AIR QUALITY IMPACT ASSESSMENT OF TRANSPORT-RELATED AIR POLLUTANTS

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ABSTRACT

Transportation sources make a major contribution to atmospheric pollutant concentrations particularly in the urban environment. Air quality impact assessment (AQIA) can be defined as a method of determining the relative contributions to ground level concentrations of current or future source emissions at receptor sites of interest. The methodology of AQIA has been reviewed by means of a study of monitoring and modelling methods. In this context two environmental problems have been studied.

Airports, because of the various activities that take place, are a complex source of air pollution consisting of many individual mobile and stationary sources. A review of previous measurement studies has been performed. In addition, measurements of carbon monoxide hydrocarbons (both total and non-methane), oxides of nitrogen and airborne particulate lead were performed at seven locations in and around a UK Airport (Stansted). Motor vehicles were found to be a major source of air pollutants at this airport and other airports in the UK and US.

The influence of motor vehicles on air quality was assessed by means of monitoring surveys at three sites considered representative of heavily trafficked urban and motorway locations and a rural site of minimal vehicle influence. Measured concentrations were generally most significant at the urban site although high concentrations of nitric oxide and ozone were found at the motorway and rural sites, respectively. Selected statistical techniques (distribution theory and multiple regression analysis) were applied in order to derive mathematical relationships between measured concentrations and meteorological parameters and to derive a statistical model capable of predicting high percentile concentrations from three parameter censored lognormal distributions of the air quality data. Autocorrelation of the data was found to have a significant effect on both these techniques.

The decision to reduce the alkyl lead content of petrol has been a cause of concern in terms of increased emissions of aromatic and polycyclic aromatic hydrocarbons (PAH) into the atmosphere. In order to assess the impact of increased aromatic hydrocarbon emissions, analytical methods, for the measurement of these compounds (and vehicle-related halogenated hydrocarbons) in ambient air and vehicle exhaust, have been evaluated. An adsorbent sampling tube method, involving thermal desorption and analysis by gas chromatography, was found to be suitable for ambient air measurements while a photoionisation detector/gas chromatograph was suitable for vehicle exhaust measurements.

Baseline data on ambient air concentrations of vehicle-related aromatic and halogenated hydrocarbons (and also organic and particulate lead) prior to possible changes in fuel composition, were measured at the three constrasting sites. Highest concentrations were generally found at the urban site. The ratio between toluene and benzene provided information on the role of vehicle operating mode on emissions. Dynamometer studies were performed utilising test fuels of varying total aromatic hydrocarbons and lead content and constant 97 octane number and benzene content. High engine speed and total aromatic hydrocarbon content were found to be critical in defining aromatic hydrocarbon exhaust emissions particularly for benzene. It is therefore predicted that increases in aromatic hydrocarbon concentrations in ambient air will occur.

Future developments in engine design have been briefly discussed and it is concluded that vehicle emissions of aromatic hydrocarbons and PAH will be reduced in the long term.

To Terri

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CONVERSION FACTORS

1 ppm = 1 part per million (10^6)
1 ppm = 1 part per hundred million (10^8)
1 ppb = 1 part per billion (10^9)

1 ppm CO ≡ 1167 μgm^{-3}
1 ppm NMHC, THC ≡ 667 μgm^{-3} (as CH_4)
1 ppb SO_2 ≡ 2.33 $\mu g\ m^{-3}$
1 ppb O_3 ≡ 1.5 $\mu g\ m^{-3}$
1 ppbm NO ≡ 12.50 μgm^{-3}
1 pphm NO_2 ≡ 19.17 μgm^{-3}

1 ppb benzene ≡ 3.25 μgm^{-3}
1 ppb toluene ≡ 3.83 μgm^{-3}
1 ppb ethylbenzene ≡ 4.42 μgm^{-3}
1 ppb *o*-xylene ≡ 4.42 μgm^{-3}
1 ppb *m*-xylene ≡ 4.42 μgm^{-3}
1 ppb *p*-xylene ≡ 4.42 μgm^{-3}

1 ppb 1,2-dichloroethane ≡ 4.12 μgm^{-3}
1 ppb 1,2-dibromomethane ≡ 7.83 μgm^{-3}

