ ng/m}^3$ ). The soil results corresponding to anomalous soil gas sites have also been averaged and then ratioed against means calculated for all soil results (Table 42). In each instance, anomaly relief ratios (Table 43) are greater than unity suggesting that the soil gas levels of mercury are somewhat dependent on soil levels of mercury.

To date, the only other results available to the writer on the presence of mercury in soil gas over Pb-Zn occurrences are those found in Table 28 of U.S.G.S. Professional Paper 713 (see Table 31 in Chapter Six). Here, ground measurements (40 in number) disclosed a maximum mercury concentration in air of  $68 \text{ ng/m}^3$  over soils in the Coeur d'Alene mining district, Wallace, Idaho. It should be noted that this value is not a true comparison with the Keel soil gas results as Crosby (1968) has indicated that the technique employed to collect soil air was that of McCarthy *et al.* (1969) and thus represents "soil respired Hg" rather than actual "Hg in soil gas".

No results are given by McCarthy *et al.* (1970) on any accompanying soil analyses to the soil gas studies in Idaho, but the investigation by Crosby on primary halos indicates that mercury levels in Pb-Zn ores, altered products, and brecciated rock of the Coeur d'Alene mining district are somewhat lower than similarly

Table 43. Anomalous soil gas sites and corresponding levels of mercury in soil, 1970 investigations

| Date of field trip |                              | Mercury in soil gas <sup>1</sup><br>(ng/m <sup>3</sup> ) |                     | Mercury in soil <sup>2</sup><br>(ppb) |              |
|--------------------|------------------------------|----------------------------------------------------------|---------------------|---------------------------------------|--------------|
|                    |                              | Near-surface                                             | From depth          | 4 inches                              | 18-24 inches |
| March-             | No. of samples               | -                                                        | 8                   | 8                                     | 8            |
| April,             | Range                        | -                                                        | 124-495             | 680-6850                              | 560-11000    |
| 1970               | Mean                         | -                                                        | 197                 | 3195                                  | 4050         |
|                    | Anomaly relief ratio (soils) | -                                                        | N.C.                | 2.8                                   | 3.0          |
| July-              | No. of samples               | 6                                                        | 8                   | 8                                     | 7            |
| Aug.,              | Range                        | 24-210 <sup>3</sup>                                      | 74-850 <sup>3</sup> | 940-7000                              | 540-12200    |
| 1970               | Mean                         | 108                                                      | 246                 | 3205                                  | 4460         |
|                    | Anomaly relief ratio (soils) | N.C.                                                     | N.C.                | 1.5                                   | 2.0          |
| Sept.-             | No. of samples               | 2                                                        | 3                   | 2                                     | 3            |
| Oct.               | Range                        | 47-57                                                    | 20-60 <sup>3</sup>  | 6200-7800                             | 4900-8800    |
| 1970               | Mean                         | 52                                                       | 42                  | 7000                                  | 6635         |
|                    | Anomaly relief ratio (soils) | N.C.                                                     | N.C.                | 3.5                                   | 3.4          |

<sup>1</sup> Soil gas results > Threshold (Table 42)

<sup>2</sup> Mercury in soil values corresponding to anomalous soil gas results

<sup>3</sup> Includes one result less than the threshold value. Designated as anomalous from a comparative experiment(s).

Anomaly relief ratio (soils) =  $\frac{\text{Mean of anomalous sites}}{\text{Mean of all sites (Table 42)}}$

N.C. = Not Calculated

occurring products at Keel.

### 7.5.3 Additional Experiments

During the course of collecting soil gas for mercury determination, several selected experiments were attempted to provide ancillary information on both the analytical procedures employed and the gaseous (bio)geochemistry of mercury.

#### 7.5.3.1 The effect of water vapour on the collecting efficiency of Ag gauze

It is easily appreciated that other volatile substances may be present in soil gas that could adversely affect the amalgamation of Hg vapour/volatile Hg compounds with Ag gauze. The potential influence of some sulphur gases has already been noted. However, the most latent interference when collecting Hg from soil gas would appear to be water vapour. Condensation has been observed inside hoods during and after sampling.

Following a method employed by Rathje (1969) to separate mercury vapour from water vapour, a short bed of dessicant (anhydrous  $\text{MgClO}_4$ ) was positioned after the hood attachment and before the Ag gauze. The results of test pumpings are presented in Table 44 and suggest water vapour may have a profound effect on inactivating Ag gauze. However, the writer believes that these results may reflect contamination from the  $\text{MgClO}_4$  (analysis indicates about 200 ppb in Analar reagent) and not a separation of water vapour from anomalous soil gas. Further research is required to establish this claim and, also, the influence of water vapour on the amalgamation process.

#### 7.5.3.2 Consecutive pumping tests

The total amount of Hg vapour/volatile Hg compounds in soil gas at any one site may be limited by equilibria with naturally-occurring compounds and/or ionic or sorbed species of the element. It is also

Table 44. The possible effect of water vapour on the amalgamation of mercury vapour and/or mercury-containing compounds with 60 mesh silver gauze

| Test site                       | Experimental procedure <sup>1</sup> | Mercury in soil gas (ng/m <sup>3</sup> ) |            | Mercury in soil (ppb) |            |
|---------------------------------|-------------------------------------|------------------------------------------|------------|-----------------------|------------|
|                                 |                                     | Near-surface                             | From depth | 4 in.                 | 18-24 inc. |
| Anomalous peaty, gleysolic soil | 1st pumping                         | 90                                       | <10        | 4200                  | 1140       |
|                                 | 2nd pumping                         | 2550*                                    | 75         |                       |            |
|                                 | 3rd pumping                         | 1680*                                    | 40         |                       |            |
|                                 | 4th pumping                         | 550*                                     | <10        |                       |            |
| Anomalous basin peat            | 1st pumping                         | 120                                      | 4400*      | 448                   | 328        |
|                                 | 2nd pumping                         | 85                                       | <10*       |                       |            |
|                                 | 3rd pumping                         | 30                                       | 130*       |                       |            |
| Anomalous peaty, gleysolic soil | 1st pumping                         | -                                        | 795*       | 6400                  | 3900       |
|                                 | 2nd pumping                         | -                                        | 230*       |                       |            |

<sup>1</sup> Consecutive soil gas sampling from same site preparation ( 2 and 2.5 l/m for 60 or 90 minutes)

\* Determinations of mercury in soil gas collected by 60 mesh Ag gauze after water vapour has been removed by anhydrous MgClO<sub>4</sub>. The comparative results were obtained by normal sampling procedures.



possible that a reservoir of volatile Hg in soil gas (again in equilibrium with Hg-rich soils and/or a sub-till source) may be available and constitute a "mercury-table" that is drawn upon during soil pumping.

Consecutive pumping at the same sites (Table 45) suggests that the amount of volatile Hg in soil gas at any one site may be limited, but no real conclusions can be drawn. It is postulated that complex soil/soil gas equilibria exist in soils at Keel. Considerable time may be required to produce more Hg-containing volatiles.

#### 7.5.3.3 Bacterial evolution of Hg vapour/volatile Hg compounds

Barber et al. (op. cit.) have reported on mercury volatilization from bacterial cultures. Suspensions of Pseudomonas fluorescens were treated with mercuric chloride solution and then killed with a commercial disinfectant (Dettol). Atmospheres above the suspension were pumped off through CdS-impregnated fibre glass filter pads or Ag gauze filters and in each instance raised levels of mercury were recorded against similarly treated controls. This stimulation of mercury was also detected with cultures of a bacterium isolated from a high mercury-containing soil from Keel.

The writer has attempted similar "in-situ" experiments at anomalous field sites. Soils at pumping sites were pre-treated with a 30% Dettol solution and soil gases collected in the normal manner. No positive stimulation of mercury was detected in these tests. The writer regards this approach to be a worthy avenue of research that could eventually yield rewarding information on the microbial biogeochemistry of mercury.

#### 7.5.3.4 Pyrolysis of soil gas vapours

The possibility that naturally-occurring volatile compounds of mercury pumped from Keel soils were not collected by 60 mesh Ag gauze at the temperature range encountered in the field (2 to 15°C) has been

Table 45. Results of consecutive pumping experiments

| Date of field trip | Mercury in soil gas, from depth (ng/m <sup>3</sup> ) |                             | Mercury in soil (ppb) |           |
|--------------------|------------------------------------------------------|-----------------------------|-----------------------|-----------|
|                    | First pumping <sup>1</sup>                           | Second pumping <sup>1</sup> | 4 in.                 | 18-24 in. |
| March-April, 1970  | 128                                                  | 127                         | 700                   | 610       |
|                    | 132                                                  | 63                          | 1020                  | 910       |
|                    | 153                                                  | 103                         | 5700                  | 6200      |
|                    | 27                                                   | 24                          | 560                   | 730       |
| July-August, 1970. | 850                                                  | 355, 315 <sup>2</sup>       | 4520                  | 3720      |
|                    | 74                                                   | 63                          | 1080                  | 1100      |
|                    | 43                                                   | 37                          | -                     | 3350      |
|                    | (20) <sup>3</sup>                                    | (13) <sup>3</sup>           |                       |           |
|                    | 43                                                   | 37                          | 3840                  | 1700      |
|                    | <10                                                  | <10                         | 4000                  | 2800      |
|                    | 25                                                   | <10                         | 4000                  | 2800      |
|                    | 59                                                   | 89                          | 1560                  | 2300      |

<sup>1</sup> 2.5 and 2 l/m for 60 or 90 minutes

<sup>2</sup> Third pumping

<sup>3</sup> Near-surface soil gas measurements

investigated by pre-pyrolyzing soil vapours before contact with Ag filters. Hopefully, a thermal breakdown of natural volatiles would allow mercury vapour amalgamation to proceed normally.

A 24 Watt heater (simply a three foot winding of nichrome wire about a section of pyrex tubing supplied with a current from a conventional 12 V DC battery) was positioned after the hood and before the Ag filters. The results are presented in Table 46 and show some improvement on the amount of mercury collected. There would seem room for improvement on pyrolyzing soil vapours (perhaps differential heating experiments) and additional research could prove useful.

#### 7.5.3.5 Mercury in atmospheric air at Keel

Several attempts were made to measure Hg in atmospheric air at Keel. All results showed levels of less than  $10 \text{ ng/m}^3$ , even over the small pile of mineralized waste rock.

Although the results were totally negative, the writer believes that the technique employed here is not a suitable one to properly monitor atmospheric air for Hg vapour. Barren winds and breezes probably dilute any atmospheric halo below the detection limit of the test. It is also possible that any atmospheric anomaly could be defined in a range below  $10 \text{ ng/m}^3$ . Direct-reading of atmospheric air mercury levels would seem required here to determine the presence of an air halo.

#### 7.5.4 Meteorological Considerations on the Presence of Mercury in Soil Gas at Keel

The Irish climate is most unpredictable. Unsettled periods of weather may occur at any time of the year. Figures 48 and 49 show mean monthly temperature ranges and mean monthly rainfall over a 30-year period at Newtown Forbes, Co. Longford, the closest recording station to Keel. Temperature and rainfall are seasonally cyclic and indicate that the months of March through July to be the best part of the year for

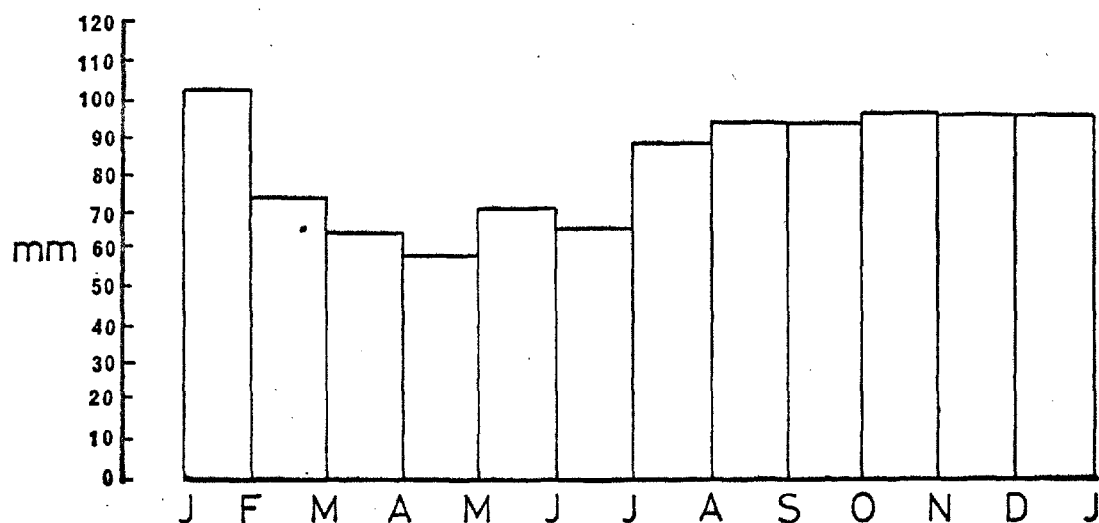


Fig. 48 Mean monthly rainfall at Newtown Forbes,<sup>1</sup> Co. Longford for the period 1916-1950

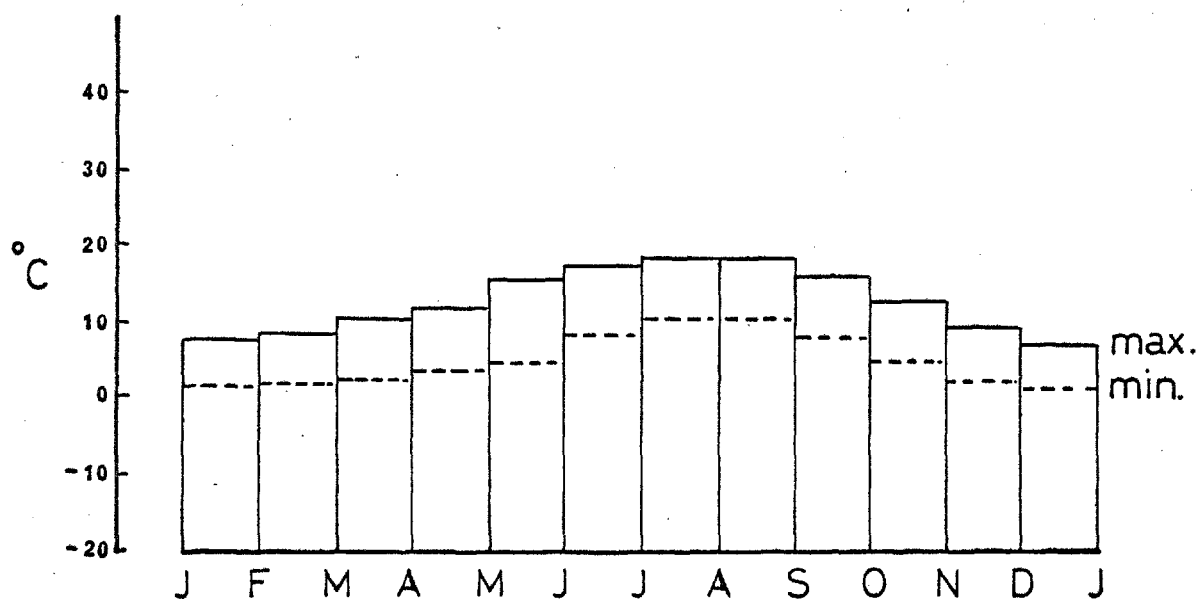


Fig. 49 Mean monthly temperature ranges at Newtown Forbes,<sup>1</sup> Co. Longford for the period 1916-1950

<sup>1</sup> 146 ft. msl, Keel at 400 ft. msl

Table 46. Results of pyrolysis experiments

| Date of field trip | Mercury in soil gas, from depth (ng/m <sup>3</sup> )   |                                   | Mercury in soil (ppb) |        |
|--------------------|--------------------------------------------------------|-----------------------------------|-----------------------|--------|
|                    | Pyrolyzed vapours <sup>1</sup>                         | Control <sup>2</sup>              | 4"                    | 18-24" |
| May, 1971          | 130                                                    | < 10                              | 4200                  | 1140   |
|                    | 370                                                    | 10                                | 900                   | 680    |
|                    | 120                                                    | < 10                              | 1680                  | 960    |
|                    | < 10                                                   | < 10                              | 25600                 | 20000  |
|                    | 150                                                    | 140                               | 130                   | 116    |
|                    | 380                                                    | 440                               | 900                   | 2050   |
|                    | 420                                                    | 195                               | 940                   | 3800   |
|                    | 60                                                     | < 10                              | 9600                  | 480    |
|                    | 70                                                     | 25                                | 1860                  | 5560   |
|                    | Mercury in soil gas, near-surface (ng/m <sup>3</sup> ) |                                   | Mercury in soil (ppb) |        |
|                    | Pyrolyzed vapours <sup>1</sup>                         | Control <sup>2</sup> (from depth) | 4"                    | 18-24" |
|                    | 25                                                     | < 10                              | 620                   | 3360   |
|                    | 250                                                    | 70                                | 620                   | 3360   |
|                    | 160                                                    | < 10                              | 1520                  | 2060   |
|                    | 250                                                    | 195                               | 1940                  | 6400   |

<sup>1</sup> at 24 watts<sup>2</sup> soil gas collected in the normal manner

soil gas sampling. A recording barograph and thermograph have been employed to gather additional basic meteorological information during soil gas sampling at Keel.

McCarthy et al. (1969) are of the opinion that mercury vapour release from soils may be dependent on diurnal variations in barometric pressure and have shown some evidence in support of their claim. Further, McCarthy et al. (1970) state "the daily content of Hg in air (atmospheric air) is a function of the diurnal change in barometric pressure resulting in the exhalation of Hg through the earth's 'breathing process'. The effect of temperature is less obvious; the maximum daily temperature commonly occurs 2-4 hours later than the time when maximum mercury is found in air."

Currie (1970) says that soil gases (here referring mainly to oxygen and carbon dioxide) respond to barometric pressure and soil respiration is a common occurrence. Respiration rates show a ten-fold seasonal change, mainly associated with soil temperature. Further, Currie states that rain can act as a piston and drive air into soil and induce mass flow. Wind may also cause mass flow in soil.

Magos (1966) reports that temperature is a more important factor than air pressure when considering vapour pressure and volatilization of metallic mercury. A. R. Barringer (pers. comm.) reports from findings in Australia that the ambient air temperature appears to be a major factor influencing mercury vapour evolution from a sulphide occurrence.

At Keel, barograph recordings showed little more than daily to weekly fluctuations, probably reflecting advancing weather fronts from over the Atlantic Ocean. Diurnal variations in air pressure related to daily temperature changes were rarely observed.

Other than the broad seasonal pattern exhibited by mercury soil gas levels (Sept.-Oct. levels much less than March-April and July-August results) there would seem to be little evidence that barometric

pressure or temperature changes influence the presence of Hg vapour/volatile Hg compounds in soil gases at Keel. On this basis, the writer is of the opinion that gaseous diffusion (opposed to mass flow which occurs only in response to external stimuli) is a more important aspect of any soil gas movement at Keel.

#### 7.5.5 Physical, Hydrological, and Chemical Considerations on the Presence of Mercury in Soil Gas at Keel

As meteorological controls on the presence of Hg in soil gas at Keel are somewhat inconclusive, physical, hydrological, and chemical controls would appear to be appropriate for comment on the generation of volatile Hg/Hg-containing compounds.

In Chapter Four, mercury distribution in soils at Keel was shown to differ from freely-drained to poorly-drained sites to peats. It has been postulated that the gaseous movement of Hg in unconsolidated overburden at Keel is independent of air pressure and temperature controls. It is proposed that the distribution and accumulation and/or depletion of Hg in soil gas at Keel must be dependent on certain physio-chemical conditions.

Physical conditions for movement of gaseous mercury from sub-till sources at Keel would seem relatively unfavourable. The clay-rich and highly compacted drift may effectively block Hg vapour movement. Currie (op. cit.) has demonstrated how diffusion of gases in various soil and artificial matrices is affected by the shape and size of material. Figure 50 (after Currie, op. cit.) shows that plate-like micas are not a conducive environment for gaseous movement.

Certain hydrological factors (i.e. water-table depth and ground water composition) are other important features when considering gaseous dispersion of mercury from depth. Williston (1962) states that mercury vapour has the ability to migrate through a layer of water and A. R. Barringer (pers. comm.) has confirmed this from unpublished work.