* conversion factors based on an ambient temperature of 20°C and pressure of 760 mm Hg

1. INTRODUCTION

Air pollution has been defined as 'the presence in the outdoor atmosphere of one or more contaminants, such as dust, fumes, gas, mist, odour, smoke or vapour in quantities of characteristics and of duration such as to be injurous to human, plant or animal life or to property, or which unreasonably interfere with the comfortable enjoyment of life and property' (Bishop, 1957). Concern over the effects of air pollution was expressed as early as 1661 by John Evelyn in his book 'Fumifugium' (Evelyn, 1661). Air pollution remains an important scientific, social and political issue as has been demonstrated recently by the arguments concerning the possible environmental consequences of reducing the content of alkyl lead additives in petrol (Anon, The London Times, 1982; Pearce, 1983).

The most common air pollutants are associated with various combustion processes (i.e. power generation and transportation) and include: oxides of sulphur (SOx), oxides of nitrogen (NOx), carbon monoxide (CO); hydrocarbons (HC) and particulates. Other air pollutants are generally associated with specific industries, some of which are listed in Table 1 (Perry and Slater, 1975).

Table 1 : Specific air pollutants and their sources
(after Perry and Slater, 1975)

Pollutant	Sources
Ammonia	Ammonia works
Sulphur trioxide	Sulphuric acid works, brickworks
Sulphides, sulphur	Generating stations, metal smelting, rubber vulcanizing, coke ovens
Chlorine and hydrogen chloride	Chlorine works, aluminium works, metal recovery plants, refuse incinerators
Chlorinated hydrocarbons	Dry cleaning establishments
Bromides	Motor vehicle emissions
Fluorine and fluorides	Brickworks, glassworks, aluminium smelting, iron works
Mercaptans	Oil refineries, coke ovens
Metals	Specific to appropriate works

Air quality impact assessment (AQIA) can be defined as a method of determining the relative contribution to ground level pollutant concentrations of specific current or future source emissions at receptor sites of interest. As a decision-making tool it is applicable when some type of emission alteration is involved (such as reducing the alkyl lead content in petrol and increasing the capacity of airports). These emission alterations have been recently summarized by Youngblood (1982) as:

(i) a change in the mass emission rate from one or more existing sources;

(ii) a change in the physical parameters of the emissions from one or more existing sources (such as release height, temperature, volume flow-rate, etc.);

(iii) the introduction or deletion of one or more sources; and

(iv) a change in the relative contributions of specific sources or source types to the total emissions.

Emissions alterations resulting from changes (ii), (iii) and (iv) can be regarded as 'engineering changes'.

Of central interest in AQIA studies are a number of factors which include:

(i) distinguishing, with sufficient accuracy, the relative impact on current air quality of specific source emissions over background concentrations (Core _et al._, 1982);

(ii) obtaining a reasonable estimate of the probable impact on future air quality of a proposed emission alteration;

(iii) estimating current and future "worst-case" pollutant concentrations and the expected frequency of their occurrence;

(iv) identifying current and potential future sites where maximum ground level concentrations are likely to occur (Bryan, 1977; Yamartino _et al._, 1980) particularly with respect to potential population exposure;

(v) comparing alternatives, including alternative sites for development;

(vi) comparing the air quality estimates with appropriate air quality standards or guidelines, as a means of placing the data in perspective with regard to possible health or other effects (Perry and Williams, 1981).

The principle activities in AQIA are (a) observation (monitoring), to determine current air quality and (b) prediction (modelling), to identify the likely future state of air quality (Johnson and Ruff, 1975). The choice of techniques applicable in a particular situation is intimately related to the situation to be assessed and requires three categories of information: emission characteristics, air quality standards or criteria, and environmental characteristics. Emission characteristics are needed to provide information on the source or sources, manner of release, and the behaviour or nature of the pollutants. Air quality standards or criteria for the pollutant (or pollutants) of interest help to define the exposure times to be considered and the distance scales over which pollutant concentrations need to be assessed. Environmental characteristics may affect the dispersion and depletion of the pollutant and may also define sites of particular air quality importance which require consideration.

Ambient air can be defined as that to which the general public is exposed, since it is the potential effects of air pollution on man which are usually of prime consideration (Larsen, 1973). Ambient air quality can therefore be defined as the quality of the ambient air near ground level, expressed as concentrations of air pollutants (Weber, 1982). The term monitoring is properly applied to the measurement of ambient air quality with time to discern any changes produced by alterations in various factors such as emissions, meteorology, etc. (Reay, 1979).

In respect to AQIA, ambient air quality monitoring (AAQM) can provide valuable information in defining 'baseline' data. Subsequent analysis can yield information on the probable levels of background concentrations, and on the temporal and spatial distribution of the particular pollutants monitored. It is then possible to infer average and worst case pollutant concentrations and the expected frequency of their occurrence (Yamartino et al., 1980), for the specific sites monitored and existing source emission situations. However, only limited information can be obtained from such surveys for determining the contribution of specific source emissions to ambient pollutant concentrations, or for identifying sites of maximum ground level concentrations and critical receptor sites.

AAQM is generally not sufficient in predicting air quality of proposed future actions (Core et al., 1982) except in the simplest situations. Such cases could include, for instance, the problem of identifying the contribution to observed ground level concentrations of the emissions released from a single source, when this is the only source of a particular pollutant. Provided adequate information is available on mass emission rates, an assessment could possibly be based solely on the results of a properly designed monitoring survey.

To obtain statistically reliable information on the relative contribution to ground level concentrations of pollutant emissions from a number of sources, or the results of 'engineering changes', would require the setting-up of a very dense and therefore, probably prohibitively expensive monitoring network (Weber, 1982). However, the availability of baseline monitoring data can prove to be an important factor in AQIA studies, not only for determining current air quality but also to ensure that modelling estimates are obtained in the most comprehensive manner.

The contribution of baseline data can be significant by serving as a basis for model validation. Comparison between measured and modelled pollutant concentrations generally require that the value of background concentrations is taken into consideration - since this will not be incorporated in the model predictions (Core et al., 1982). An estimate can be obtained, however, if monitors are suitably located for this purpose (Williams et al., 1981).

Baseline data can provide valuable supportive information with regard to model input assumptions. Interpretation of the data on a directional basis (e.g. pollution roses) (Sutton, 1982), or on the basis of specific source emission chemical or physical characteristics, may result in the identification of emission inventory errors (Core et al., 1982). Appropriate analysis of the observed pollutant concentrations in relation to meteorological parameters may indicate particular aspects of the local dispersion characteristics. Corresponding adjustments of the relevant internal model assumptions can then be made.

Validation procedures for assessing model accuracy usually depend on direct comparisons between measured and estimated values and statistical evaluation of the observed differences. However particular temporal and spatial distribution characteristics of the monitored pollutant concentrations can also be used as a basis of comparison (Keddie et al., 1979). Such characteristics can be used to test the ability of a model to reproduce the observed pollutant distribution patterns, and thus aid in assessing the performance of the model with respect to its application in a given situation.

AAQM is also important in the formation of statistical models which can be used for short-term forecasts in an area where concentration values are measured (Weber, 1982). They can also be used in determining background concentrations in other air quality simulation models.

The objectives of AAQM with respect to AQIA can therefore be summarised as follows:

(i) characterisation of present air quality as derived from particular sources;

(ii) comparison of present air quality with air quality standards or criteria;

(iii) provision of background data for air quality simulation models;

(iv) validation of air quality simulation models; and

(v) formation of statistical models for short-term forecasts of air quality.

The design of an AAQM survey is clearly dependent on the aims of the AQIA to be performed, the nature of the problem, the instruments available, the staff available and the financial constraints. However, some general guidelines are available.

Spatial scales of interest in impact assessment are usually related to the location of maximum ground level concentrations (Mahoney and Spengler, 1975), or the presence of critical receptor points such as hospitals. Preliminary dispersion modelling is often applied in defining these locations, taking into account important topographical features. For tall chimneys, an approximate evaluation of the location of maximum ground level concentration can be given by $H^2/12$, where H is the plume height at the average wind speed (Moore, 1969).