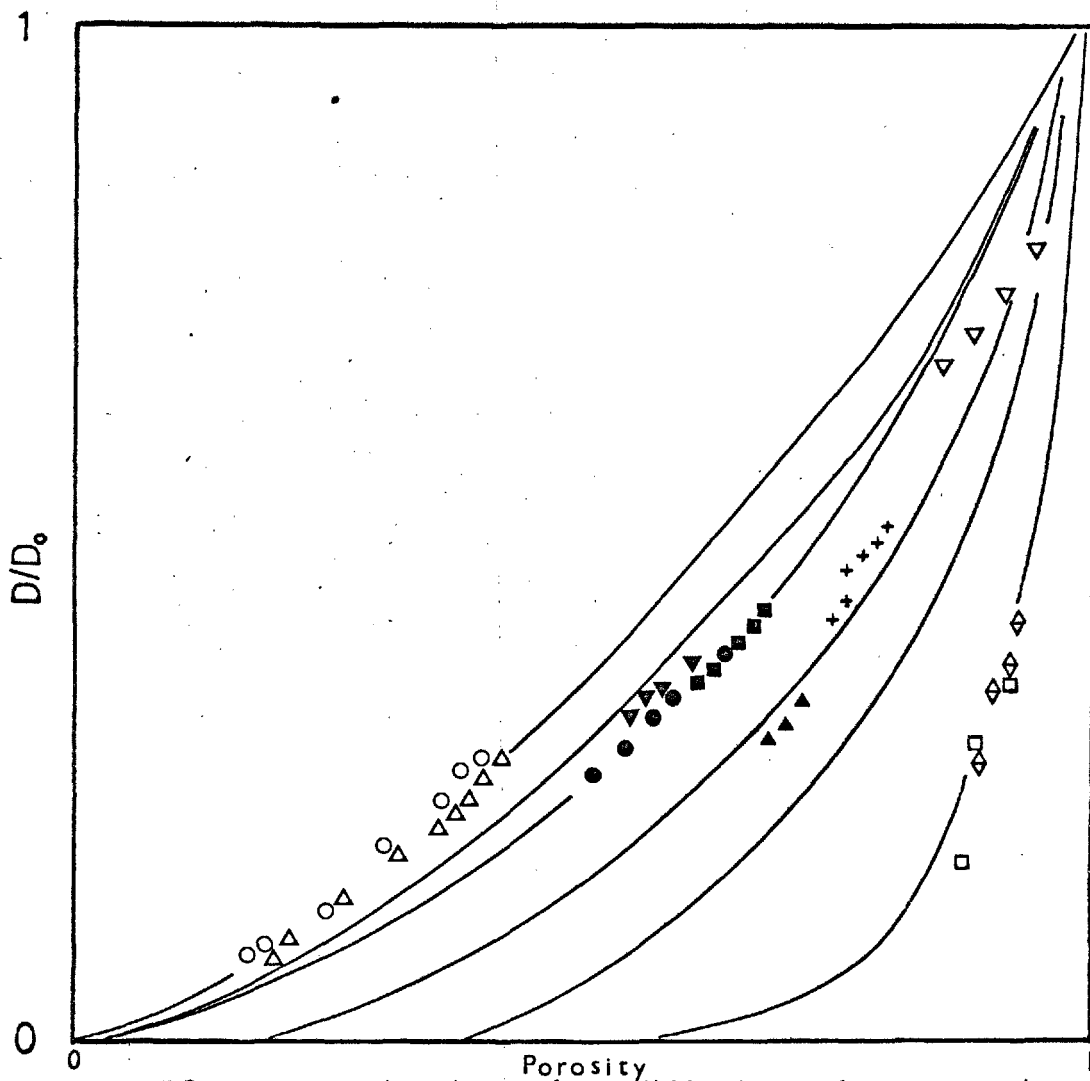


Fig. 50 Measured values for diffusion of gases through dry granular materials with a family of curves from the theoretical relationship  $D/D_0 = e^m$  for various values of  $m$

$e$  = Porosity  
 $D/D_0$  = Diffusion ratio

$m = 1.5$  ○ glass beads △ sand  
 $m = 2$  ● ▼ ■ soil crumbs  
 $m = 3$  ▲ pumice + kaolin  
 ▼ diatomaceous earth  
 $m = 10$  ◇ vermiculite □ mica



Metallic mercury is regarded as virtually insoluble in water, but some inconsistencies are revealed when attempts are made to measure its solubility (Wallace *et al.*, *op. cit.*). At room temperature in deaerated water its solubility is 20-30 ppm; at the same temperature but with water saturated with oxygen, it is around 40,000 ppm. The increase is thought to be oxidation to mercuric oxide, with subsequent hydrolysis to the relatively soluble mercuric hydroxide. From this, it would seem possible that mercury could enter into metal-ionic-gaseous equilibria reactions to complete dispersion through a layer of water or water-saturated unconsolidated overburden.

Other chemical factors (including geochemical and biochemical mechanisms) may be important in controlling mercury levels in soil air. At Keel, mercury soil anomalies correlate well with those of Pb and Ag at most sites and all elements show a preference to accumulate in the near-surface horizons of peaty gleys. This feature suggests the enrichment of Hg through ionic and/or complex movement as Ag and Pb both have extremely low vapour pressures and gaseous migration of these two metals seems unlikely. The writer ascribes to "Goldschmidt enrichment" of Hg-Pb-Ag through seasonal retention by pasture grasses and subsequent accumulation and fixing by humic and fulvic acids. Once mercury has accumulated in the near-surface horizons, equilibria are established between gaseous forms and naturally-occurring inorganic and organo-metallic compounds. Some vapours are lost through gaseous diffusion to the atmosphere. Equilibrium is maintained (to produce more volatiles of mercury) and biogeochemical enrichment ensures continued metal accumulation in the near-surface horizons from sources in till.

The presence of naturally-occurring gaseous organo-metallics of mercury in soils at Keel has not been directly established. However, the low-temperature pyrolyzing of soil vapours has improved levels of mercury detected at anomalous sites and is considered an encouraging

sign of biochemically generated and released volatile Hg-containing organo-metallies.

The nature of mercury has been determined in the clay-rich horizon immediately underlying the organic-rich  $A_0$  and  $A_1$  horizons of an anomalous, peaty, gleyed, and podzolized soil profile (see Table 18). Using a continuous heating technique (monitored with a thermocouple) and plasma emission spectroscopy analysis, mercury vapour release was identified to peak at  $200^{\circ}\text{C}$ . This peak corresponds to the temperature at which a  $\text{HgCl}_2$  standard thermally decomposes to Hg vapour.

Mercuric chloride is a relatively powerful oxidizing agent, and can be reduced by many organic materials. Numerous such reducing compounds would be present in normal soils.

Frear and Dills (op. cit.) have investigated the insecticidal action of mercuric chloride and mercurous chloride and have established several facts concerning the chemical behaviour of mercury salts when mixed with soil. In all their experiments they reported that Hg salts, whether in the mercuric or mercurous state, are readily reduced under favourable conditions to metallic Hg. In addition, several factors were found to affect reduction of mercury salts to metallic Hg.

Briefly, these were:

- i) The presence of organic matter in soil is required. Without soil organic matter the reduction of mercury salts proceeds slowly, if at all.
- ii) The reduction requires moisture, and is thus presumably effected in an aqueous medium.
- iii) The reduction proceeds more rapidly as the soil pH is increased.

At pH 5.25 the reduction of mercuric chloride was negligible whereas at pH 6.4 there was considerable reduction. Hydroxides of Na and Ca were used to adjust the soil pH, and were of equal effect on the reduction of mercury salts.

iv) Like other chemical reactions, the speed of reduction of mercury salts in soil increased with increases in the temperature. Below 25°C the reduction reaction proceeded at a relatively slow rate.

At Keel, the presence of soil organic matter, ample moisture, a slightly acid pH, and relatively suitable temperature controls appear favourable for the reduction of  $\text{HgCl}_2$  to metallic Hg.

The possibility of naturally-occurring volatile organo-metallics of mercury in soils at Keel cannot be dismissed lightly. Kimura and Miller (1964) state that metallic mercury vapour and volatile ethyl and methyl organo-metallics of Hg are present in air surrounding soils treated with organomercury fungicides. Naturally-occurring volatile organo-metallic compounds of mercury may be similarly generated. Recently, Imura *et al.* (1971) have shown that mercuric chloride can be chemically methylated to dimethylmercury with methylcobalamin (a vitamin  $\text{B}_{12}$  analog). Also, dimethylmercury may be converted into methylmercuric chloride (also a volatile) by further reactions with mercuric chloride.

## 7.6 SUMMARY

Important findings from laboratory experiments and soil gas investigations at Keel have been summarized here.

The application of mercury pathfinding to mineral exploration is believed to be aided by gaseous dispersion of the element in both the primary and secondary environment. This aspect of mercury geochemistry is often referred to by applied investigators as an important dispersion mechanism; but, little direct measurement has been reported in the geological literature. However, studies by Sergeev (1961), McCarthy *et al.* (1969), McCarthy *et al.* (1970), and the direct-reading of atmospheric mercury anomalies by Barringer Research Ltd., Canada have recorded gaseous halos of Hg in soil gas and/or in atmospheric air in the

vicinity of mineralized occurrences.

Laboratory experiments by the writer using a dynamic sampling system and noble metal (60 mesh Ag gauze) amalgamation of mercury vapour has indicated good collecting efficiency and reproducibility can be obtained on laboratory atmospheres when using low air flow rates.

Collecting mercury from soil gas at Keel employing a dynamic sampling technique (possibly similar to that originally used by Sergeev, *op. cit.*) has been successful and some anomalous soil gas levels of Hg have been recorded.

Soil gas levels of mercury appear to be dependent on the soil levels of Hg. Thus, air anomalies at Keel do not necessarily represent actively oxidizing sulphides at depth (see Chapter Four on soil anomaly formation). The form of the mercury in soil gas has not been directly determined but indirect evidence suggests the presence of Hg vapour, perhaps organo-metallic vapours (biochemically generated?), and possibly inorganic vapours ( $\text{HgCl}_2$  has a slight vapour pressure) in mineralized soils at Keel.

Meteorological controls on the presence or absence of Hg in soil gas seem less important in Ireland than in the Western United States where McCarthy *et al.* (1969 and 1970) have produced evidence strongly supporting mass flow of Hg vapour during "soil respiration" processes at reduced air pressures. Physical, hydrological, and (bio)(geo)chemical conditions and considerations are commented on and concluded as being relatively more important environmental influences contributing to solid-ionic-gaseous mercury equilibria in anomalous soils at Keel. Mercury vapour and Hg-containing volatiles are thought to be released to the atmosphere by gaseous diffusion.

The soil gas collection methods and techniques employed by the writer would seem cumbersome and, more important, inappropriate for use in mineral exploration in the Longford district as soils suitably define

anomalous areas. Productivity of soil gas sampling was poor (four sites/day/man) and considerable analytical expertise was required to obtain results. Direct-reading of mercury in soil gas (perhaps linking the writer's soil gas attachments to the high sensitivity (one ng/m<sup>3</sup>) mercury spectrometers as employed by Barringer Research Ltd., Canada) presents a better opportunity for prospecting. The definition of anomalous levels of mercury in atmospheric air may provide useful data for the regional approach to mineral exploration (notwithstanding the present situation regarding mercury pollution in the environment).

The writer's method of collecting and determining mercury may be of some use to those investigating Hg pollution in industrial atmospheres.

## CHAPTER 8

### CONCLUSIONS AND RECOMMENDATIONS - PART B

#### 8.1 GENERAL

Like Chapter Five, Chapter Eight is a concluding summary with accompanying suggestions for continued applied and research investigations. The subject matter referred to here is that contained in Chapters Six and Seven. Discussion and comment is not entirely divorced from the previous conclusions and recommendations, but emphasis has been placed on the writer's findings regarding the usefulness of Hg pathfinding in mineral exploration. Particular reference is made to the gaseous migration of the element and related analytical aspects. Some comment is made on the secondary dispersion of Hg at large.

#### 8.2 CONCLUSIONS

i) A dynamic sampling technique has been developed to determine Hg in laboratory atmospheres. Sixty mesh silver gauze is employed to amalgamate Hg vapour and/or Hg-containing compounds and dusts. The selective nature of 60 mesh silver gauze for Hg has not been investigated, but interferences are thought to be limited to some sulphur-containing gases. Control experiments indicate that a low air flow rate (2.5 l/m or less) is required to obtain reproducible results.

ii) The application of dynamic sampling and 60 mesh Ag gauze amalgamation to the collection of Hg from soil gas vapours using specially designed and modified attachments and storage battery-powered vacuum pumps has also proved successful. "Near-surface" and "at depth" soil gas Hg has been collected.

iii) The content of Hg vapour/Hg-containing compounds in soil gases from soils covering the range 150 to 40,000 ppb Hg exhibits a somewhat erratic relationship. Only after "statistically" treating all the data (averaging and ratioing) has the influence of the level of Hg in soil been demonstrated to broadly correlate with Hg soil gas levels. Simply stated, an anomalous Hg-containing soil does not ensure the accompanying presence of anomalous soil gas concentrations of Hg using the methods and techniques applied by the writer.

iv) The writer is of the opinion that complex soil/soil gas equilibria exist in the anomalous (and background) Hg-containing soil profile. At Keel, the presence of similarly raised levels of Ag and Pb at moderately and strongly anomalous Hg sites suggests that hydro-morphic and/or biogeochemical factors rather than upward gaseous dispersion of mercury are responsible for the surficial enrichment of elements. Subsequent to or coincident with metal accumulation (believed to be biogeochemical "Goldschmidt" cycling of metals) a Hg soil/soil gas equilibria is established.

v) Plasma emission spectrometry has identified the presence of a compound in the anomalous, near-surface, inorganic horizons having a thermal dissociation temperature similar to that of  $\text{HgCl}_2$ . Experimental results reported by Frear and Dills (1967) coupled with the known environmental conditions at Keel suggest the degradation of mercuric chloride to volatile metallic Hg.

vi) The presence of volatile organomercurials in soil air cannot be dismissed lightly. Pyrolysis of soil gases at Keel has shown some improvement in levels of Hg collected. Mercury is known to take part in many organo-metallic interactions and to form many organo-metallic compounds. "The Organic Compounds of Mercury" by L. G. Makarova and A. N. Nesmeyanov, North Holland Publishing Co., 1967 is a 540 page book attesting to the affinity of Hg for organo-metallic

bonding. The term "mercuration" is a well-known phenomena describing the reaction between aromatic compounds with mercuric acetate, an important process in the preparation of arylmercury compounds (Coates, 1956). Further, Coates states that although mercury-carbon bonds are not formed with significantly greater ease than bonds between many other metals and carbon, they tend to remain intact, whereas most organo-metallic compounds are generally distinguished by high reactivity. Organomercurials introduced to soils are known to degradate to mercury vapour but some organo-metallic volatiles are also known to escape.

vii) A critical review of literature sources supports the writer's results and opinion of a complex metal-ion-gas equilibria of Hg in the secondary environment.

In the hydrosphere (including soil solution) simple inorganic complexes and ionic forms of mercury are present, somewhat dependent on pH and composition of the naturally-occurring water. Mercuric chloride (aq), mercuric hydroxide (aq), metallic mercury (aq), mercuric ion, anionic tri and tetrachloro complexes, anionic monomercuric hydroxide and mixed anionic chloro-hydroxides are inorganic species known or postulated as existing in naturally-occurring solutions.

The influence of the biosphere superimposes organo-metallic bioconversions on inorganic mercury and current evidence has shown the presence of biologically generated methyl and dimethylmercury(ic) compounds in naturally-occurring ecosystems. Mercury adsorption (chelating) with sulphhydryl (mercapto) groupings is another important bio-interaction phenomena and probably accounts for mercury retention and/or the long half life of the element in humus as well as in some biological systems.

viii) A cursory examination of the present circumstances surrounding Hg pollution in the environment suggests that while



current emphasis is being placed on the obvious hazards to man, eventual contamination problems may influence the use of the element as a geochemical pathfinding in mineral exploration.

ix) The application of new and superior analytical methods and techniques (opposed to classical methods of determination) has been a primary stimulus in the present interest and research shown in Hg (bio)(geo)chemistry. Undoubtedly, chromatographic techniques (particularly thin-layer and gas-liquid methods) have provided the most advanced data on the nature and occurrence of mercury in ecosystems. Tin (II) reduction of mercuric ion to metallic mercury for determination by flameless atomic absorption is an inexpensive, rapid, and precise method of analysis for total Hg.

### 8.3 RECOMMENDATIONS

#### 8.3.1 Suggestions for Applied Geochemical Usage of Mercury in Soil/Soil Air/Atmospheric Air in Mineral Exploration

i) The writer contends that the soil gas sampling technique as developed and applied by him is not efficient or adequate for present prospecting requirements and refers to comments in the Chapter Seven Summary outlining a recommendation that future soil gas investigations employ direct-reading Hg spectrometers.

ii) The application of soil gas/atmospheric air for prospecting seems to hold most promise for those areas covered by alluvium or loose residual soils. Such overburdens are usually associated with hot, dry climates in which Hg may readily and easily degas from soils in response to reduced air pressures (mass flow) and/or gaseous diffusion. Transported and water-saturated overburdens tend to be more compact and may physically suppress Hg migration by aqueous or gaseous forms.

iii) The prospecting application of the atmophilic component

of an ore and/or pathfinding element in naturally-occurring equilibria currently demands the analysis of associated soil, rock, water, and plants to fully interpret gaseous anomalies. In this respect, "atmogeochemical" prospecting must be regarded as a dependent tool, an infant daughter of mineral exploration technology; hence, great care is necessary for present implementation and future upbringing. The writer is of the opinion that the monitoring of metal-containing gases cannot as yet be given much priority in prospecting until both research and applied investigations have established more firmly the relative importances of (bio)(geo)chemical and meteorological influences on atmogeochemical dispersion. At present, the approach can only be regarded as a "potentially useful" regional and detailed mineral exploration aid.

### 8.3.2 Additional Research Requirements

i) The writer has noted the relatively unproductive nature of his sampling techniques for collecting and analysis of Hg in soil gas. Research and development is recommended for the adapting of the existing modification of the James-Webb (1964) flameless atomic absorption spectrophotometer for the direct-reading determination of Hg vapour in air and soil gas. This adaptation requires some improvement of instrument stability at low mV ranges, additional amplification, and perhaps, actual changes in the collapsed double cell arrangement. The writer envisages changing the existing instrument from parallel photocells to a single photomultiplier valve, a "mechanical chopper" and/or modulated UV source, and the necessary mirror focusing of the double beams. Gratings and slits may also be required to reduce line-broadening effects. Implementation of the above-mentioned modifications should greatly improve both instrument stability and sensitivity and, when provided with a suitable DC power

source (or DC-AC alternator), direct-reading measurements may be possible.

ii) The data collected by the writer and others investigating Hg in soil gas and air suggests sufficient scope for continued and comparative research on mineralized soils and associated environments. The importance of bacterial action on the retention and dispersion of Hg in naturally-occurring environments needs attention.

iii) Further thermal dissociation experiments seem required on a wide range of naturally-occurring inorganic and organic materials; not only to identify mercury compounds, but also to obtain some information on the relative energies required for the release of Hg, particularly in humus and peats. Some work has already been reported (Koksoy et al., 1967) but the emphasis was directed toward investigating simple inorganic forms of Hg. Thermal dissociation experiments could be run concurrently or comparatively with gas-liquid chromatography. Here the writer envisages identification of the Hg-containing organo-metallic using gas-liquid chromatography, pyrolysis of the vapours, and flameless atomic absorption determination of total Hg. Carefully selected partial extraction experiments (perhaps similar to those reported by the writer in Chapters Four and Five) coupled with thin-layer chromatography may also be of some use in comparative identification of naturally-occurring forms of Hg.

iv) Abundance and profile distribution studies should be made on some soils known to have been treated with inorganic and organic mercurials during agricultural practices to assess both lateral dispersion and vertical penetration characteristics of introduced metals. Not only would this provide some information on "spheres of influence" regarding Hg pollution, but may also provide useful data on the incorporation of Hg into the biogeochemical cycle.

v) When the direct-reading "in-situ" determination of Hg

vapour in soil air becomes possible, the following experimental tests would seem to have priority.

a) The rate of formation of soil gas mercury. Measurements by the writer have indicated that the amount of gaseous Hg may be limited at any one site (re: consecutive pumping experiments). The direct-reading of mercury in soil air would enable the estimation of the relative amount of the soil gas component in a naturally-occurring equilibrium. Such tests may well show that a relatively short pumping time is all that is required to establish the presence of an anomalous mercuriferous site.

b) The pyrolysis of soil gas vapours (preferably over a range of temperatures) may enable the field separation and/or identification of Hg/Hg-containing soil gases. Selected "in-situ" experiments similar to the writer's attempts to stimulate the release of Hg harboured by microorganisms may also find some application here.

c) Modifications on the "soil gas site-preparation" should be examined in some detail. The shallow holes employed by the writer can be criticized on the basis that the soil air system tends to be open to dilution by atmospheric air. A larger diameter and deeper hole (possibly using a power auger similar to that described by Saum and Caneer (op. cit.) for extracting Rn gas from soil) may prove more useful when investigating "at depth" Hg soil gas. The advantages gained by pumping from a deep, large diameter hole are quite obvious. Any anomalous Hg vapour could be linked more closely with "sulphide mineralization degassing" and, in addition, the soil air system would suffer from considerably less dilution from the atmosphere (i.e. a closed system).

vi) Research and development on the application of the gaseous component of those potentially favourable ore and pathfinding

elements (As, Sb, I, S, Te, and perhaps, some metal-containing organo-metallics) should proceed wherever possible to direct-reading determinations. The above listed recommendations and associated experiments hold for these gases as well.

# SELECTED REFERENCES

- A.G.R.G. Technical Communication No. 46 (1963) The statistical control of routine analysis.
- A.G.R.G. Technical Communication No. 17 (1965) Determination of antimony in soil and sediment samples.
- A.G.R.G. Technical Communication No. 48 (1965) Determination of gold in soil and sediment samples.
- A.G.R.G. Technical Communication No. 49 (1965) Determination of arsenic in soil and sediment samples.
- A.G.R.G. Technical Communication No. 50 (1965) Decomposition of samples with nitric and perchloric acids.
- A.G.R.G. Technical Communication No. 51 (1965) Determination of selenium in soils and sediments.
- A.G.R.G. Technical Communication No. 52 (1966) Determination of phosphorus in soil, sediment and rock samples.
- A.G.R.G. Technical Communication No. 32 (1967) Determination of organic carbon in soil and sediment samples.
- A.G.R.G. Technical Communication No. 55 (1967) Abbreviated operating instructions for the A.G.R.G. mercury vapour meter.
- A.G.R.G. Technical Communication No. 56 (1967) The determination of molybdenum in soil and sediment samples.
- Aidin'yan, N.Kh. (1962) The content of mercury in certain natural waters. Trudy Instituta Geologii Rudnykh Mestorozhdeniy, Petrografii, Mineralologii i Geokhimii -- Voprosy Geokhimii, No. 70, (III), pp 9-14. Translation in Studies on Mercury Deposits, Office of Technical Services, Joint Publications Research Service, U.S. Dept. of Commerce (1964).
- Aidin'yan, N.Kh., Troitskii, A.I., and Belavskaya, G.S. (1964) Distribution of mercury in the soils of the U.S.S.R. and Vietnam. Geochemistry International, No. 4, pp 670-675.
- Almond, H. (1953) Field method for determination of traces of arsenic in soils -- confined spot procedure using a modified Gutzeit apparatus. Anal. Chem., 25, pp 1766-1767.
- American Conference of Governmental Industrial Hygienists (1958) Manual of analytical methods. Determination of mercury in air, a dithizone method, 6 p.
- Analytical Methods Committee (1965) The determination of small amounts of mercury in organic matter. Analyst, 90, No. 1074, pp 515-530.
- Andersson, A.A. (1967) Kvicksilvret i marken. Grundforbättring, 20, pp 95-105. (English summary)

- Angino, E.E. and Billings, G.K. (1967) Atomic absorption spectrophotometry in geology. Elsevier Publishing Co., 144 p.
- Anon. (1970) The mad hatter's legacy. Newsweek, April 20, pp 42-43.
- Anon. (1970) The quicksilver crisis. Newsweek, August 3, pp 55.
- Anon. (1971) Mercury in the air. Environment, 13, No. 4, pp 24-33.
- Azzaria, L.M. (1966) A method of determining traces of mercury in geologic materials. Geological Survey of Canada, Paper 66-54, pp 13-26.
- Bails, J.D. (in press) Environmental mercury contamination.
- Baily, E.H. and Barnes, J.W. (1968) Geology and ore deposits of the Lakan lead-zinc District, Iran. Third Session CENTO Training Program Geological Mapping Techniques, pp 18-28.
- Baily, E.H. and Smith, R.M. (1964) Mercury--its occurrence and economic trends. U.S. Geological Survey Circular 496, 11 p.
- Barakso, J.J., Rowles, C.A., and Lavkulich, L.M. (1969) Geochemical prospecting in B.C. Western Miner, June.
- Barakso, J.J. and Tarnocai, C. (1970) A mercury determination method and its use for exploration in British Columbia. Canadian Mining and Metallurgical Bulletin, 63, No. 696, pp 501-506.
- Barber, J., Beauford, W., and Shieh, Y.J. (in press) Some aspects of mercury uptake by plant, algal and bacterial systems in relation to its biotransformation and volatilisation.
- Barringer, A.R. (1966) Interference-free spectrometer for high-sensitivity mercury analyses of soils, rocks and air. Trans. Inst. Min. Met., 75, Section B, pp B120-B124.
- Barringer, A.R. (1969) Remote-sensing techniques for mineral discovery. Ninth Commonwealth Mining and Metallurgical Congress, Mining and Petroleum Geology Section, Paper 20, 42 p.
- Belcher, R., Dagnall, R.M., and West, T.S. (1964) An examination of the atomic absorption spectroscopy of silver. Talanta, 11, pp 1257-1263.
- Benes, P. (1969) On the state of mercury (II) traces in aqueous solutions. Colloidal behaviour of mercury. J. Inorg. Nucl. Chem., 31, pp 1923-1928.
- Benes, P. (1970) Radiochemical study of the sorption of trace elements. VI. Adsorption and desorption of bivalent mercury on glass. Coll. Czech. Chem. Comm., 35, pp 1349-1355.
- Benes, P. and Rajman, I. (1969) Radiochemical study of the sorption of trace elements. V. Adsorption and desorption of bivalent mercury on polyethylene. Coll. Czech. Chem. Comm., 34, pp 1375-1386.
- Bent, K.J. (1969) Fungicides in perspective. Endeavour, 28, No. 105, pp 129-134.

- Blanchard, R. (1968) Interpretation of leached outcrops. Nevada Bureau of Mines, Bulletin 66, 196 p.
- Bloomfield, C. (1952) The distribution of iron and aluminum oxides in gley soils. *J. Soil Sc.*, 3, No. 2, pp 167-171.
- Boorer, J.R. (1944) The behaviour of mercury compounds in soil. *Annals of Applied Biology*, 31, pp 340-359.
- Boyle, R.W. (1968) The geochemistry of silver and its deposits. *Geological Survey of Canada Bulletin* 160, 264 p.
- Boyle, R.W. (1971) The land environment. *Canadian Mining and Metallurgical Bulletin*, 64, No. 712, pp 46-50.
- Boyle, R.W. and Garrett, R.G. (1970) Geochemical prospecting--a review of its status and future. *Earth Science Reviews*, 6, pp 51-75.
- Bratt, J. (1967) Mercury and mercury compounds. *Kirk-Othmer Encyclopedia of Chemical Technology*, Second Edition, 13, pp 218-249.
- Butt, C.R.M. (1971) The influence of environment on regional geochemical patterns in Northern Ireland. Unpublished Ph.D. thesis, University of London.
- Cannon, H.L. (1955) Geochemical relations of zinc-bearing peat to the Lockport Dolomite, Orleans County, New York. *U.S. Geological Survey Bulletin* 1000-D, pp 119-185.
- Charlesworth, J.K. (1957) The Quaternary era. Edward Arnold, London, 1700 p.
- Christie, A.A., Dunsden, A.J., and Marshall, B.S. (1967) Field methods for determining organomercurial vapours in air. *Analyst*, 90, pp 185-191.
- Coates, G.E. (1956) Organo-metallic compounds. Methuen and Co. Ltd., London, pp 43-51.
- Cole, M.M. (1968) Report of biogeochemical orientation studies at Keel, Drumming and Ardagh. Unpublished consultant's report, Riofinex.
- Commonwealth Bureau of Soils (1969) Determination of zinc and zinc availability in soils (1969-1965). Harpenden, England, 18 p.
- Craven, C.A.U. (1954) Statistical estimation of the accuracy of assaying. *Trans. Inst. Min. Met.*, 63, Part 12, pp 551-563.
- Crosby, G.M. (1969) A preliminary examination of trace mercury in rocks, Coeur d'Alene District, Idaho. *Quarterly of the Colorado School of Mines*, 64, No. 1, pp 169-194.
- Currie, J.A. (1970) Movement of gases in soil respiration. Society of Chemical Industry, London, Monograph No. 37, pp 152-169.
- Dept. of Transport and Power Meteorological Service (Dublin). Averages of rainfall for stations in Ireland 1916-1950, 7 p.



- Dept. of Transport and Power Meteorological Service (Dublin). Mean and extreme values of air temperature for stations in Ireland 1921-1950, 18 p.
- Dickson, F.W. (1968) The origin of mercury haloes. Twenty-third International Geological Congress, 7, pp 357-365.
- D'Itri, F.M. (in press) Sources of mercury in the environment.
- Donovan, P.R. (1965) Geochemical dispersion in relation to base metal deposits in glacial terrain in West-Central Eire. Unpublished Ph.D. thesis, University of London.
- Donovan, P.R. and James, C.H. (1966) Geochemical dispersion in glacial overburden over the Tynagh (Northgate) base metal deposit, West-Central Eire. Geological Survey of Canada, Paper 66-54, pp 89-110.
- Durum, W.H., Hem, J.D., and Heidel, S.G. (1971) Reconnaissance of selected minor elements in surface waters of the United States, October, 1970. U.S. Geological Survey Circular 643, 49 p.
- Dyck, W. (1969a) Uranium exploration using radon in soils. Canadian Mining J., August, pp 45-49.
- Dyck, W. (1969b) Radon determination apparatus for geochemical prospecting for uranium. Geol. Survey of Canada, Paper 68-21, 30 p.
- Erickson, R.L., Marranzino, A.P., Oda, U., and Janes, W.W. (1966) Geochemical reconnaissance in the Pequop Mountains and Wood Hills, Elko County, Nevada. U.S. Geological Bulletin 1198-E, 20 p.
- Evans, D.S. (1969) Research, development, and progress on the application of mercury geochemistry to geochemical prospecting. Unpublished report, A.G.R.G.
- Fernandez, F.J. and Manning, D.C. (1971) The determination of arsenic at sub-microgram levels by atomic absorption spectrophotometry. Atomic Absorption Newsletter, 10, No. 4, pp 86-88.
- Fishbein, L. (1970) Chromatographic and biological aspects of organo-mercurials. Chromatographic Reviews, 13, No. 2, pp 83-162.
- Fleming, G.A., Walsh, T., and Ryan, P. (1968) Some factors influencing the content and profile distribution of trace elements in Irish soils. Trans. Ninth Int. Cong. Soil Science, 2, pp 341-350.
- Frear, D.E.H. and Dills, L.E. (1967) Mechanism of the insecticidal action of mercury and mercury salts. J. Econ. Ent., 60, No. 4, pp 970-974.
- Friedrich, G.H. and Hawkes, H.E. (1966a) Mercury as an ore guide in the Pachuca-Real Del Monte District, Hidalgo, Mexico. Econ. Geol., 61, pp 744-753.
- Friedrich, G.H. and Hawkes, H.E. (1966b) Mercury dispersion halos as ore guides for massive sulfide deposits, West Shasta District, California. Mineralium Deposita, 2, pp 77-88.

- Fujita, M., Takeda, Y., Terao, T., Hosino, O., and Ukita, T. (1968) Microdetermination of mercury by the oxygen bomb combustion-method. *Anal. Chem.*, 40, No. 13, pp 2042-2043.
- Fursov, V.Z. (1958) Mercury dispersion haloes as a prospecting guide at the Achisai lead-zinc deposit. *Geokhimiya*, No. 3, pp 267-272.
- Furukawa, K., Suzuki, T., and Tonomura, K. (1969) Decomposition of organic mercurial compounds by mercury-resistant bacteria. *Agr. Biol. Chem.*, 33, No. 1, pp 128-130.
- Gardiner, M.J. and Ryan, P. A new generalised soil map of Ireland and its land-use interpretation. *Irish J. Agric. Res.*, 8, pp 95-109.
- General Soil Map (1969) First Edition, An Foras Taluntais, Dublin.
- Geological Map of Ireland (1962) Third Edition, Irish Geological Survey.
- Ginzburg, I.I. (1960) Principles of geochemical prospecting. Pergamon Press, New York, 311 p.
- Goulden, P.D. Mercury pollution and its detection. Unpublished information.
- Goulden, P.D. and Afghan, B.K. (1970) An automated method for determining mercury in water. Dept. of Energy, Mines and Resources, Ottawa, Canada, Technical Bulletin No. 27, 21 p.
- Hansuld, J.A. (1966) Eh and pH in geochemical prospecting. Geological Survey of Canada Paper 66-54, pp 172-187.
- Hawkes, H.E. and Webb, J.S. (1962) Geochemistry in mineral exploration. Harper and Row, New York, 415 p.
- Hawkes, H.E. and Williston, S.H. (1962) Mercury vapor as a guide to lead-zinc deposits. *Mining Cong. J.*, 48, pp 30-32.
- Hem, J.D. (1970a) Chemical behaviour of mercury in aqueous media. U.S. Geological Survey Professional Paper 713, pp 19-23.
- Hem, J.D. (1970b) Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water Supply Paper 1473, Second edition, p 11.
- Hornbrook, E.H.W. (1970) Effectiveness of geochemical and biogeochemical exploration methods in the Cobalt area, Ontario. *Proceedings, Third International Geochemical Symposium, Toronto*, pp 435-443.
- Hoshara, K. (1961) Mercury content of deep-sea water. *Nippon Kagaku Zasshi*, 82, pp 1107-1108 (in Japanese), *Chem. Abs.*, 56, p 4535, 1962.
- Imura, N., Sukegawa, E., Pan, S., Nagao, K., Kim, J., Kwan, T., and Ukita, T. (1971) Chemical methylation of inorganic mercury with methylcobalamin, a vitamin B<sub>12</sub> analog. *Science*, 172, pp 1248-1249.
- James, C.H. (1962) A review of the geochemistry of mercury (excluding analytical aspects) and its application to geochemical prospecting. *Geochemical Prospecting Research Centre Tech. Comm. No. 41*, 42 p.

- James, C.H. (1964) The potential role of mercury in modern geochemical prospecting. *Min. Mag.*, July, pp 23-32.
- James, C.H. (1970) A rapid method for calculating the statistical precision of geochemical prospecting analysis. *Trans. Inst. Min. Met.*, 79, No. 762, Section B, pp B88-B90.
- James, C.H. and Webb, J.S. (1964) Sensitive mercury vapour meter for use in geochemical prospecting. *Trans. Inst. Min. Met.*, 73, Part 9, pp 633-641.
- Jenne, E.A. (1968) Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. *In* *Advances in Chemistry Series*, No. 73, "Trace Inorganics in Water". American Chemical Society, pp 337-387.
- Jensen, S. and Jernelov, A. (1969) Biological methylation of mercury in aquatic organisms. *Nature*, 223, No. 5207, pp 753-754.
- Jernelov, A. (1968a) The menace of mercury. *New Scientist*, 40, No. 627/12, pp 627.
- Jernelov, A. (1968b) Turnover of mercury in aquatic ecosystems. *Swedish Water and Air Pollution Research Bulletin*, 3 p.
- Jernelov, A. (1968c) Laboratory experiments concerning the conversion of mercury compounds. *Swedish Water and Air Pollution Research Bulletin*, 7 p.
- Jernelov, A. (1969) Are there any differences between "biologically" and "chemically" synthesized methyl mercury? *Vatten*, 3, pp 304-309.
- Johnson, P.H. and Bhappu, R.B. (1969) Chemical mining - a study of leaching agents. *New Mexico Bureau of Mines and Mineral Resources Circular* 99, 10 p.
- Jolly, J.L. and Heyl, A.V. (1968) Mercury and other trace elements in sphalerite and wallrocks from central Kentucky, Tennessee and Appalachian zinc districts. *U.S.G.S. Bulletin* 1252-F, 29 p.
- Jonasson, I.R. (1970) Mercury in the natural environment: a review of recent work. *Geological Survey of Canada Paper* 70-57, 39 p.
- Kalb, G.W. (1970) The determination of mercury in water and sediment samples by flameless atomic absorption. *Atomic Absorption Newsletter*, 9, No. 4, pp 84-87.
- Karasik, M.A., Goncharov, Yu., and Vasilevskaya, A. Ye. (1965) Mercury in waters and brines of the Permian salt deposits of Donbas. *Geochemistry International*, 2, No. 1, pp 82-87.
- Karasik, M.A. and Gerasimova, L.I. (1967) Mode of vaporization of mercury over cinnabar. *Doklady*, 173, No. 2, pp 199 (abstract only).
- Kelly, W.C. (1958) Topical study of lead-zinc gossans. *New Mexico Bureau of Mines and Mineral Resources Bulletin* 46, 80 p.

- Kimura, Y. and Miller, V.L. (1960) Vapor phase separation of methyl- or ethylmercury compounds and metallic mercury. *Anal. Chem.*, 32, No. 3, pp 420-424.
- Kimura, Y. and Miller, V.L. (1964) The degradation of organomercury fungicides in soil. *Agric. Food Chem.*, 12, No. 3, pp 253-257.
- Kitamura, S., Tsukamoto, T., Hayakawa, K., Sumino, K., and Shibata, T. (1966) Application of gas chromatography to the analysis of alkyl-mercuric compounds. *Medicine and Biology (Jap.)*, 75, No. 5, pp 274-281.
- Koksoy, M., Bradshaw, P.M.D., and Tooms, J.S. (1967) Notes on the determination of mercury in geological samples. *Trans. Inst. Min. Met.*, 76, Section B, pp B121-B124.
- Kosta, L. and Byrne, A.R. (1969) Activation analysis for mercury in biological samples at nanogram level. *Talanta*, 16, pp 1297-1303.
- Krauskopf, K.P. (1956) Factors controlling the concentration of 13 rare metals in sea waters. *Geochem. et Cosmochim. Acta*, 9, p 1-32.
- Kraynov, S.R., Volkov, G.A., and Korol'kova, M.Kl. (1966) Distribution and the mode of migration of trace elements Zn, Cu, Hg, Li, Rb, Cs, As, and Ge. *Geochemistry International*, 3, No. 1, pp 108-123.
- Kurayuki, Y. and Kusamoto, K. (1967) *Japan Analyst*, 16, p 815 quoted by Fishbein (1970).
- Lagerwerff, J.V. and Specht, A.W. (1970) Contamination of roadside soil and vegetation with cadmium, nickel, lead, and zinc. *Environ. Sci. Tech.*, 4, No. 7, pp 583-585.
- Larsson, J. (1970) Mineralogical and geochemical studies in areas of blanket peat in Western Ireland. Unpublished Ph.D. thesis, University of London.
- Leggo, M.D. (1970) Further studies in mercury. Unpublished D.I.C., University of London.
- Linch, A.L., Stalzer, R.F., and Lefferts, D.T. (1968) Methyl and ethyl mercury compounds - recovery from air and analysis. *Amer. Industr. Hyg. Assoc. J.*, 29, pp 79-86.
- McCarthy, J.H. Jr., Meuschke, J., Ficklin, W.H., and Learned, R.E. (1970) Mercury in the atmosphere. U.S. Geological Survey Professional Paper 713, pp 37-39.
- McCarthy, J.H. Jr., Vaughn, W.W., Learned, R.E., and Meuschke, J.L. (1969) Mercury in soil gas and air - a potential tool in mineral exploration. U.S. Geological Survey Circular 609, 16 p.
- Magos, L. (1966) Radiochemical determination of metallic mercury vapour in air. *Brit. J. Industr. Med.*, 23, pp 230-236.
- Magos, L. (1967) The effect of halide ions on the  $\text{Hg} \rightleftharpoons {}^{203}\text{Hg}$  exchange reaction between air and aqueous solution. *J. Chem. Soc., Section A*, pp 545-546.

- Magos, L. and Cernik, A.A. (1969) A rapid method for estimating mercury in undigested biological samples. *Brit. J. Industr. Med.*, 26, pp 144-149.
- Makarova, L.G. and Nesmeyanov, A.N. (1967) The organic compounds of mercury. North Holland Publishing-Co., Amsterdam, 540 p.
- Manning, D.C. (1970) Non-flame methods for mercury determination by atomic absorption, a review. *Atomic Absorption Newsletter*, 9, No. 5, pp 97-99.
- May and Baker, a catalogue entitled "Chemicals for Industry".
- Millman, A. (1966) Core samples of decomposed rock. Unpublished consultant's report, Riofinex.
- Mitchell, G.F. (1957) Geology of Ireland. In *A View of Ireland*, edited by Meenan, J. and Webb, D.A., British Association for the Advancement of Science, Dublin, 254 p.
- Morris, D.F.C. and Killick, R.A. (1964) The determination of mercury in rocks by neutron-activation analysis. *Talanta*, 11, pp 781-788.
- Morrissey, C.J. and Whitehead, D. (1969) Origin of the Tynagh residual orebody, Ireland. Paper 24, Ninth Commonwealth Mining and Metallurgical Congress, 15 p.
- Motycka, J. (1970) Airborne mercury spectrometer. *Barringer Research*, 3, No. 3, pp 6-7.
- Newbould, P.J. (1958) Peat bogs. *New Biology*, No. 26, pp 88-105.
- Ng, S.K. and Bloomfield, C. (1962) The effect of flooding and aeration on the mobility of certain-trace elements in soils. *Plant and Soil*, 16, No. 1, pp 108-135.
- Nichol, I. and Henderson-Hamilton, J.C. (1965) A rapid quantitative spectrographic method for the analysis of rocks, soils and stream sediments. *Trans. Inst. Min. Met.*, 74, pp 955-961.
- Omang, S.H. (1971) Determination of mercury in natural waters and effluents by flameless atomic absorption spectrophotometry. *Anal. Chim. Acta*, 53, pp 415-420.
- Ozerova, N.A. (1962) Primary dispersion haloes of mercury. *Tr. IGEM AN SSSR*, No. 72, 135 p. (Translation by P.R. Donovan)
- "Panel on Mercury", Committee on Technical Aspects of Critical and Strategic Materials (1970) Trends in usage of mercury. *J. Metals*, May, pp 28-38.
- Patterson, J.M. (1970) Geology and mineralization of the Keel area, Co. Longford, Republic of Ireland. Unpublished Ph.D. thesis, University of London.
- Peacock, J.D. and Williamson, R. (1961) Radon determination as a prospecting technique. *Trans. Inst. Min. Met.*, 71, pp 75-85.