Sampling sites should be placed in a ring (or concentric rings if resources are sufficient) around discrete sources in the zone of maximum ground level concentrations with the sites separated by at least 13° (Moore, 1977).

In large urban areas, with many individual sources, a significance factor can be calculated for areas of maximum concentrations which can be used in assigning an order of priority for various monitoring sites (Munshi and Patil, 1982). Alternatively, collection of a small number of random samples at multiple locations in urban areas offers a method of obtaining more spatially-representative air quality data, less expensively than fixed-site approaches (Ott and Mage, 1981).

In determining air quality in large inhomogeneous areas, two approaches can be adopted (Keddie et al., 1979). A grid system can be defined with monitoring sites located at the corners of the grid squares. Typically a 1 km grid is adopted in urban or industrial areas and a 5-10 km grid in rural areas free from major sources of emissions. Alternatively, monitoring sites are located in areas of differing emission characteristics having regard to the likely spatial variability and prevailing meteorological conditions.

Fast-response continuous monitoring instruments and remote sensing equipment can be incorporated into a mobile sampling facility which has the advantages of acquisition of greater spatial resolution of air pollutants and differentiation between large high level sources and nearby local sources (Moore, 1976).

A number of physical constraints exist in the selection of monitoring sites. Sites should be chosen so that sampling errors due to absorption of air pollutants by vegetation (e.g. hedges, trees, etc.) can be avoided. In addition, monitoring sites should not be sheltered from the effects of distant sources or be overly influenced by local sources. It is also important that monitoring sites should be secure and adequately protected from vandalism.

A transportable monitoring system has a number of advantages which make it particularly useful for AQIA. Sites may be changed if they are found unsuitable; there is greater flexibility of geographical placement and adaptability for assessments of different air quality impact situations.

The time scales appropriate for AQIA are determined by the time scales of effects of pollutant emissions, regulatory standards or criteria, meteorological variability and emission variability (Mahoney and Spengler, 1975). In most cases the minimum time scale of the information desired is determined by the time periods specified in the applicable air quality standards or criteria, and the duration of the AAQM survey on the number of samples needed to define adequately air quality resulting from changes in the aforementioned factors. The choice of methods and instrumentation is dependent on the minimum time scale and on a number of other considerations which include: sensitivity and limits of detection, accuracy and precision, specificity, reliability, field or laboratory analysis, versatility, operation and maintenance, data output and costs of running and purchase (Reay, 1979).

A variety of mathematical techniques can be applied to data collected from an AAQM survey in order to assist AQIA. Air quality data can often be best described by simple frequency distributions (Larsen, 1971; Bencala and Seinfeld, 1976). A recent review by Georgopoulos and Seinfeld (1982) has presented the methodologies and their limitations in describing air quality through statistical distributions (such as lognormal, Weibull, three-parameter lognormal, Pearson IV (gamma) etc.). The lognormal distribution has often been applied successfully to air quality data from single point sources and homogeneous area sources (when the number of individual sources is greater than 10) (Benarie, 1980). However, deviations may occur in other situations and other distributions may be more accurately applied. Computer techniques have been developed in order to best fit distributions to air quality data (Holland and Fitz-Simmons, 1982) but simpler graphical methods may also be used.

Frequency distributions of air quality are important in AQIA in that they can be used to describe fully air quality data and can provide background concentration values and comparisons with air quality standards or criteria. Cats and Holtstag (1980) have described an empirical procedure, based on a lognormal approach, which is capable of estimating changes in frequency distributions due to the introduction of new sources in a complex industrial area, when the contribution of the new sources to the long-term average concentration within wind direction sectors can be estimated (using a Gaussian plume model). In addition, Nieuwstadt (1980) demonstrated, using the same data set, that high percentile 24 hr SO_2 values could be better calculated than by a Gaussian plume model using the relationship

$$C_{\alpha\%} = \bar{C} \exp(x_\alpha \sigma - \sigma^2/2) \qquad (1)$$

where $\bar{C}$ = long-term average

x_α = the value at which the normal distribution function $p(x_\alpha) = \alpha\%$

$C_{\alpha\%}$ = the percentile short-term concentration and

σ = the empirically derived logarithmic standard deviation of short-term concentrations.