- Pertel, R. and Gunning, H.E. (1959) Photochemical separation of mercury isotopes. II. The reaction of  $\text{Hg}^{206}\text{6}(3\text{P}_1)$  atoms, photoexcited in natural mercury vapor, with water vapor and other  $\text{HgO}$ -forming substrates. *Can. J. Chem.*, 37, pp 35-42.
- Phillips, G.F., Dixon, B.E., and Lidzey, R.G. (1959) The volatility of organo-mercury compounds. *J. Sci. Food Agric.*, 10, pp 604-610.
- Pickard, J.A. and Grainger, J. (1962) Annual Report Agric. Hort. Res. Stn., Long Ashton, Bristol, p. 65.
- Presant, E.W. (1966) A trace element study of podzol soils, Bathurst district, New Brunswick. Geological Survey of Canada Paper 66-54, pp 222-232.
- Randhawa, N.S. and Broadbent, F.E. (1965a) Soil organic matter-metal complexes: 5. Reactions of zinc with model compounds and humic acid. *Soil Science*, 99, No. 5, pp 295-300.
- Randhawa, N.S. and Broadbent, F.E. (1965b) Soil organic matter-metal complexes: 6. Stability constants of zinc-humic acid complexes at different pH values. *Soil Science*, 99, No. 5, pp 362-366.
- Rankama, K.K. and Sahama, Th. G. (1950) *Geochemistry*. University of Chicago Press, Chicago, 912 p.
- Rasmussen, R.A. (1970) Isoprene: identified as a forest-type emission to the atmosphere. *Environ. Sci. Tech.*, 4, No. 8, pp 667-671.
- Rathje, A.O. (1969) A rapid ultraviolet absorption method for the determination of mercury in urine. *Amer. Industr. Hyg. Assoc. J.*, 30, pp 126-132.
- Ravikovitch, S., Margolin, M., et al. (1968) Zinc availability in calcareous soils: I. Comparison of chemical extraction methods for estimation of plant "available" zinc. *Soil Sc.*, 105, pp 57-61.
- Reed, B.L. and Miller, R.L. (1971) Orientation geochemical soil survey at the Nixon Fork Mines, Medfra Quadrangle, Alaska. *U.S. Geological Survey Bulletin* 1312-K, 21 p.
- Ruzicka, J. and Lamm, C.G. (1969) Automated determination of traces of mercury in biological materials by substoichiometric radioisotope dilution. *Talanta*, 16, pp 157-168.
- Ryan, P. and Walsh, T. (1966) Character study of soils developed on Weichsel glacial deposits in Ireland. *Proc. Roy. Irish Acad.*, 64, Section B, No. 24, pp 465-507.
- Salmi, M. (1955) Prospecting for bog-covered ore by means of peat investigations. *Bull. de la Commission Geologique de Finlande*, No. 169, 34 p.
- Salmi, M. (1956) Peat and bog plants as indicators of ore minerals in Vihanti ore field in western Finland. *Bull. de la Commission Geologique de Finlande*, No. 175, 22 p.
- Saukov, A.A. (1946) The geochemistry of mercury. In: *t Geol. Nauk, AN SSR Tr. No. 78, Mineralovo-geokhim. Ser. No. 17*, 129 p. (Translation brief by the Geological Survey of Canada).

- Saum, N.M. and Caneer, W.T. (1969) Radon gas used to find uranium. *The Northern Miner*, Nov. 27, pp 81 and 84.
- Schnitzer, M. and Skinner, S.I.M. (1964) Organo-metallic interactions in soils. 3. Properties of iron- and aluminium-organic-matter complexes, prepared in the laboratory and extracted from a soil. *Soil Sci.*, 98, pp 197-203.
- Schofield, R.K. (1950) Effect of pH on electric charges carried by clay particles. *J. Soil Sci.*, 1, pp 1-8.
- Schultz, R.W. (1971) Mineral exploration practice in Ireland. *Trans. Section B Inst. Min. Met.*, 80, No. 777, pp 238-258.
- Sergeant, G.A., Dizon, B.E., and Lidzey, R.G. (1957) The determination of mercury in air. *Analyst*, 82, No. 970, pp 27-33.
- Shacklette, H.T. (1970) Mercury content of plants. *U.S. Geological Survey Professional Paper* 713, pp 35-36.
- Shacklette, H.T., Boerngen, J.G., and Turner, R.L. (1971) Mercury in the environment -- surficial materials of the conterminous United States. *U.S. Geological Survey Circular* 644, 5 p.
- Silcock, B. (1971) Limpets reveal metal poison danger. *The Sunday Times*, June 6.
- Sjostrand, B., Ljunggren, K., Johnels, A.G., Olsson, M., Otterlind, G., and Westermark, T. (1971) Activation analysis of mercury and other environmental pollutants in water and aquatic ecosystems. Reprint from "Nuclear Techniques in Environmental Pollution", a symposium held under the auspices of the International Atomic Energy Agency, Vienna, 1970, pp 373-405.
- Smart, N.A. (1968) Use and residues of mercury compounds in agriculture. *Residue Reviews*, 23, pp 1-36.
- Sutherland Brown, A. (1966) Investigation of mercury dispersion haloes around mineral deposits in central British Columbia, *Geological Survey of Canada, Paper* 66-54, pp 73-83.
- Suzuki, T., Furukawa, K., and Tonomura, K. (1968) Studies on the removal of inorganic mercury. Compounds in waste by the cell-reused method of mercury-resistant bacterium. *J. Ferment. Technol.*, 46, No. 12, pp 1048-1055.
- Swaine, D.J. and Mitchell, R.L. (1960) Trace-element distribution in soil profiles. *J. Soil Science*, 11, No. 2, pp 347-368.
- Synge, F.M. and Stephens, N. (1960) The Quaternary period in Ireland - an assessment. *Irish Geog.*, 4, pp 121-130.
- Tanaka, H., Sugiura, Y., and Yokoyama, A. (1968) Radioisotope dilution method for determination of inorganic and organic mercury by paper chromatography. *Bunsoki Kagaku*, 17, No. 11, pp 1424-1427, (English translation by B.K. Bowes).

- Thilliez, G. (1968) Determination precise et rapide par absorption atomique de-traces de mercure dans l'air et dans les milieux biologiques. *Chimie Analytique (Fr.)*, 50, No. 5, pp 1-7.
- Toribara, T.Y., Shield, C.P., and Koval, L. (1970) Behaviour of dilute solutions of mercury. *Talanta*, 17, pp 1025-1028.
- Trost, P.B. and Bisque, R.E. (1970) Differentiation of vaporous and ionic mercury in soils. *Proceedings, Third International Geochemical Symposium, Toronto*, pp 276-278.
- Turney, W.G. (1970) (in press) The mercury pollution problem in Michigan and the Lower Great Lakes area.
- Turney, W.G. (1970) Mercury pollution: Michigan's action program. *J. Wat. Poll. Contr. Fed.*, 43, No. 7, pp 1427-1438.
- Udo, E.J., Bohn, H.L., and Tucker, T.C. (1970) Zinc adsorption by calcareous soils. *Soil Sc. Soc. Amer.-Proc.*, 34, No. 3, pp 405-407.
- U.S. Dept. of Commerce (1964) Studies on mercury deposits, U.S.S.R. A translation of nine-articles from various issues of the Russian-language periodical *Trudy Instituta Geologii Rudnykh Mestorozhedeniy, Petrografii, Mineralogii, i Geokhimii*, JPRS: 23, 931, 118 p.
- Vaughn, W.W. (1967) A simple mercury vapor detector for geochemical prospecting. *U.S. Geological Survey Circular* 540, 8 p.
- Vinogradov, A.P. (1959) The geochemistry of rare and dispersed chemical elements in soils. *Consultants Bureau, New York*, 209 p.
- Wallace, R.A., Fulkerson, W., Shults, W.D., and Lyon W.S. (1971) *Mercury in the Environment*. Oak Ridge National Laboratory, ORNL NSF-EP-1, 61 p.
- Walsh, T. and Barry, T.A. (1958) The chemical composition of some Irish peats. *Proc. Royal Irish Academy*, 59, Section B, No. 15, pp 305-328.
- Ward, F.N., Lakin, H.W., Canney, F.C., and others (1963) Analytical methods used in geochemical exploration by the U.S. Geological Survey. *U.S. Geological Survey Bulletin* 1152, 100 p.
- Ward, F.N., Nakagawa, H.M., Harms, T.F., and Van Sickle, G.H. (1969) Atomic-absorption methods of analysis useful in geochemical exploration. *U.S. Geological Survey Bulletin* 1289, 45 p.
- Warren, H.V. (1962) Background data for biogeochemical prospecting in British Columbia. *Trans. Royal Soc. Canada*, 56, Third Series, Section Three, pp 21-30.
- Warren, H.V. (1966) Some aspects of lead pollution in perspective. *J. Coll. Gen. Practit.*, 11, pp 135-142.
- Warren, H.V. and Delavault, R.E. (1960) Observations on the biogeochemistry of lead in Canada. *Trans. Royal Soc. Canada*, 54, Third Series, Section Four, pp 11-20.



- Warren, H.V. and Delavault, R.E. (1969) Mercury content of some British soils. *Oikos*, 20, pp 537-539.
- Warren, H.V., Delavault, R.E., and Barakso, J.J. (1966) Some observations on the geochemistry of mercury as applied to prospecting. *Econ. Geol.*, 61, No. 6, pp 1010-1028.
- Weiss, O. (1970) Airborne geochemical prospecting. *Proceedings, Third International Geochemical Exploration Symposium, Toronto*, pp 502-514.
- Westoo, G. (1966) Determination of methylmercury compounds in food-stuffs. I. Methylmercury compounds in fish, identification and determination. *Acta. Chem. Scand.*, 20, No. 8, pp 2131-2137.
- Westoo, G. (1967) Determination of methylmercury compounds in food-stuffs. II. Determination of methylmercury in fish, egg, meat, and liver. *Acta. Chem. Scand.*, 21, No. 7, pp 1790-1800.
- Westoo, G. (1968) Determination of methylmercury salts in various kinds of biological material. *Acta. Chem. Scand.*, 22, No. 7, pp 2277-2280.
- White, D.E. (1967) Mercury and base-metal deposits with associated thermal and mineral waters. *In Geochemistry of Hydrothermal Ore Deposits (Chapter 13)*, Holt, Rinehart and Winston, Inc., edited by H.L. Barnes, 670 p.
- White, D.E., Hinkle, M.E., and Barnes, I. (1970) Mercury content of natural thermal and mineral fluids. *U.S. Geological Survey Professional Paper 713*, pp 25-28.
- Wiklander, L. (1970) The content of mercury in Swedish ground and river water. *Geoderma*, 3, pp 75-79.
- Williston, S.H. (1964) The mercury halo method of exploration. *Engineering and Mining J.*, 165, No. 5, pp 98-101.
- Williston, S.H. (1968) Mercury in the atmosphere. *J. Geophys. Research*, 73, No. 22, pp 7051-7055.
- Wood, J.M., Kennedy, F.S. and Rosen, C.G. (1968) Synthesis of methylmercury compounds by extracts of a methanogenic bacterium. *Nature*, 220, pp 173-174.
- Wotjalik, T.A. (1971) Accumulation of mercury and its compounds. *J. Wat. Poll.-Contr. Fed.*, 43, No. 6, pp 1280-1292.
- Zimmerman, P.W. and Crocker, W. (1933) The injurious effect of mercury vapor from bichloride of mercury in soil of rose houses. *Boyce Thompson Inst. Prof. Paper*, 1, No. 23, pp 222-225.

## APPENDIX 1

### SAMPLE COLLECTION AND PREPARATION

#### A1.1 SOILS

Soil samples were collected with the commonly-used "T" steel-piece tipped with a conventional wood twist-auger.

Samples to confirm and augment the original work by Riofinex were selected at 18 to 24 inch depths, depending on local conditions. Augering during August and September usually met with some difficulty due to the partial development of a "hardpan" (usually at the base of the A<sub>2</sub> horizon) in well-drained areas. Two-depth sites (10 inch and 20 to 30 inch) were collected in areas of detailed study.

Soils were placed in water-proof kraft bags (3 x 5 in.) with metal wire sealing clasps. Pertinent data was recorded on the bag with a black felt pen. This information was transferred to permanent record sheets during laboratory work.

#### A1.2 PITS

Pits were excavated at critical sites with the aid of local help. Ideally, a rectangular plot four feet by six feet was selected and dug out to a depth of six or more feet. Profile walls were cleaned, visually examined, and usually photographed for later reference. Channel samples of the observed horizons were then collected. On-site Eh and pH measurements were made during the field examination of two pits.

#### A1.3 STREAM SEDIMENTS

A small number of stream sediments were collected in the Ardagh area by normal sampling procedures. Fine-grained inorganic

material was selected from the active channel and placed in a kraft bag with the aid of a stainless steel hand trowel. Excess water was drained off and required field data written on the bag with a black felt pen.

#### A1.4 PLANTS

Approximately 30 grass and/or reed samples were collected in the Keel area. A sampling station of approximately ten feet diameter was chosen and sufficient grass cut using stainless steel scissors to fill a large kraft bag (5 x 10 in.).

#### A1.5 WATER

Water was collected in borosilicate glass bottles with bakelite caps. Bottles were detergent and acid washed in the laboratory and then pre-rinsed with the station site water before sample collection. Two hundred and fifty ml was sufficient for Cd, Zn, Pb, Fe, Mn, Ca, K, Na, and Mg determinations but one litre was required for Hg analysis alone. Solutions were stabilized by the additional of double-distilled, "low-in-lead" concentrated nitric acid (Hopkin and Williams).

#### A1.6 DECOMPOSED ZONE AND ROCKS

Through the kind permission of Riofinex, samples of the Decomposed Zone and associated rocks were collected from existing drill core at the Keel site.

Usually, three spot and/or mixed samples of oxidized and leached material were selected from one 15 foot core box. This procedure had to be extensively modified to consider the overall poor core recovery, lost or previously analyzed lengths and short, locally weathered sections.

Limited rock sampling was again from drill core. Core splits were collected from unweathered lengths associated with the Decomposed Zone and also from graphitic and shaley horizons in the upper part of the stratigraphic succession.

#### A1.7 PREPARATION

Soil, pit, and stream sediment samples were air-dried at room temperature in the collecting kraft bags. Peats and organic-rich soil samples were dispersed during drying to prevent excessive hardening.

The dried samples were gently disaggregated by pestle action in a porcelaine mortar and sieved through selected nylon meshes. Normally, only -80 mesh was retained but a few soil samples were split into -38 to -80, -80 to -197, and >-197 fractions (all dry sieved). Fines were placed in appropriately numbered coin envelopes.

Grass samples were air dried (two to three weeks) and pulped in a rotary Wiley mill through a 40 mesh screen.

Decomposed Zone samples usually required only gentle disaggregation to reduce weathered rock, sandy clays, and limonites to fines. Sieving (-80) mesh was again through nylon mesh.

Rock samples were reduced to about one-half inch units and fed into a "chipmunk" jaw crusher. A crushed sample was continually recycled as the jaw openings were progressively reduced to the finest setting. Eventually, -80 mesh was separated (Hg analysis only) and the remaining +80 mesh ground in a tungsten-carbide "Tema" mill for 30 to 40 seconds. A split of the second pulp was then reduced in an agate mortar until all the split passed through a -80 mesh sieve. Mercury again, and the remaining elements were determined on the second pulp.

## APPENDIX 2

### MERCURY ANALYSIS

#### A2.1 GENERAL

Description and discussion of analytical methods and techniques in this appendix is intimately related with the research and development of atmospheric air and soil air Hg analysis in Chapter 7. Appendix Two is primarily devoted to known and applied techniques for Hg analysis in materials other than air as studied in this research.

#### A2.2 INSTRUMENTATION

The original James-Webb (1964) prototype instrument, a double-cell flameless atomic absorption spectrophotometer, was used during initial Hg studies, but later research was performed on a modified instrument manufactured by Instrument Research Laboratories Ltd., Corsham, Wiltshire.

The new instrument contains the essential features of the prototype. Improvements and modifications include a collapsed double-cell arrangement to reduce instrument size, mains-powered photocells, and electronic balancing to assist optical balance. Also, the Hg-free air source and by-pass was modified to reduce the length of the air flow path.

Additional changes have been introduced for the pre-treatment of air. Magnesium perchlorate replaces "self-indicating" silica gel as a water dessicant and iodized activated charcoal is used in place of  $\text{PdCl}_2$  as the de-mercurifying agent for atmospheric air. The palladium chloride impregnated glass wool is still retained as the Hg absorbent for the reference cell. The above changes were introduced to improve the atmospheric air drying and cleaning procedure.

### A2.3 CALIBRATION PROCEDURES

Operating parameters have been optimized for analysis of Hg vapour and prepared standards. These include:

- i) Instrument equilibration (warm-up) and optically balanced with moving air flow
- ii)  $5\frac{1}{2}$  l/m air flow for each cell
- iii) Calibration by injection of known amounts of Hg vapour-saturated air over the range of 0 to 7000 mV.
- iv) 30 second radio frequency (RF) induction heating of natural standards on steel trays

Operating procedures generally follow those described by James and Webb (1964) and repeated in detail in A.G.R.G. Technical Communication No. 55.

A calibration constructed by injecting known amounts of Hg vapour is shown in Figure A1. Note the bending of the curve towards the concentration axis above 2000 mV. This is in accordance with observations from flame atomic absorption (such as Zn) and probably reflects self-absorption and line-broadening phenomena. The prototype instrument calibration has been quoted as linear to 10,000 mV., but J. Watling (pers. comm.) reports graph curvature above 3000 mV.

A statistical series prepared for control of flame atomic absorption work proved unsatisfactory for a Hg analysis precision plot. Instead, a natural standard containing 1.6 ppm Hg was used with differing weights (10 to 60 mg) and results are included in Figure A1.

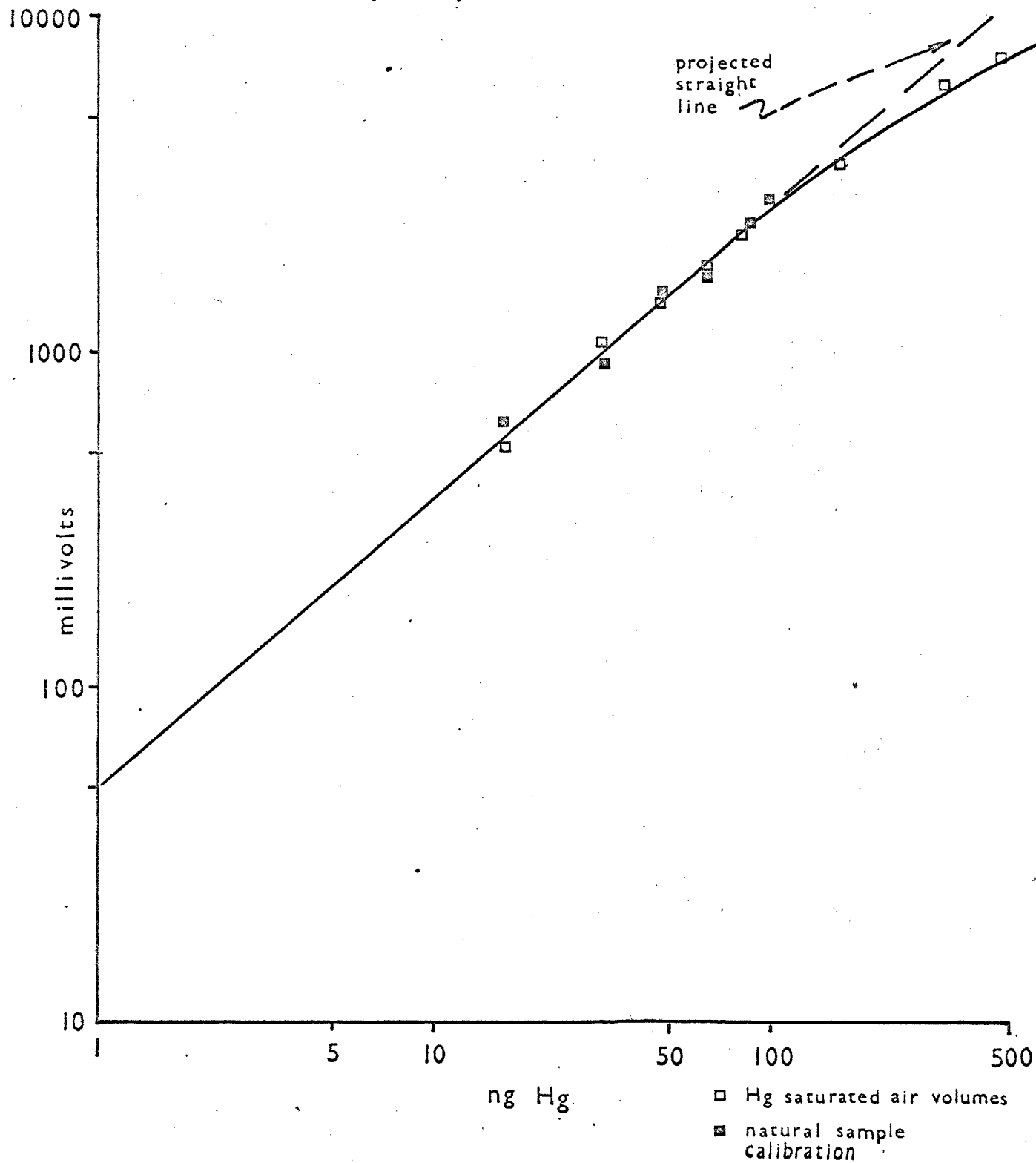
### A2.4 MERCURY DETERMINATION

#### A2.4.1 Soils, Rocks and Oxidized Material

Twenty-five or 50 mg portions of sample are weighed in

Fig. A1

Calibration curve of  
mercury vapour  
spectrophotometer



duplicate on to pre-ignited ( $450^{\circ}\text{C}$ ) steel trays. Trays are then heated for 30 seconds by RF induction (300 mA) in a sealed pyrex ignition tube. An optical pyrometer measurement has indicated a peak temperature greater than  $700^{\circ}\text{C}$ . Volatiles are swept from the heating chamber into the air flow system, equally divided into reference and measuring cells and the relative absorption is indicated by the voltmeter. The mean of duplicate analyses is taken as the amount of Hg present. A detection limit of 25 ppb is possible with a 50 mg weight and a precision of better than  $\pm 30$  per cent at the 95 per cent confidence level is usually obtainable from replicate analyses (see Table A1). Samples must be well-mixed to ensure good reproducibility. Experience by the writer indicates clay-rich soils and tills duplicate more precisely than do sandy or gritty materials.

#### A2.4.2 Grass, Organic-rich Soils, and Peats

Dried and pulped grass samples (1.00 gm) are leached overnight with 10 ml concentrated "low-in-lead" nitric acid (Hopkin and Williams) and 2 ml of concentrated sulphuric acid (ANALAR grade). Eight ml of demineralized water is added, the solution mixed and refluxed gently for 30 seconds, and a 5 ml (or 2 ml, if necessary) aliquot (cooled) transferred to a clean 125 ml dreschel bottle fitted with a sintered glass bubbler. Sufficient demineralized water is added (50 ml) followed by the listed reagents in order.

- i) 1 ml of 1% cysteine hydrochloride in 1N  $\text{HNO}_3$
- ii) 3 drops of 5% silicone 'anti-foam' mixture
- iii) 1 ml of 20% stannous chloride in 6N HCl
- iv) 5 ml of 30% NaOH

Immediately upon addition of the NaOH, the dreschel bottle is sealed and bubbling of Hg-free air commenced. The released Hg vapour is flushed via a  $\text{MgClO}_4$  dessicant, into the spectrophotometer and a



Table A1. Precisions of mercury in soil<sup>1</sup> analyses based on replicate determinations

| N | $\bar{A}$ (ppb) | Precision <sup>2</sup> |
|---|-----------------|------------------------|
| 6 | 336             | $\pm 23\%$             |
| 6 | 1,000           | $\pm 12\%$             |
| 6 | 1,360           | $\pm 15\%$             |
| 4 | 5,080           | $\pm 11\%$             |
| 6 | 10,000          | $\pm 13\%$             |
| 6 | 13,500          | $\pm 4.2\%$            |

<sup>1</sup> Samples are naturally-occurring, well-mixed, clay-rich soils of glacial till origin.

<sup>2</sup> 95% confidence level (after A.G.R.G. Tech. Comm. No. 46)

voltmeter reading recorded. Standard solutions containing mercuric ion are treated in a similar manner and Figure A2 shows a calibration graph. A substantial blank value, presumably Hg introduced with the acids, was subtracted from all calculated results.

Tin (II) reduction of mercuric ion to mercury and subsequent flameless atomic absorption determination of released Hg vapour has been recently popularized by many investigators researching mercury pollution problems. The technique described above differs from other reduction techniques in that mercuric ion is first complexed with a sulphhydryl bond (cysteine) and then released (as Hg vapour) at a pH greater than 7. This technique would seem to be very well suited for the analysis of organic-rich samples as some mercury is probably bound by natural protein groupings and may not be easily released to solution by the nitric/sulphuric leach. In such cases, Hg naturally bound as mercapto complexes may be reduced by stannous chloride at a high pH. Jonasson (1970) implies mercury geochemistry and dispersion may be highly influenced by organic sulphur complexes and naturally-occurring proteins.

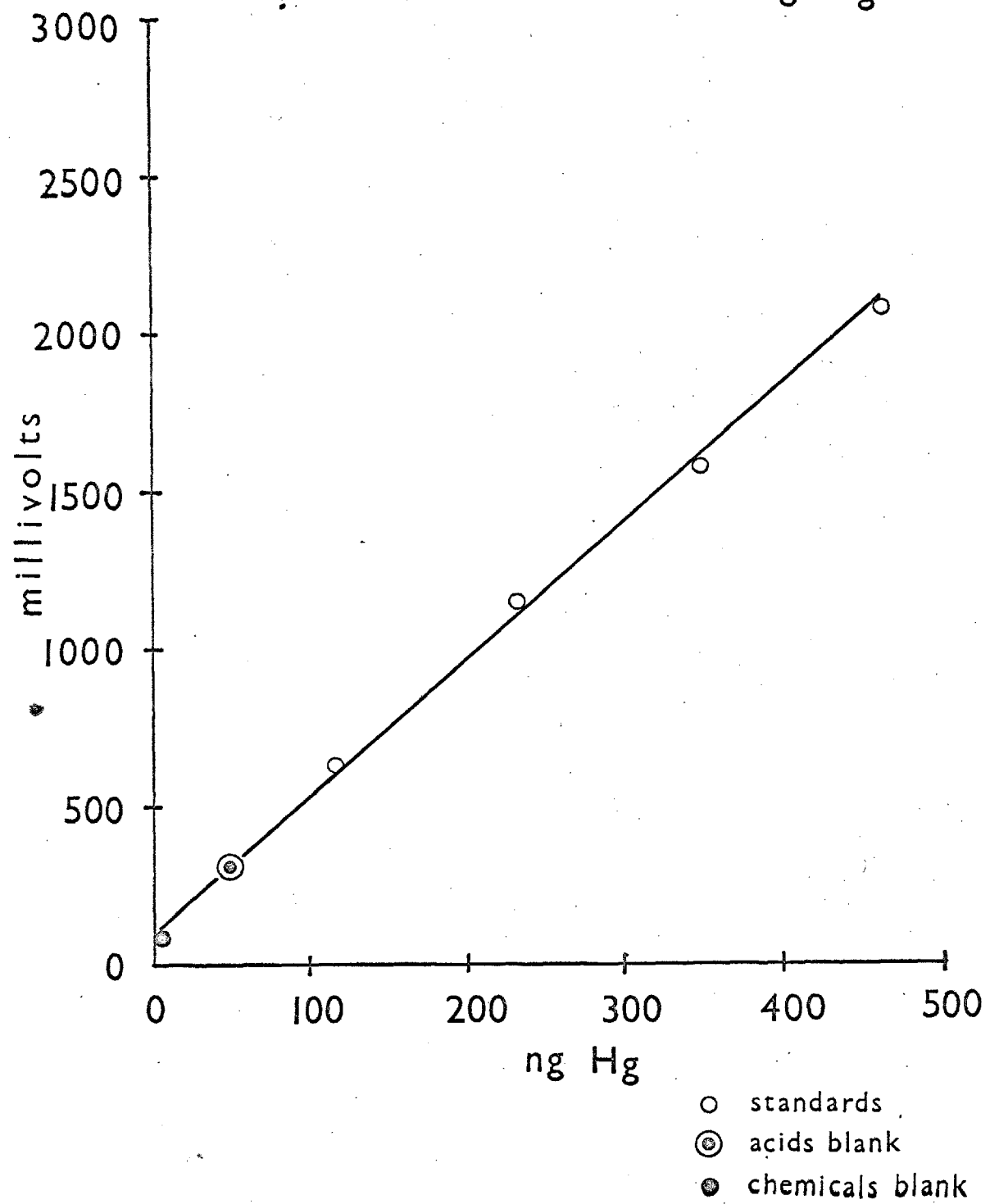
The above analytical method was originally reported by Magos and Cernik (1969) as applied to the analysis of urine. The use of magnesium perchlorate as a dessicant for separating water vapour from Hg vapour has been reported by Rathje (1969).

Nitric/sulphuric leaching and vapour release of Hg has also been applied to a limited number of peats, organic-rich soils and sulphide minerals from the Keel area. The efficiency of the concentrated acid leach has not been investigated. A total digestion would require both hot acid oxidation and lengthy refluxing in a Bethge apparatus or an equivalent efficient volatile trap (Analytical Methods Committee, 1965).

A detection limit of approximately 50 ppb is possible with a

Fig. A 2

Calibration graph,  
SnCl<sub>2</sub> release technique  
for determining Hg



one gram sample by the method applied here. A precision of  $\pm 50$  per cent at the 95 per cent confidence level has been calculated from limited replicate analyses.

#### A2.4.3 Water

Mercury analysis of water presents a number of difficulties. The problems surrounding sample pre-filtering, container type, stabilizing additive, use of bactericides, and length of stay in container before analysis (by any method) have all received comment in the literature. It is not within the scope of this appendix to discuss literature findings, but additional study appears warranted.

On reviewing published sources, the most satisfactory water sampling technique appeared to be collection of one litre in glass bottles and the solution stabilized with nitric acid (see Appendix One). Hopefully, all ionic complexes, colloid bound Hg, and Hg harboured by microorganisms would be oxidized and mercury fixed as mercuric ion.

As the analytical technique of Magos and Cernik introduces contamination, this approach was soon ruled out as a method of Hg analysis of natural waters. Instead, addition of  $\text{SnCl}_2$  solution only (pH now less than 7) is directly followed by bubbling to release Hg vapour. This method has produced only partially satisfactory results, but quite similar techniques have shown good recovery and analytical precision (Rathje, op. cit., Omeng, 1970, and Kalb, 1970). Mercury determination by  $\text{SnCl}_2$  reduction/Hg vapour release from solution employing the James-Webb instrument suggests the volatilization of nanogram amounts of mercury from natural waters is, perhaps, a more involved and complex analytical procedure than has been reported in the literature. Certainly the quality of reagents is

important, but reaction times, temperature factors, and potentially suppressing and enhancing substances (particularly naturally-occurring) have received little reported investigation.

#### A2.4.4 A Modified Procedure for Organic-rich Samples

For several years now, small mercury 'sniffers' have been manufactured for the analysis of soil and rock. These instruments are basically single, short-length absorption cells. It is well known that water vapour, sulphur dioxide, and 'organic smoke' (small unburned carbon particles) are potentially interfering substances which can induce false signals (James and Webb, op. cit.). These problems have been partially solved in using short-cell Hg vapour meters by pre-filtering volatiles with a fibre-glass pad.

In an attempt to study the effect of organic smoke on the double-cell instrument, an in-line filter holder (Hawksley-Gelman) containing a one inch fibre-glass filter pad was positioned in the vapour flow path. Calibration with and without the filter showed negligible differences. However, analysis of organic-rich soils revealed the double-cell instrument liable to some enhancing interferences from 'organic smoke'. When contrasted with unfiltered vapours and acid digestion/mercury release results, filtered soil volatiles showed much better agreement with the acid digestion/mercury release values.

Figure A3 shows results of the three analytical techniques on a traverse across the mineralized peat at Keel. A Hg anomaly reflects the subcropping ore in both lower and upper horizons. The anomaly is shown to be clearly identifiable with all three analytical techniques. It would appear from this data that pre-filtration of soil volatiles an advantage when a more absolute Hg determination is required, but of less value in applied investigations or in prospecting.

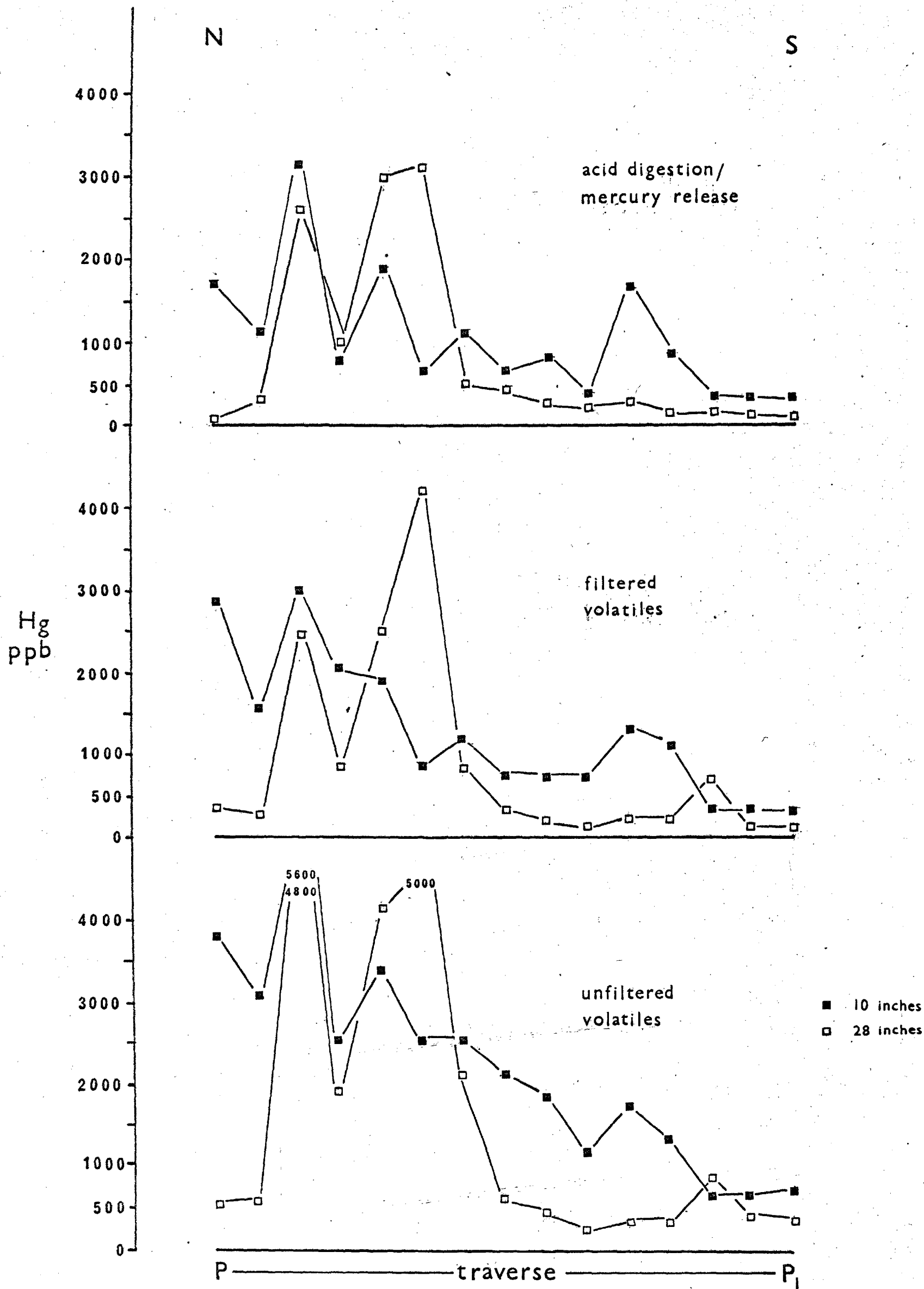


Fig. A3

A comparison of analytical techniques for determining Hg in organic-rich, mineralized soils

APPENDIX 3ATOMIC ABSORPTION AND FLAME EMISSION PROCEDURESA3.1 GENERAL

The study of Hg dispersion required sensitive and precise analysis of additional trace and minor elements in soils and associated material. Fortunately, the elements of main concern are all easily estimable by atomic absorption and flame emission spectrophotometry.

A3.2 TOTAL ATTACK PROCEDUREA3.2.1 Inorganic Material and Peats (Ref. A.G.R.G. Tech. Comm. No. 50)

Samples were weighed with a single beam torsion balance, placed in pyrex test-tubes (16 x 150 mm with rim), and 5 ml of concentrated nitric perchloric acid mixture (4:1) added. Tubes were then placed in an air-bath and the temperature gradually raised to about 200°C. Digestion was completed when all traces of perchloric acid had been distilled off.

The cooled sample was leached with 10 ml of 1N HCl to bring metals into solution. Gentle warming on a sand-bath was applied to facilitate dissolving of the residue. Iron and manganese-rich residues required prolonged heating to dissolve completely. In such cases, 25 to 50 mg of potassium metabisulphite were added to the leach to reduce Fe and Mn oxides to free ions. Eventually, digested samples were leached with 2 ml of 6N HCl which proved more effective in dissolving Fe and Mn residues. This solution was then brought up to 10 ml with demineralized water.

A3.2.2 Grass

One gram of accurately weighed, dried and pulped grass was

leached over-night in concentrated nitric acid. Enough concentrated perchloric acid was then added to make a 4:1 nitric-perchloric mixture. Heat was applied, gently at first, and then more strongly to evaporate all traces of perchloric acid. Digestion was completed when residues turned white or near white. The cooled flasks were gently warmed with 10 ml of 1N HCl to bring metals into solution.

### A3.2.3 Water

One hundred ml of the collected sample was filtered into a 250 ml conical flask. Two glass beads were introduced and the flask covered with a watch glass. Heating was applied and the sample evaporated to dryness. The cooled residue was leached with 10 ml of 1N HCl (warmed) to bring metals into solution.

### A3.3 DETERMINATION

The leached residues were allowed to settle and considered ready for atomic absorption and flame emission analysis. Cadmium, Zn, Pb, Mn, Cu, and Fe (atomic absorption) were determined directly (with required dilutions) on the 10 ml leach.

Calcium and Mg (atomic absorption) were analyzed for on 1 ml aliquots diluted to 10 ml with one per cent lanthanum solution in normal hydrochloric acid.

Sodium and K (flame emission) were determined on suitable aliquots diluted with basic ammonium carbonate solution. The pre-precipitated Fe and Al hydroxides were allowed to settle before sample aspiration. Rubidium (also flame emission) was determined directly on the original 1N HCl leach volumes.

Total Ag was estimated by a modified procedure. Samples (0.5 gm) were digested in mercuric nitrate-stabilized concentrated nitric acid (Ward et al., 1969). The leach and residue were centri-



fuges and the supernatant analyzed by atomic absorption.

Calibration curves (except Ag) were constructed from synthetic standards prepared in 1N HCl. Silver standards were prepared in dilute nitric acid. In the case of Cd and Ag, strong solutions of Ca and Na (1000 ug /ml ) were sprayed to observe any molecular absorption effects. In both cases small, but measurable, signals were obtained and sample results judged accordingly. Angino and Billings (1967) indicate Cd determination by atomic absorption is influenced by Ca and Na molecular absorption. Belcher et al. (1964) report no interference on the atomic absorption determination of silver with 1,000 fold mole excesses of Ca and Na.

#### A3.4 COLD-EXTRACTABLE PROCEDURE

The following cold-extractable solutions were used:

- i) 1N KCl
- ii) 3% glacial acetic acid
- iii) 0.1 M EDTA (Diammonium salt)

Sample weights of 100 or 200 mg were placed in 18 x 180 mm test-tubes. Ten ml of extractant were added and the sample thoroughly mixed by the vortex action of a test-tube shaking instrument ('Whirl-i-mixer' - Gallenkamp). This operation was repeated five or six times over three hours after which solutions were centrifuged and supernatants decanted into clean test-tubes. Cold-extractable leach volumes were sprayed directly for Cd, Zn, Pb, Mn, and Fe. Chemical blank values were determined and subtracted from the calibration graph for corrected results. Other than some trace impurities, the extractants gave no observable enhancement or suppression to calibration graphs compared with standards prepared in 1N HCl.