Concentration values over specific periods of time (parts of day, seasons, years) may be averaged to investigate diurnal, seasonal or annual variations. For example, traffic-related air pollutants such as CO, at roadside monitoring sites, demonstrate a significant diurnal variation (Seifert and Ullrich, 1978) and can be correlated with diurnal variation in vehicle numbers. Similarly, sub-division of concentration values by meteorological parameters can provide interesting information. Particularly useful techniques are the use of normalised concentration roses and concentration boxplots (Graedel, 1977) which relate concentration values with horizontal wind direction and can provide remote identification and semiquantitative estimation of both sporadic and continuous sources and their relative emission rates. Using pollution rose techniques, Sutton (1982) has described a method of estimating an ambient sulphur dioxide emission inventory technique for the Southampton city area.

Multiregression techniques have been successfully applied to AAQM data which relate concentrations to meteorological parameters such as temperature, wind speed, etc. (Marsh and Foster, 1967; Smith and Jeffrey, 1972; Witz et al., 1982) and can be applied successfully in calculating pollutant concentrations.

It has been demonstrated that time series of air quality data over a number of years are strongly autocorrelated (Hirtzel and Quon, 1979). As a result, empirically-derived relationships can be demonstrated between maximum concentrations and long-term mean concentrations (Drufuca and Giugliano, 1978) and the probability distribution of the maximum concentration can be estimated as a function of the autocorrelation function, the number of measurements and certain statistical descriptors of the air pollutant concentration measurements.

An important role of AAQM is to validate modelling techniques. Numerous statistical techniques have been described (Bencala and Seinfeld, 1979; Benarie, 1980; Rao and Visalli, 1981) to validate fully a model's performance in comparison with monitored data which include the use of cumulative frequency distributions, temporal correlations, spatial alignments, extreme value statistics, time series analysis etc. However these statistical comparisons between observed and predicted concentrations are compromised by difficulties in generating accurate emission inventories, by limitations in the accuracy of the AAQM data and by other factors. They provide little direct evidence of the model's ability to approximate actual impacts from specific sources (Core et al., 1982). Using chemical mass balance studies of monitored particulate concentrations, Core et al. (1982) identified major errors in emission data bases which, when corrected, drastically improved the dispersion model's performance. Ultimately, validation procedures enable judgements to be made as to the quality of the study and as to the level of confidence that might therefore be assigned to the results.

Air quality simulation models have become an important technique in AQIA over the last twenty five years (Turner, 1979; Stern, 1980). The aim of models is to provide information on ambient air concentrations of one or more species of pollutants in space and time as related to varying emission and meteorological parameters and removal and transformation processes (Weber, 1982). The Clean Air Act Amendments of 1977 (Government of the United States of America, 1977) provided in the United States specific impetus to employ air quality models to assist in AQIA and their use has become widespread around the world with the introduction of similar legislation.

Models can be classified as deterministic, statistical or physical (Weber, 1982). A deterministic model, in terms of dispersion, was defined by Turner (1979) as 'a mathematical expression of the effects of the atmosphere upon air pollutants'. Statistical models employ an empirically derived relationship between meteorological and other parameters on measured ambient air concentrations. A physical model is a simulation of actual meteorological and topographical conditions on a laboratory scale.

A general review of all the modelling techniques is not feasible thus emphasis has been placed on the simplest deterministic models and those with a wide range of applicability with respect to AQIA.

The most commonly used model in AQIA is the Gaussian plume model and its use has been validated in numerous studies (Weil and Jepsen, 1977; Barker, 1979: Harrison and McCartney, 1980). Hanna <u>et</u> <u>al.</u> (1981) have listed the following properties that have led to the Gaussian plume model achieving a "blessed" status in the United States (United States Environmental Protection Agency, 1978) and in other countries:

(i) it has the ability to produce results that agree well with experimental data;

(ii) it has reasonable ease of calculation;

(iii) it is appealing conceptually;

(iv) it is consistent with the random nature of turbulence;

(v) it is a solution to the Fickian diffusion equation; and

(vi) other methods often contain a large amount of empiricism in their final stages.