### A3.5 PRECISION OF ANALYSES

A statistical series of 11 samples was prepared (after Craven, 1954) for analytical control of Cd, Zn, Pb, Mn, and Fe determinations. Table A2 summarizes precision data by atomic absorption analysis for total (nitric-perchloric digestion) and partially extracted (EDTA and glacial acetic acid) elements. Precisions have not been determined for 1N KCl extractable elements as initial experiments showed the leach to be ineffective on Keel samples. Such studies were terminated very early on; hence, only a limited number of values are included in the text.

Batch control was implemented with occasionally duplicated samples (2 every 50), some replication (5 every 150) and chemical blanks (1 every 50).

Calcium, Mg, K, and Rb precisions have been calculated using replicate analyses (see Table A3). Individual determinations were made on selected samples and precision (at the 95 per cent confidence level) estimated with the following formula:

$$\sqrt{\frac{\sum (A - \bar{A})^2}{N - 1}} \times \frac{200}{\bar{A}}$$

N = number of determinations

$\bar{A}$  = arithmetic mean of determinations

A = individual determinations

(after A.G.R.G. Tech. Comm. No. 46)

### A3.6 ADDITIONAL NOTES

Sample weights were selected according to the type of material analyzed and the range of values expected. Soil weights of 100 and 200 mg and Decomposed Zone weights of 50 and 100 mg were normally selected. Rock weights were 100 mg. Metal extraction on

Table A2. Precisions<sup>1</sup> of atomic absorption analyses (Zn, Cd, Pb, Fe, Mn)

| Element | HNO <sub>3</sub> /HClO <sub>4</sub> digestion |           | 0.1 M EDTA leach |           | 3% acetic acid leach |                   |
|---------|-----------------------------------------------|-----------|------------------|-----------|----------------------|-------------------|
|         | Range ppm                                     | Precision | Range ppm        | Precision | Range ppm            | Precision         |
| Zn      | 6 - 2200                                      | ± 7.0%    | 2 - 570          | ± 33%     | 2 - 240              | ± 1.8%            |
| Cd      | 3 - 42                                        | ± 13%     | 1 - 26           | ± 24%     | <0.5 - 17            | ± 32%             |
| Pb      | <10 - 3000                                    | ± 15%     | <10 - 1500       | ± 16%     | all values<br><100   | not<br>calculated |
| Fe      | (< 0.01 - 2.9%)                               | ± 5.4%    | 50 - 1050        | ± 25%     | all values<br><200   | not<br>calculated |
| Mn      | 10 - 10,000                                   | ± 2.3%    | 3 - 4850         | ± 16%     | all values<br><200   | not<br>calculated |

<sup>1</sup> after James (1970), 95% confidence level

Table A3. Precisions<sup>1</sup> of atomic absorption (Ca, Mg) and flame emission (K, Rb) analyses

| Element | N | $\bar{A}$ (ppm) | Precision    |
|---------|---|-----------------|--------------|
| Ca      | 5 | 32800           | $\pm 2.2\%$  |
| Ca      | 5 | 7170            | $\pm 1.1\%$  |
| Mg      | 5 | 4930            | $\pm 3.2\%$  |
| Mg      | 5 | 18500           | $\pm 5.8\%$  |
| K       | 4 | 4275            | $\pm 12.0\%$ |
| Rb      | 4 | 47              | $\pm 13.0\%$ |

<sup>1</sup> at the 95% confidence level

small weights appeared marginally more effective with the nitric-perchloric attack.

All chemicals used were of analytical grade ('ANALAR' or equivalent) and water was demineralized by a cation/anion exchange column.

Atomic absorption and flame emission determinations were performed on Perkin-Elmer '303' and '403' instruments employing direct-reading digital accessories for calibration and element determination.

APPENDIX 4SPECTROGRAPHYA4.1 GENERAL

Semi-quantitative spectrographic analysis has been employed to increase data of secondary and tertiary importance. The method used is basically that described by Nichol and Henderson-Hamilton (1964). Sixteen elements (Ag, Ba, Bi, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sn, Sr, Ti, V, and Zn) were sought in soils, rock, Decomposed Zone, and peats. Instrument specification and method briefs are outlined in Table A4 while the useful ranges of the respective elements of the analytical wave lengths are shown in Table A5.

A4.2 SAMPLE PREPARATION

All samples were pre-ignited in a muffle furnace at 450°C for five hours. Soils, Decomposed Zone material, and rocks were ignited using the already prepared -80 mesh fraction while peats were ignited on whole air-dried portions and followed by disaggregation and sieving to -80 mesh.

A4.3 CONTROL AND PRECISION OF ANALYSES

The authors of the method state that precisions averaging  $\pm 35$  per cent to  $\pm 45$  per cent at the 95 per cent confidence level can be obtained. Here, plate control was established using an internal-external checking system. Germanium (400 ppm), as an internal standard, was determined on each sample and an operator's reference sample was included on each plate. In addition, a prepared statistical series coupled with replicate analyses (see Table A6) were used for control of Keel samples. Generally, this approach

to quality control has indicated precisions somewhat poorer, usually approximating  $\pm 60$  per cent at the 95 per cent confidence level. Abnormally high (poor) levels of precision on any one element can usually be attributed to samples containing amounts close to the detection or upper limit of the method.

Table A4. Spectrograph specifications and operating parameters

|                  |                                                                                                        |
|------------------|--------------------------------------------------------------------------------------------------------|
| Source unit      | Hilger and Watts FS 131                                                                                |
| Spectrograph     | Hilger and Watts Large Quartz FS 55                                                                    |
| Arc stand        | Hilger and Watts FS 56                                                                                 |
| Comparator       | Hilger J. A. Co. L. 90                                                                                 |
| Wavelength range | 2800-4950 Å                                                                                            |
| Emulsion         | Ilford N. 30                                                                                           |
| Anode            | Morganite SG. 305H - 5 mm Carbon<br>2.91 mm diameter and 5 mm crater                                   |
| Cathode          | Morganite SG. 305H - flat ended                                                                        |
| Exposure         | 20 seconds                                                                                             |
| Gap              | 3 mm                                                                                                   |
| Arc current      | 12.5 A                                                                                                 |
| Slit             | 15 μ                                                                                                   |
| Collimator       | Internal                                                                                               |
| Step sector      | Two steps giving three intensities in<br>proportion 1: 1/4: 1/16                                       |
| Processing       | 5 min. Kodak developer at 20°C, 10 sec.<br>stop, 10 min. fix, wash 30 min.                             |
| Sample buffer    | Spec-pure graphite, lithium carbonate,<br>germanium dioxide mixture. Mixed 1:1<br>with ignited sample. |

(after Nichol and Henderson-Hamilton, 1964)



Table A5. Spectral wave lengths and useful ranges of elements determined

| Element                                | Wave length (Å) | Range (ppm)       |
|----------------------------------------|-----------------|-------------------|
| Ag                                     | 3382.9          | 0.2 - 1000        |
| Ba                                     | 4554.0          | 20 - 10,000       |
| Bi                                     | 3067.7          | 5 - 200           |
| Co                                     | 3453.5          | 5 - 10,000        |
| Cr                                     | 4254.3          | 2 - 500           |
| Cu                                     | 3274.0          | 2 - 200           |
| Cu                                     | 2961.2          | 200 - 10,000      |
| Fe(as Fe <sub>2</sub> O <sub>3</sub> ) | 3233.1          | 1% - 30%          |
| Ga                                     | 2943.6          | 2 - 10,000        |
| Ge                                     | 3039.0          | Internal Standard |
| Mn                                     | 4034.5          | 2 - 500           |
| Mn                                     | 2933.0          | 500 - 10,000      |
| Mo                                     | 3170.3          | 2 - 10,000        |
| Ni                                     | 3414.8          | 5 - 200           |
| Ni                                     | 3050.8          | 200 - 10,000      |
| Pb                                     | 2833.1          | 2 - 100           |
| Pb                                     | 2873.3          | 100 - 10,000      |
| Sn                                     | 2840.0          | 5 - 10,000        |
| Sr                                     | 4077.7          | 20 - 10,000       |
| Ti                                     | 3377.6          | 50 - 10,000       |
| V                                      | 3185.4          | 2 - 10,000        |
| Zn                                     | 3345.0          | 50 - 10,000       |

(modified after Larsson, 1970)

N.B. Iron, Mn, Pb, and Zn analyses were used only when atomic absorption results were not available.

Table A6. Precisions<sup>1</sup> of semi-quantitative spectrographic analyses by replicate determinations.

| Element | No. of Samples | No. of Determinations | Range of Mean Values ppm | Range of Precisions | Mean Precision Value | Notes                                                                                                           |
|---------|----------------|-----------------------|--------------------------|---------------------|----------------------|-----------------------------------------------------------------------------------------------------------------|
| Ag      | 10             | 4                     | 3 - 29                   | 10 - 108%           | 48%                  | A statistical series (<0.2 to 5.0 ppm) gave a precision of $\pm 81\%$ at the 95% confidence level. <sup>2</sup> |
| Ba      | -              | -                     | (50 - 1600)              | -                   | (36%)                | A statistical series used to calculate precision. <sup>2</sup>                                                  |
| Bi      | 10             | 4                     | Not detected             | -                   | -                    |                                                                                                                 |
| Co      | 10             | 4                     | <2 - 55                  | 21 - 158%           | 89%                  | Large proportion of determinations less than 10 ppm                                                             |
| Cr      | 10             | 4                     | 11 - 42                  | 21 - 79%            | 46%                  |                                                                                                                 |
| Cu      | 10             | 4                     | 22 - 275                 | 26 - 105%           | 65%                  |                                                                                                                 |
| Ga      | 10             | 4                     | <2 - 8                   | 23 - 170%           | 62%                  | Most determinations less than 10 ppm                                                                            |
| Ge      | 10             | 4                     | 300 - 400                | 10 - 43%            | 31%                  | Internal standard                                                                                               |
| Mo      | 10             | 4                     | 4 - 14                   | 21 - 145%           | 68%                  |                                                                                                                 |
| Ni      | 10             | 4                     | 90 - 165                 | 10 - 62%            | 34%                  |                                                                                                                 |
| Sn      | 10             | 4                     | <5 - 20                  | -                   | -                    | All samples less than 20 ppm, most less than 5 ppm. Precisions not calculated                                   |
| Sr      | 10             | 4                     | 32 - 215                 | 40 - 110%           | 68%                  |                                                                                                                 |
| Tl      | 10             | 4                     | 800 - 5200               | 10 - 104%           | 46%                  |                                                                                                                 |
| V       | 10             | 4                     | 16 - 50                  | 24 - 95%            | 64%                  |                                                                                                                 |

<sup>1</sup> after Tech. Comm. No. 46, 95% confidence level

<sup>2</sup> after James (1970)

APPENDIX 5COLORIMETRIC AND TITRIMETRIC PROCEDURESA5.1 GENERAL

Atomic absorption and emission spectrography have been supplemented by colorimetric procedures for As, Sb, Se, P, Au and titrimetric methods for carbonate and organic carbon.

The methods used are briefly discussed with some accompanying notes.

A5.2 COLORIMETRIC PROCEDURESA5.2.1 Arsenic (Ref. A.G.R.G. Tech. Comm. No. 49)

A modification of the Gutzeit test has been used to analyze soil, rock, and oxidized material. Normally, samples were fused with bisulphate and acid leached. As organic-rich samples and peats tended to congeal on heating into a solid, and perhaps, not fully attacked melt, such samples were fluxed with potassium hydroxide (after Almond, 1953). Pit samples were digested with a  $\text{HNO}_3\text{-HClO}_4$  mixture (4:1) (unpublished method, Barakso and Delavault), acid leached and As determined as above. The reference quotes a precision of  $\pm 25$  per cent at the 95 per cent confidence level. A graphical plot of precision using a prepared statistical series confirmed precision estimates, but also indicated precision somewhat less (i.e.  $> \pm 25$  per cent) with values less than 50 ppm.

A5.2.2 Antimony (Ref. A.G.R.G. Tech. Comm. No. 17)

Antimony analysis of soil, rock, and oxidized material required  $\text{NH}_4\text{Cl}$  fusion, acid leaching, brilliant green complexing of Sb, and solvent extraction with toluene. Precisions of  $\pm 25$  per cent at the 95 per cent confidence level are quoted by the reference.

Experience by the writer revealed good internal duplication and replication of analysis but poor external control. Overall, precision would appear to be much poorer than the quoted figure. A prepared statistical series did not respond to produce a meaningful graphical plot. The writer believes reagent quality, particularly that of toluene and perhaps brilliant green, may serverely limit the continued use of the test. Also, the possibility of As, Tl, organic carbon, and ferric iron interferences must not be ruled out.

#### A5.2.3 Selenium (Ref. A.G.R.G. Tech. Comm. No. 51)

Selenium in soil, rock, and oxidized material was determined using a 3,3'-diaminobenzidine method. A nitric/perchloric (4:1) digestion is followed by several filtration, precipitation, and masking operations before Se complexing, solvent extraction, and colorimetric estimation. A precision of  $\pm 25$  per cent at the 95 per cent confidence level is obtainable by this technique over the 0.2 to 500 ppm range.

#### A5.2.4 Phosphorus (Ref. A.G.R.G. Tech. Comm. No. 52)

Phosphorus in soil, till, and oxidized material was determined by a vanadate-molybdate method. A bisulphate fusion is acid leached and a suitable aliquot is allowed to develop the phosphate/vanadate-molybdate coloured complex. Results within  $\pm 25$  per cent at the 95 per cent confidence level may be obtained over the range 20 ppm to 10 per cent.

#### A5.2.5 Gold (Ref. A.G.R.G. Tech. Comm. No. 48)

A few samples were analyzed for gold using a brilliant green colorimetric method. The initial acid digestion is followed by separation procedures, buffering, complexing, and solvent extraction. Precision is quoted at  $\pm 40$  per cent at the 95 per cent confidence

level. The lower limit of detection is 50 ppb.

### A5.3 TITRIMETRIC PROCEDURES

#### A5.3.1 Organic Carbon (Ref. A.G.R.G. Tech. Comm. No. 32)

Organic carbon in soil was estimated by a modification of a method originally reported by Schollenberger in 1927. Simply, organic matter is oxidized in a dichromate-sulphuric acid leach and the excess dichromate titrated with ferrous ammonium sulphate. A precision has not been reported but internal and external duplication by the writer has shown the test to be extremely reliable on samples containing less than ten per cent organic carbon.

#### A5.3.2 Carbonate (Ref. A.G.R.G. Tech. Comm. No. 53)

Carbonate in soil and oxidized material has been determined by base (sodium hydroxide) titration of excess acid (hydrochloric) remaining from a sample leached in known acid strength. No precision has been reported but duplicate analyses suggest the test satisfactory for semi-quantitative analysis.

## APPENDIX 6

### DATA RECORDS

|    |                        |                            |
|----|------------------------|----------------------------|
| As | ppm                    |                            |
| Sb | ppm x 10 <sup>-1</sup> |                            |
| Hg | ppb x 10               |                            |
| Cd | ppm                    |                            |
| Pb | ppm x 10               |                            |
| Zn | ppm x 10 <sup>2</sup>  |                            |
| Mn | ppm x 10 <sup>-1</sup> |                            |
| Fe | % x 10 <sup>-2</sup>   |                            |
| Ca | % x 10 <sup>-2</sup>   | (x 10 <sup>-1</sup> rocks) |
| Mg | % x 10 <sup>-2</sup>   | (x 10 <sup>-1</sup> rocks) |
| Cu | ppm                    |                            |
| Ag | ppm x 10 <sup>-1</sup> |                            |
| Ba | ppm x 10 <sup>2</sup>  |                            |
| Sr | ppm                    |                            |
| Ni | ppm                    |                            |
| Co | ppm                    |                            |
| Cr | ppm                    |                            |
| Ga | ppm                    |                            |
| V  | ppm                    |                            |
| Mo | ppm                    |                            |
| Ti | ppm                    |                            |

Table A7 Elemental data on Decomposed Zone material used to calculate relative enrichment ratios

| Drillhole / |           | Calculate relative enrichment ratios |     |      |      |     |          |    |    |       |     |     |     |     |    |    |       |        |        |     |    |    |
|-------------|-----------|--------------------------------------|-----|------|------|-----|----------|----|----|-------|-----|-----|-----|-----|----|----|-------|--------|--------|-----|----|----|
| Footage     |           | As                                   | Sb  | Hg   | Cd   | Pb  | Zn       | Mn | Fe | Ca    | Mg  | Cu  | Ag  | Ba  | Sr | Ni | Co    | Cr     | Ga     | V   | Mo | Ti |
| 83 25       | 25120910  | 1320                                 | 5   | 35   | 49   | 85  | 28       | 14 | 85 | 60    | 40  | 40  | 40  | 20  | 2  | 85 | 20    | 130    | 11600  |     |    |    |
| 83 54       | 56 3 5    | 44                                   | 110 | 9    | 500  | 350 | 50       | 7  | 10 | 2     | 60  | 30  | 20  | 30  | 2  | 13 | 4     | 20     | 1      | 850 |    |    |
| 83 58       | 64 50160  | 225                                  | 250 | 22   | 920  | 530 | 100      | 12 | 28 | 5     | 40  | 60  | 50  | 85  | 10 | 30 | 5     | 30     | 21600  |     |    |    |
| 83 66       | 66250 45  | 445                                  | 210 | 20   | 920  | 950 | 165      | 22 | 4  | 5     | 60  | 60  | 50  | 100 | 20 | 16 | 5     | 20     | 81000  |     |    |    |
| 83 67       | 70 45 5   | 2                                    | 210 | 10   | 860  | 900 | 140      | 26 | 14 | 2     | 60  | 60  | 20  | 40  | 2  | 10 | 2     | 10     | 6      | 500 |    |    |
| 83 79       | 79 13 5   | 250                                  | 150 | 8    | 690  | 750 | 115      | 17 | 15 | 2     | 130 | 170 | 20  | 30  | 2  | 16 | 5     | 20     | 21300  |     |    |    |
| 83 85       | 85 70200  | 950                                  | 180 | 111  | 760  | 450 | 90       | 50 | 35 | 20    | 130 | 60  | 60  | 50  | 10 | 20 | 5     | 40     | 51000  |     |    |    |
| 83 88       | 88 43180  | 850                                  | 170 | 93   | 1000 | 380 | 70       | 15 | 15 | 20    | 85  | 100 | 85  | 100 | 10 | 16 | 5     | 20     | 5      | 850 |    |    |
| 83115       | 115 45 60 | 450                                  | 150 | 50   | 1200 | 50  | 95462200 | 20 | 85 | 100   | 60  | 40  | 10  | 20  | 6  | 30 | 61000 |        |        |     |    |    |
| 86 61       | 61 55150  | 395                                  | 30  | 360  | 160  | 55  | 28       | 2  | 74 | 30    | 13  | 10  | 20  | 10  | 10 | 85 | 40    | 130    | 13000  |     |    |    |
| 86 65       | 70170380  | 1800                                 | 50  | 370  | 988  | 49  | 133      | 1  | 12 | 130   | 160 | 100 | 20  | 85  | 20 | 30 | 13    | 40     | 104000 |     |    |    |
| 86 72       | 75 45 85  | 380                                  | 150 | 220  | 588  | 27  | 53       | 1  | 12 | 10    | 40  | 20  | 40  | 50  | 5  | 20 | 8     | 30     | 22000  |     |    |    |
| 86 77       | 80 85180  | 310                                  | 170 | 12   | 794  | 28  | 53       | 1  | 10 | 10    | 85  | 10  | 30  | 85  | 10 | 8  | 5     | 20     | 2      | 850 |    |    |
| 86 82       | 88 58270  | 900                                  | 330 | 22   | 2100 | 77  | 133      | 5  | 46 | 13    | 130 | 100 | 20  | 100 | 30 | 20 | 5     | 40     | 41600  |     |    |    |
| 86 95       | 100 55100 | 825                                  | 60  | 200  | 168  | 25  | 33       | 5  | 55 | 20    | 20  | 4   | 20  | 5   | 10 | 40 | 13    | 40     | 12000  |     |    |    |
| 86102       | 107 38 65 | 225                                  | 60  | 1200 | 600  | 330 | 58       | 5  | 32 | 30    | 85  | 2   | 30  | 40  | 2  | 20 | 10    | 30     | 21300  |     |    |    |
| 86111       | 115 95190 | 175                                  | 40  | 220  | 425  | 140 | 51       | 5  | 67 | 40    | 20  | 13  | 20  | 40  | 20 | 40 | 20    | 85     | 23000  |     |    |    |
| 86116       | 118 58190 | 350                                  | 70  | 780  | 413  | 390 | 80       | 2  | 29 | 40    | 85  | 100 | 20  | 60  | 30 | 30 | 8     | 40     | 51600  |     |    |    |
| 86123       | 123 55170 | 410                                  | 30  | 750  | 350  | 350 | 73       | 3  | 44 | 30    | 20  | 30  | 20  | 60  | 20 | 30 | 10    | 50     | 22000  |     |    |    |
| 86135       | 135 18 95 | 700                                  | 170 | 400  | 850  | 520 | 112      | 10 | 51 | 20    | 30  | 40  | 40  | 40  | 2  | 30 | 6     | 40     | 11600  |     |    |    |
| 86147       | 150 63 35 | 1370                                 | 360 | 2200 | 1688 | 980 | 203      | 28 | 33 | 30    | 200 | 100 | 40  | 100 | 20 | 40 | 10    | 40     | 202000 |     |    |    |
| 117 33      | 36 5 35   | 420                                  | 84  | 875  | 1125 | 640 | 150      | 7  | 13 | 200   | 85  | 170 | 200 | 130 | 50 | 30 | 5     | 85     | 163000 |     |    |    |
| 117 38      | 42 45110  | 102                                  | 88  | 82   | 325  | 340 | 65       | 2  | 3  | 40    | 30  | 170 | 200 | 85  | 20 | 40 | 10    | 40     | 104000 |     |    |    |
| 117 58      | 58180 50  | 1500                                 | 31  | 290  | 1730 | 14  | 300      | 4  | 2  | 160   | 40  | 10  | 50  | 130 | 2  | 40 | 10    | 20     | 12000  |     |    |    |
| 117 62      | 62 60 43  | 3000                                 | 64  | 285  | 712  | 150 | 93       | 2  | 22 | 00300 | 170 | 130 | 85  | 10  | 20 | 5  | 30    | 21600  |        |     |    |    |
| 117 64      | 64 48 5   | 175                                  | 736 | 13   | 1870 | 660 | 225      | 2  | 31 | 00300 | 170 | 40  | 130 | 10  | 20 | 2  | 20    | 101300 |        |     |    |    |
| 117 66      | 66180 45  | 300                                  | 711 | 25   | 1830 | 680 | 250      | 5  | 31 | 00200 | 170 | 40  | 160 | 10  | 20 | 1  | 20    | 101300 |        |     |    |    |
| 117 71      | 75 45 55  | 168                                  | 406 | 35   | 1700 | 520 | 98       | 5  | 22 | 20    | 130 | 170 | 40  | 130 | 20 | 40 | 5     | 60     | 21600  |     |    |    |
| 117 75      | 77 45 55  | 775                                  | 350 | 7    | 900  | 540 | 93       | 5  | 5  | 20    | 200 | 80  | 60  | 130 | 10 | 13 | 5     | 20     | 31300  |     |    |    |
| 117 88      | 88190 55  | 65                                   | 171 | 18   | 1080 | 320 | 102      | 63 | 36 | 40    | 160 | 80  | 85  | 160 | 20 | 20 | 8     | 30     | 81600  |     |    |    |
| 117112      | 112140 45 | 33                                   | 266 | 31   | 1125 | 420 | 155      | 17 | 18 | 30    | 130 | 50  | 50  | 130 | 5  | 10 | 3     | 30     | 5      | 850 |    |    |