The basic Gaussian plume equation, whose origin can be found in the work of Sutton (1932), Pasquill (1961, 1974) and Gifford (1961, 1968) assumes that material is carried downwind of the source giving rise to a plume; in this plume, lateral and vertical concentration profiles are described by Gaussian distributions characterised by standard deviations σ_y and σ_z in the horizontal and vertical directions respectively. The values of σ_y and σ_z are specified as monotonically increasing functions of distance downwind from the source for a series of different atmospheric stability conditions corresponding to different intensities of turbulent diffusion.

The basic equation for a release from a point source at height h

$$C(x,y,z) \;=\; \frac{Q}{2\pi u\sigma_y\sigma_z}\exp\left(\frac{-y^2}{2\sigma_y{}^2}\right)\left(\exp\left[\frac{-(z-h)^2}{2\sigma_z{}^2}\right] + \exp\left[\frac{-(z+h)^2}{2\sigma_z{}^2}\right]\right) \tag{2}$$

where C(x,y,z) = the concentration at distance x downwind from the source, crosswind distance y from the plume axis at height z and

u = wind speed

Q = source strength

h = source height.

The two exponential terms in the closed brackets assume that the plume is effectively reflected at the ground. A temperature inversion acting as an impenetrable ceiling for the plume may be similarly treated with downwards reflection of the plume (Clarke, 1979):

$$C(x,y,z) \;=\; \frac{Q}{2\pi u\sigma_y\sigma_z}\exp\left[\frac{-y^2}{2\sigma_y{}^2}\right] F(h,z,A) \tag{3}$$

$$\text{where } F(h,z,A) \;=\; \exp\left[\frac{-(z-h)^2}{2\sigma_z{}^2}\right] + \exp\left[\frac{-(z+h)^2}{2\sigma_z{}^2}\right]$$

$$+\;\exp\left[\frac{-(2A+z-h)^2}{2\sigma_z{}^2}\right] + \exp\left[\frac{-(2A-z+h)^2}{2\sigma^2}\right]$$

$$+\;\exp\left[\frac{-(2A-z-h)^2}{2\sigma_z{}^2}\right] + \exp\left[\frac{-(2A-z+h)^2}{2\sigma_2{}^2}\right] \tag{4}$$

where A = the height of temperature inversion. When the vertical dispersion coefficient (σ_z) becomes greater than the inversion height, equation (2) simplifes to

$$C(x,y,z) = \frac{Q}{\sqrt{2\pi}\, u\, A\, \sigma_y} \exp[\frac{-y^2}{2\sigma_y^2}] \qquad (5)$$

As a result of the difficulty in measuring atmospheric turbulence, semi-empirical typing schemes have been devised to determine σ_y and σ_z which attempt to take into account atmospheric turbulence induced by mechanical friction and thermal buoyancy. These attempt to relate certain average properties of the planetary boundary layer (e.g. temperature gradient, fluctuations in wind direction, wind speed, insolation, surface roughness and heat flux) to atmospheric diffusion (Gifford, 1976). The most widely used scheme is that proposed by Pasquill (1961) which utilizes meteorological measurements of wind speed, daytime insolation and night-time cloudiness. This has been adapted to include adjustment for different surface roughness of the ground, long distances (<100 km) (Clarke, 1979), elevated and buoyant sources (Briggs, 1974) and theoretical boundary-layer stability criteria (Pasquill and Smith, 1971). They have also been extended to attempt to account for turbulence additional to that induced by mechanical and thermal buoyancy (e.g. diffusion in near-calms, very stable conditions, over cities, over water, in the lee of flow obstacles, near highways, in irregular and rugged terrain although these lie outside the limits of Pasquill's original scheme (Gifford, 1976).

Difficulties arise in the accurate measurement of wind speed (u) which should be an average value over the plume depth. In practice, the windspeed at the effective release height (h_e) is used and is usually determined by the use of the power-law formula,

$$U = U_{10}(\frac{z}{10})^n \qquad (6)$$

where z = the height in metres and U_{10} is the observed wind speed at height 10 m. The shape of the profile depends on n which is a function of surface roughness (values of n can be found in Irwin (1979)).