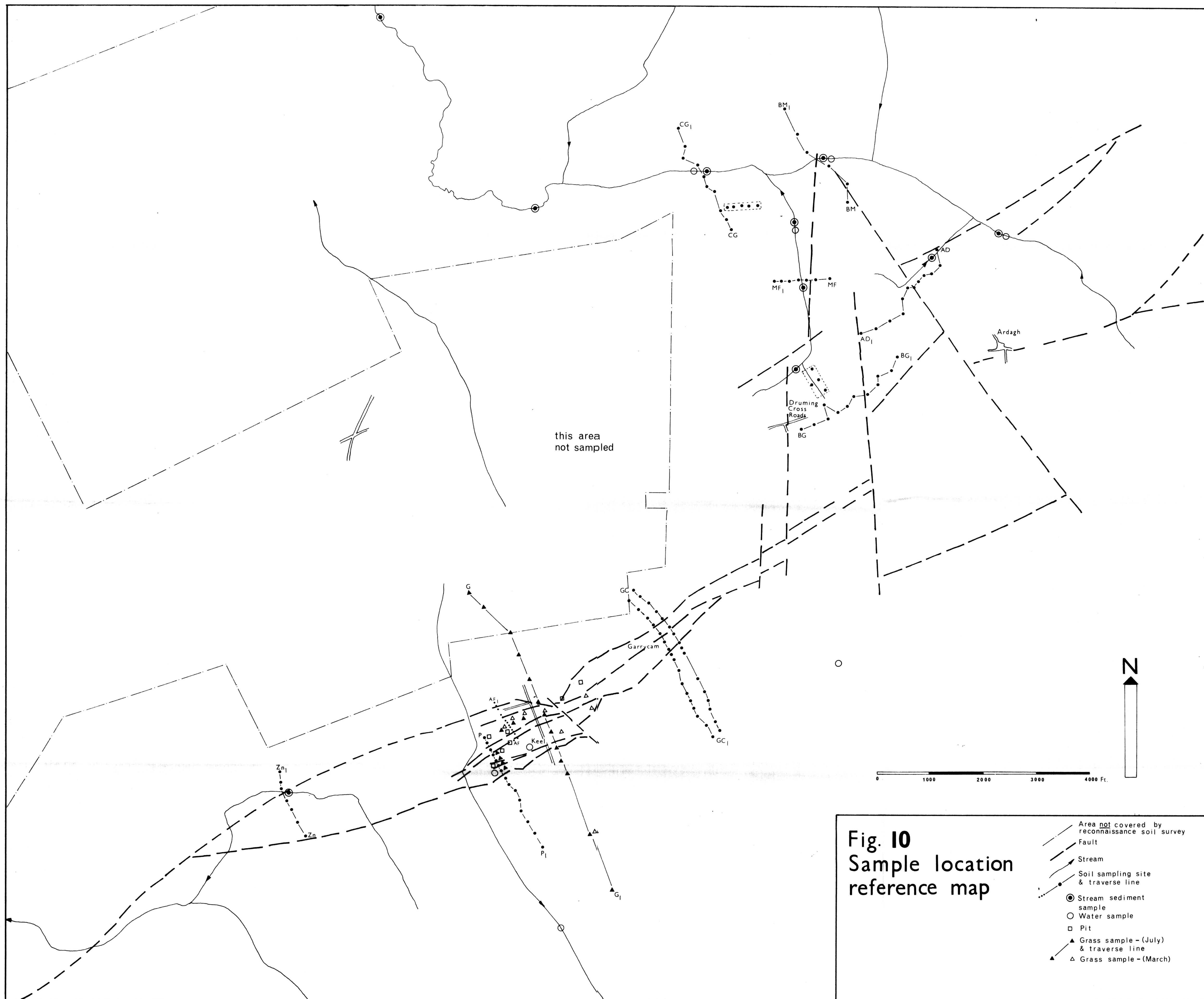
Table A8 Elemental data on mineralized tills used to calculate relative enrichment ratios

| Drillhole/<br>Footage | As | Sb  | Hg  | Cd   | Pb  | Zn  | Mn  | Fe  | Ca  | Mg  | Cu  | Ag  | Ba  | Sr  | Ni  | Co  | Cr  | Ga  | V  | Mo  | Ti    |
|-----------------------|----|-----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|-----|-------|
| 82 1                  | 1  | 43  | 35  | 113  | 10  | 80  | 91  | 3   | 23  | 18  | 34  | 30  | 10  | 5   | 40  | 30  | 20  | 30  | 10 | 40  | 52000 |
| 82 3                  | 3  | 45  | 170 | 330  | 20  | 260 | 119 | 65  | 28  | 5   | 34  | 30  | 20  | 5   | 50  | 40  | 30  | 50  | 10 | 40  | 23000 |
| 82 5                  | 5  | 70  | 285 | 700  | 30  | 650 | 300 | 230 | 38  | 3   | 32  | 40  | 40  | 30  | 20  | 30  | 50  | 30  | 10 | 40  | 81600 |
| 83 12                 | 13 | 45  | 285 | 172  | 7   | 310 | 165 | 10  | 29  | 118 | 45  | 100 | 20  | 30  | 60  | 100 | 30  | 85  | 13 | 200 | 81600 |
| 83 20                 | 20 | 93  | 330 | 480  | 101 | 900 | 650 | 482 | 62  | 10  | 43  | 85  | 16  | 40  | 30  | 85  | 130 | 40  | 13 | 40  | 21000 |
| 83 25                 | 25 | 120 | 910 | 1320 | 5   | 35  | 49  | 85  | 28  | 14  | 85  | 60  | 40  | 40  | 40  | 20  | 2   | 85  | 20 | 130 | 11600 |
| 84 10                 | 10 | 20  | 30  | 25   | 16  | 10  | 110 | 5   | 188 | 50  | 160 | 40  | 1   | 4   | 300 | 85  | 20  | 85  | 13 | 60  | 11600 |
| 84 14                 | 16 | 5   | 40  | 23   | 4   | 8   | 10  | 7   | 236 | 00  | 116 | 40  | 1   | 10  | 100 | 50  | 13  | 50  | 16 | 50  | 11000 |
| 93 1                  | 20 | 50  | 285 | 240  | 78  | 84  | 400 | 30  | 65  | 47  | 65  | 30  | 30  | 40  | 40  | 85  | 20  | 50  | 10 | 40  | 22000 |
| 93 27                 | 31 | 113 | 60  | 560  | 61  | 11  | 280 | 720 | 135 | 790 | 40  | 5   | 10  | 170 | 999 | 40  | 10  | 30  | 2  | 40  | 2 850 |
| 95 18                 | 21 | 8   | 140 | 23   | 3   | 10  | 12  | 7   | 25  | 173 | 59  | 40  | 1   | 20  | 85  | 50  | 16  | 40  | 13 | 85  | 21300 |
| 95 29                 | 38 | 43  | 285 | 1350 | 52  | 100 | 515 | 45  | 34  | 123 | 49  | 60  | 85  | 30  | 85  | 100 | 16  | 85  | 20 | 100 | 51300 |
| 96 8                  | 12 | 40  | 5   | 124  | 13  | 26  | 30  | 6   | 26  | 180 | 73  | 40  | 16  | 20  | 60  | 60  | 20  | 50  | 13 | 85  | 12000 |
| 96 12                 | 15 | 85  | 425 | 186  | 22  | 25  | 242 | 168 | 85  | 61  | 52  | 30  | 40  | 50  | 50  | 40  | 13  | 40  | 20 | 50  | 23000 |
| 96 15                 | 18 | 70  | 225 | 127  | 22  | 10  | 250 | 840 | 195 | 42  | 73  | 13  | 100 | 170 | 50  | 50  | 10  | 30  | 5  | 10  | 81300 |
| 109 10                | 12 | 20  | 150 | 22   | 10  | 28  | 124 | 6   | 34  | 93  | 84  | 50  | 13  | 16  | 60  | 130 | 30  | 85  | 20 | 100 | 31600 |
| 109 13                | 16 | 15  | 190 | 28   | 7   | 14  | 114 | 22  | 30  | 130 | 79  | 50  | 13  | 9   | 85  | 100 | 20  | 85  | 20 | 100 | 51300 |
| 109 18                | 22 | 45  | 110 | 260  | 8   | 10  | 180 | 42  | 39  | 30  | 99  | 30  | 16  | 10  | 30  | 100 | 30  | 100 | 20 | 85  | 51000 |
| 109 23                | 29 | 113 | 110 | 340  | 12  | 8   | 206 | 58  | 40  | 19  | 93  | 85  | 16  | 9   | 40  | 160 | 40  | 130 | 16 | 130 | 32000 |
| 117 12                | 15 | 15  | 30  | 28   | 3   | 10  | 19  | 5   | 27  | 192 | 58  | 40  | 1   | 10  | 60  | 85  | 20  | 40  | 10 | 85  | 21600 |
| 117 15                | 18 | 18  | 40  | 49   | 5   | 13  | 25  | 6   | 27  | 151 | 39  | 30  | 2   | 13  | 60  | 60  | 16  | 40  | 10 | 60  | 12000 |
| 117 18                | 21 | 5   | 55  | 85   | 7   | 18  | 41  | 9   | 32  | 138 | 57  | 30  | 5   | 20  | 50  | 85  | 20  | 40  | 13 | 85  | 22000 |
| 117 21                | 23 | 3   | 55  | 115  | 6   | 24  | 66  | 12  | 19  | 108 | 54  | 40  | 13  | 40  | 100 | 85  | 16  | 50  | 20 | 100 | 23000 |
| 117 31                | 32 | 1   | 11  | 71   | 4   | 98  | 250 | 95  | 45  | 7   | 2   | 20  | 30  | 13  | 40  | 50  | 16  | 13  | 10 | 20  | 11600 |
| 120 1                 | 23 | 3   | 35  | 78   | 4   | 14  | 43  | 18  | 28  | 136 | 45  | 40  | 3   | 6   | 50  | 40  | 13  | 30  | 5  | 50  | 11300 |
| 120 23                | 27 | 8   | 40  | 44   | 2   | 24  | 28  | 14  | 29  | 141 | 64  | 50  | 2   | 16  | 60  | 50  | 13  | 40  | 10 | 85  | 22000 |
| 120 27                | 29 | 5   | 65  | 54   | 3   | 13  | 31  | 15  | 27  | 125 | 48  | 40  | 2   | 13  | 50  | 60  | 16  | 40  | 10 | 50  | 21600 |
| 120 33                | 33 | 5   | 70  | 65   | 3   | 18  | 40  | 15  | 29  | 103 | 50  | 30  | 2   | 13  | 40  | 60  | 20  | 40  | 8  | 50  | 11000 |
| 120 36                | 38 | 5   | 70  | 87   | 4   | 24  | 36  | 18  | 29  | 133 | 50  | 30  | 6   | 30  | 60  | 60  | 20  | 50  | 10 | 100 | 21600 |
| 120 44                | 48 | 20  | 45  | 62   | 6   | 13  | 68  | 16  | 35  | 104 | 66  | 30  | 2   | 40  | 85  | 85  | 20  | 60  | 13 | 60  | 22000 |

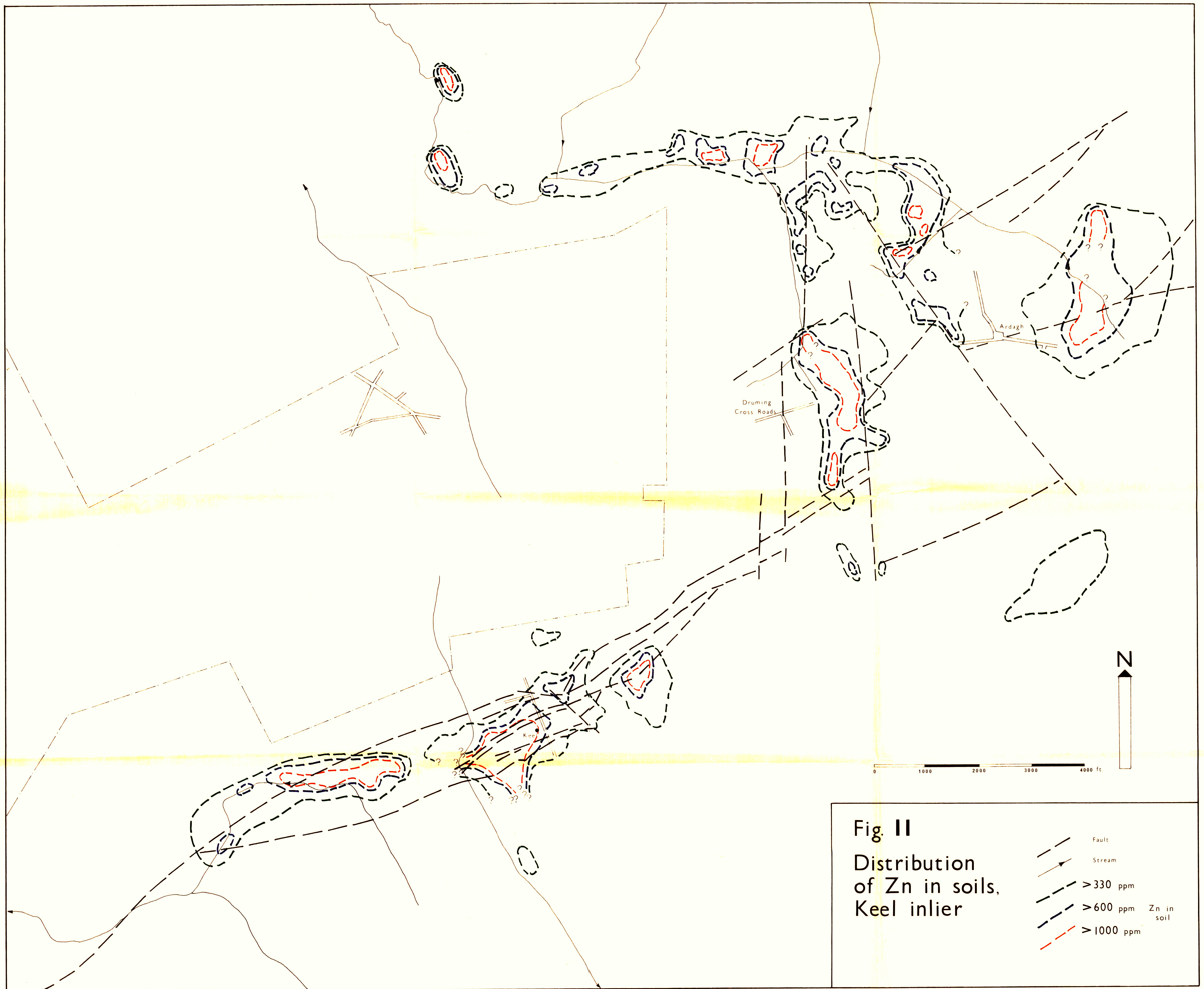


Table A9 Elemental data on rocks used to calculate relative enrichment ratios

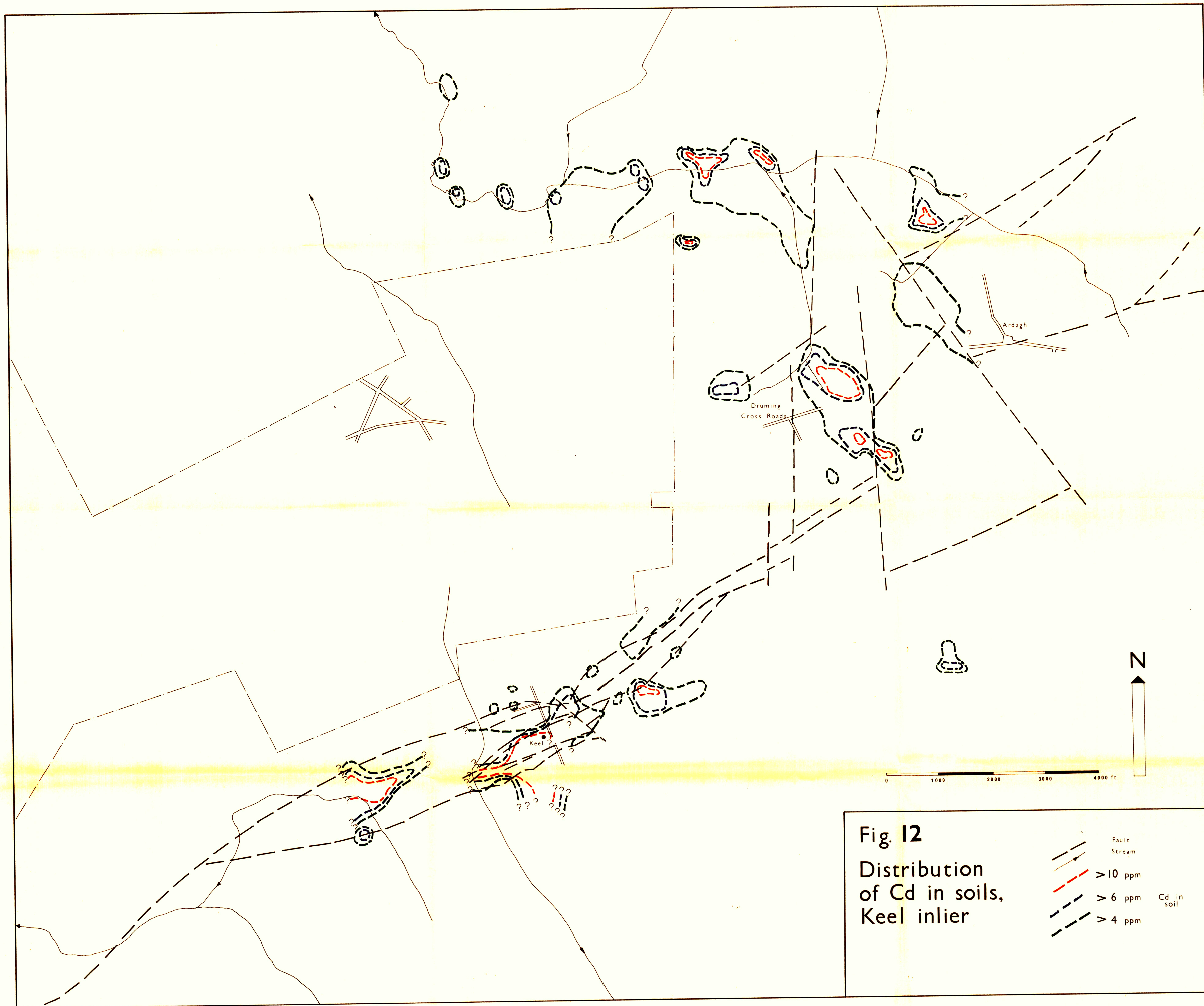
|    | Drillhole/<br>Footage |       | As     | Sb  | Hg  | Cd | Pb  | Zn  | Mn  | Fe | Ca  | Mg | Cu | Ag  | Ba    | Sr  | Ni  | Co  | Cr  | Ga  | V     | Mo    | Ti  |
|----|-----------------------|-------|--------|-----|-----|----|-----|-----|-----|----|-----|----|----|-----|-------|-----|-----|-----|-----|-----|-------|-------|-----|
| Mb | 98                    | 82 83 | 50     | 45  | 73  | 22 | 13  | 82  | 1   | 5  | 2   | 5  | 13 | 10  | 20    | 60  | 50  | 40  | 85  | 25  | 45    | 23000 |     |
| Bl | 1221                  | 2220  | 8      | 10  | 12  | 6  | 10  | 3   | 3   | 10 | 226 | 18 | 10 | 1   | 1300  | 85  | 20  | 60  | 10  | 40  | 1     | 850   |     |
| Bl | 1233                  | 0342  | 10     | 55  | 10  | 8  | 10  | 4   | 8   | 14 | 248 | 14 | 5  | 1   | 2130  | 40  | 10  | 30  | 5   | 30  | 2     | 600   |     |
| Mb | 1247                  | 8478  | 43     | 75  | 113 | 2  | 16  | 11  | 7   | 30 | 24  | 22 | 20 | 2   | 4160  | 130 | 40  | 130 | 20  | 100 | 12000 |       |     |
| Mb | 1248                  | 5490  | 58     | 65  | 50  | 6  | 23  | 11  | 13  | 24 | 133 | 18 | 40 | 8   | 16400 | 130 | 20  | 100 | 13  | 85  | 11300 |       |     |
| Bl | 1729                  | 3297  | 2      | 25  | 8   | 5  | 7   | 6   | 4   | 36 | 92  | 14 | 20 | 1   | 3200  | 60  | 30  | 60  | 16  | 40  | 11000 |       |     |
| Bl | 1731                  | 2315  | 3      | 35  | 13  | 3  | 5   | 4   | 8   | 32 | 208 | 7  | 30 | 1   | 4130  | 60  | 20  | 60  | 20  | 40  | 11300 |       |     |
| Bl | 1736                  | 6370  | 8      | 30  | 14  | 7  | 10  | 3   | 23  | 18 | 206 | 7  | 3  | 1   | 4130  | 30  | 13  | 40  | 5   | 40  | 2     | 850   |     |
| Mb | 1818                  | 5203  | 25     | 65  | 10  | 2  | 2   | 15  | 8   | 22 | 33  | 9  | 16 | 1   | 6     | 60  | 50  | 40  | 85  | 20  | 85    | 12000 |     |
| Bl | 2222                  | 2235  | 50     | 90  | 130 | 9  | 19  | 16  | 28  | 28 | 182 | 44 | 16 | 40  | 9     | 85  | 40  | 20  | 60  | 13  | 40    | 21300 |     |
| Bl | 2411                  | 2125  | 8      | 45  | 10  | 6  | 7   | 5   | 10  | 30 | 131 | 14 | 13 | 1   | 1100  | 40  | 16  | 40  | 10  | 40  | 11000 |       |     |
| Bl | 5211                  | 2118  | 3      | 25  | 17  | 5  | 2   | 5   | 7   | 23 | 183 | 13 | 10 | 1   | 3300  | 60  | 16  | 60  | 10  | 40  | 11000 |       |     |
| Mb | 5213                  | 4140  | 2      | 5   | 29  | 2  | 2   | 4   | 29  | 26 | 65  | 9  | 5  | 1   | 2     | 60  | 40  | 16  | 60  | 13  | 40    | 11600 |     |
| Mb | 5263                  | 0640  | 3      | 35  | 20  | 2  | 2   | 3   | 6   | 19 | 61  | 9  | 50 | 1   | 3     | 10  | 85  | 20  | 85  | 16  | 60    | 11600 |     |
| Mb | 5268                  | 4688  | 40     | 65  | 20  | 3  | 2   | 4   | 11  | 29 | 74  | 14 | 13 | 2   | 3     | 85  | 60  | 20  | 85  | 16  | 40    | 11600 |     |
| Bl | 6116                  | 7170  | 2      | 35  | 9   | 5  | 5   | 7   | 2   | 24 | 204 | 16 | 13 | 1   | 1400  | 50  | 16  | 60  | 10  | 40  | 2     | 850   |     |
| Mb | 66                    | 80 80 | 15     | 20  | 10  | 3  | 2   | 130 | 11  | 20 | 80  | 38 | 4  | 6   | 4     | 60  | 10  | 2   | 85  | 2   | 8     | 2     | 300 |
| Bl | 7213                  | 5153  | 5      | 35  | 30  | 6  | 2   | 10  | 5   | 31 | 121 | 19 | 30 | 1   | 9300  | 85  | 30  | 100 | 20  | 85  | 21300 |       |     |
| Mb | 7526                  | 5275  | 45     | 170 | 100 | 70 | 15  | 159 | 1   | 21 | 3   | 10 | 16 | 2   | 1     | 30  | 16  | 30  | 100 | 40  | 40    | 33000 |     |
| Mb | 7910                  | 8108  | 3      | 40  | 26  | 4  | 6   | 95  | 1   | 4  | 1   | 1  | 4  | 10  | 3     | 20  | 10  | 2   | 40  | 3   | 20    | 1     | 600 |
| Mb | 8310                  | 8108  | 2300   |     | 5   | 8  | 10  | 5   | 320 | 47 | 184 | 80 | 1  | 10  | 4     | 40  | 2   | 2   | 10  | 2   | 20    | 1     | 200 |
| Mb | 9216                  | 3163  | 45     | 35  | 19  | 10 | 15  | 8   | 6   | 24 | 135 | 58 | 3  | 20  | 2     | 85  | 20  | 10  | 30  | 2   | 20    | 8     | 400 |
| Mb | 9512                  | 4124  | 40     | 50  | 22  | 15 | 14  | 400 | 168 | 30 | 165 | 53 | 2  | 10  | 20200 | 16  | 2   | 16  | 1   | 30  | 2     | 300   |     |
| Bl | 109                   | 30 31 | 2      | 25  | 16  | 22 | 13  | 92  | 92  | 16 | 241 | 8  | 10 | 1   | 10400 | 60  | 2   | 60  | 5   | 40  | 2     | 850   |     |
| Mb | 1091                  | 60170 | 63400  |     | 116 | 17 | 176 | 200 | 52  | 35 | 11  | 10 | 50 | 100 | 6     | 50  | 160 | 40  | 160 | 20  | 60    | 24000 |     |
| Mb | 1091                  | 75180 | 450255 |     | 184 | 40 | 69  | 310 | 14  | 42 | 4   | 13 | 20 | 120 | 5     | 20  | 2   | 40  | 85  | 20  | 130   | 21600 |     |
| Mb | 1101                  | 93197 | 113180 |     | 172 | 49 | 40  | 550 | 15  | 23 | 33  | 21 | 40 | 200 | 5     | 30  | 85  | 30  | 85  | 16  | 40    | 81300 |     |
| Mb | 1102                  | 02208 | 43     | 45  | 34  | 4  | 9   | 84  | 48  | 17 | 33  | 19 | 10 | 40  | 4     | 40  | 16  | 5   | 85  | 10  | 20    | 2     | 850 |
| Mb | 1171                  | 13113 | 43     | 25  | 18  | 10 | 9   | 2   | 90  | 31 | 171 | 80 | 3  | 2   | 1     | 20  | 10  | 2   | 20  | 1   | 13    | 1     | 400 |
| Mb | 1171                  | 24124 | 43     | 30  | 18  | 14 | 10  | 17  | 266 | 46 | 180 | 38 | 10 | 20  | 13    | 85  | 13  | 2   | 16  | 5   | 20    | 1     | 600 |













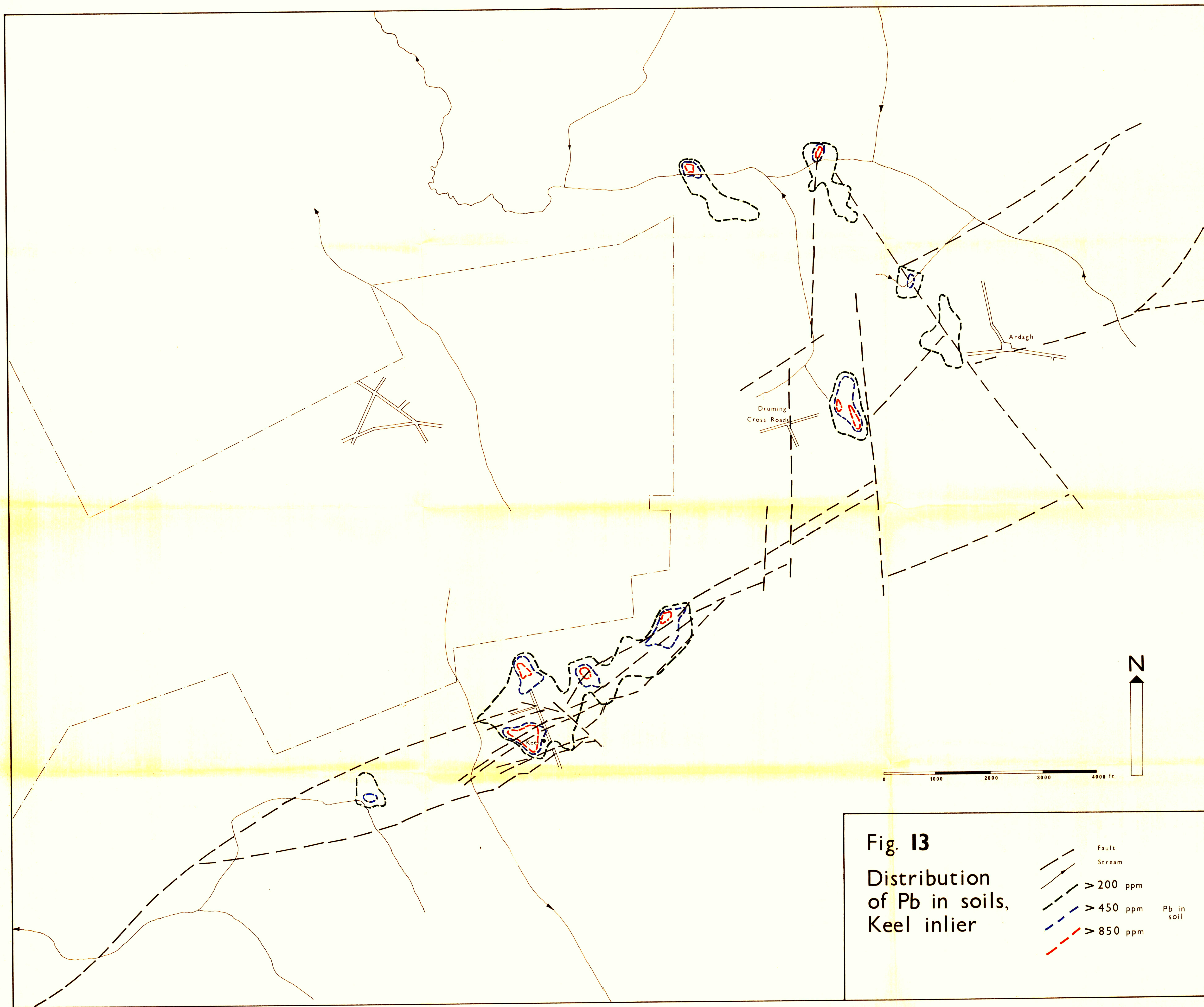


Fig. 13

Distribution  
of Pb in soils,  
Keel inlier

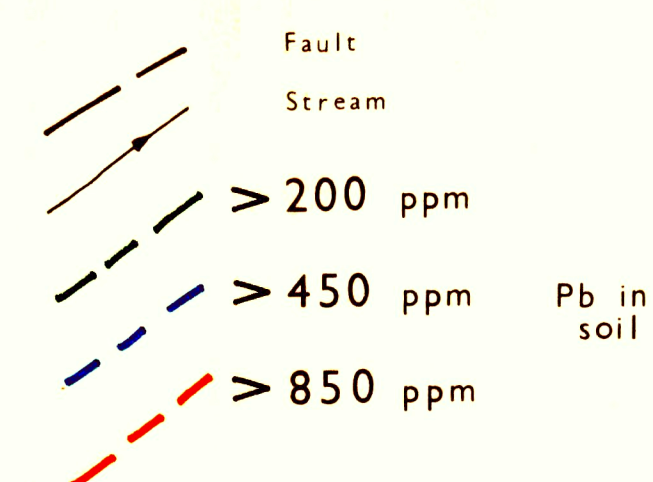
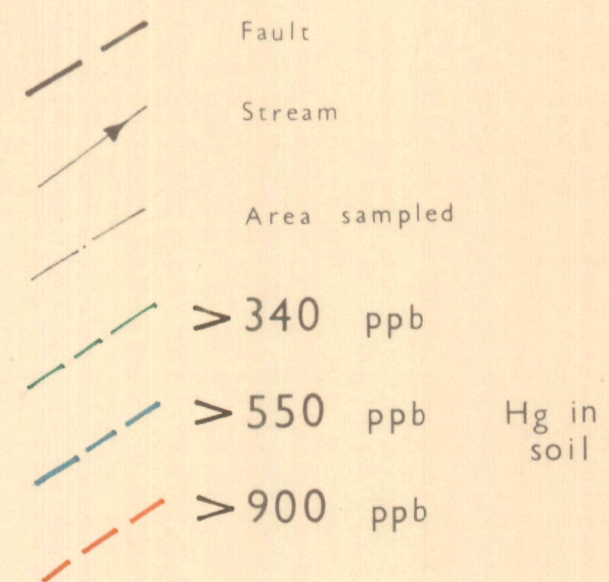


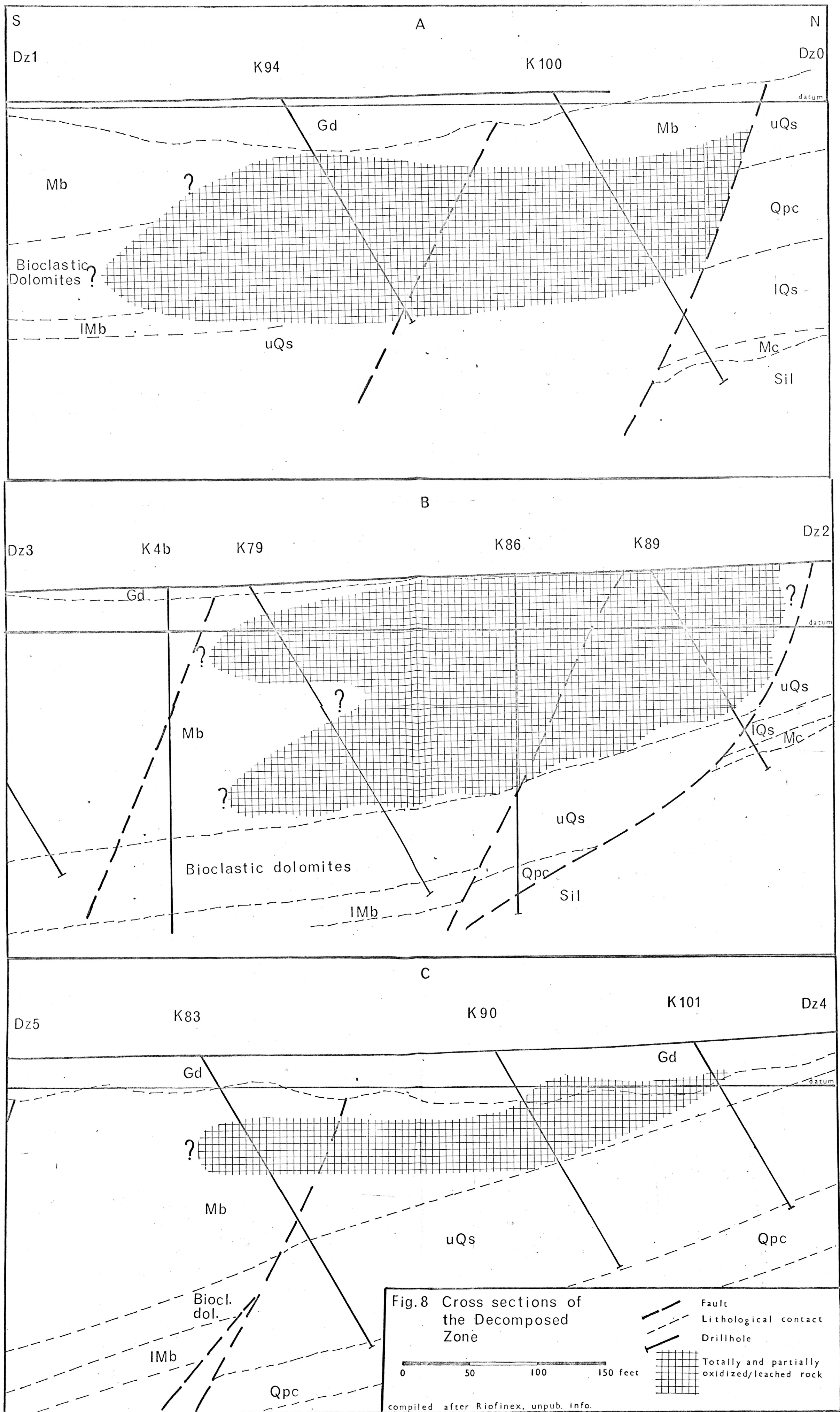


Fig. 14

Distribution  
of Hg in soils  
around Keel







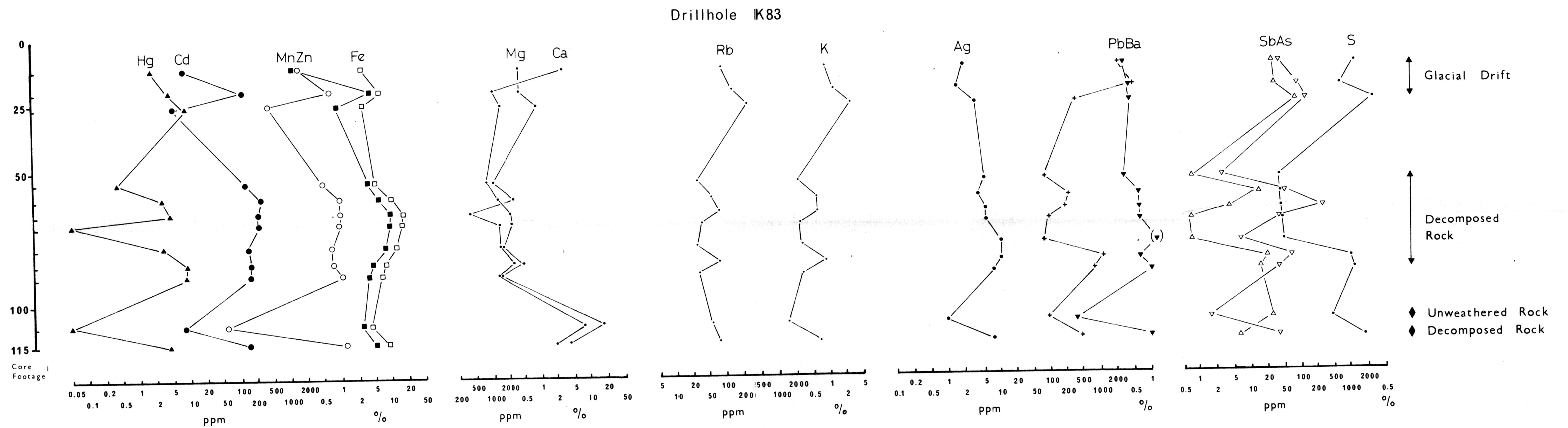


FIG. 9 Selected elements in two drillholes intersecting the Decomposed Zone