Equation (2) applies to a release over a relatively short period up to a few hours with the assumptions of a constant wind and atmospheric stability. Release over longer periods, when for example, annual average or seasonally averaged concentrations are required, can be considered in terms of the frequency distribution f(i,j) both of wind direction sectors (i) and of meteorological stability classification in those directions (j). The lateral distribution (σ_y) can be ignored and the concentration at any distance assumed to be uniform across a sector.

An instantaneous release is frequently simulated by a Gaussian puff, as opposed to a plume for a more prolonged release in steady conditions. Puff diffusion parameters (σ) have been measured in few field experiments (Hanna et al., 1981) and the consequent use of plume-derived σ's has been criticised (Gifford, 1975).

Pollutant emissions from industrial stacks often have high velocity and/or temperature. The plume rise must therefore be evaluated in order to estimate correctly the effective release height of emission (h_e) due to momentum and buoyancy effects. This rise can be estimated from the heat flux, wind speed and atmospheric stability. Methods of estimating plume rise have been extensively reviewed previously (Briggs, 1975; Hanna et al., 1981). These effects may be represented in the Gaussian plume model by adjusting the effective source height (h_e) and the dispersion parameter to account for the increased initial spreading of the plume.

Line sources, such as emissions from vehicles on a road, may be treated by integrating equation (2) along a line perpendicular to the plume axis, and replacing the source strength Q by the emission per unit length of the line source. A review of line source models has recently been presented by Chock (1982).

The Gaussian plume model is appropriate for flat homogeneous terrain, and for travel distances over which similar meteorological conditions persist. Although the model can be adjusted to account for many other conditions (complex terrain, removal processes etc.) Pasquill (1978) has documented departures from the Gaussian form in the distribution of dispersed material in the atmosphere for the

(i) vertical spread in the first km downwind of a surface release and

(ii) the vertical distribution of power-station plumes.

In the first case, models based on Lagrangian similarity theory can be applied successfully to estimate ground level concentrations from surface releases of pollutants. In the second case, a Gaussian shape can be fitted over the lower half of the power-station plume which as Pasquill (1978) points out, is the significant half in the development of the ground level concentrations to its maximum value.

Another difficulty occurs in low wind speeds (when equation (2) has a singularity). Gaussian plume models are not valid when the rate of lateral dispersion is comparable to, or larger than, the rate of advection. Comparisons between observed and expected ground level concentrations in low wind speeds have been presented (Koch and Thayer, 1971; Wilson _et al._, 1976), in which the Gaussian plume model has been found to _over_-predict concentrations. This is due to the highly variable wind direction, under low-wind speeds, which enhances horizontal and vertical diffusion. However, under near-calm conditions plume segments may become stationary which could result in higher concentrations (Benarie, 1980). Alternatives to the use of Gaussian plume models in near calm conditions can be provided by Gaussian puff models (Yamartino, 1976; Ludwig _et al._, 1977).

Diffusion in non-uniform and non-stationary wind and turbulence fields, such as may occur with sea-breeze flows and valley flows, are important to assess because it is in these areas of complex topography where much of industry is situated. As a consequence of the inhomogeneity of these local circulations, Gaussian plume models are inadequate in assessing pollutant dispersal.

As an alternative, particle trajectory models, based on G.I. Taylor's theorem (1921), can be successfully used in assessing complex flow situations (Reid, 1979; McNider and Pielke, 1980). In addition, Lagrangian similarity models have been used for shorelines fumigation studies (Kerman, 1982). Physical models provide a method of studying the flow kinetics in neutral and unstable conditions in regions of complex topography and help to define the most appropriate method of assessment (Egan, 1975).

Complex chemical reactions (such as those occurring in urban photochemical smogs) cannot be treated adequately using Gaussian plume methodology. Numerical solutions of the gradient transfer equation,

$$\frac{dC}{dt} + \frac{udC}{dx} + \frac{vdC}{dy} + \frac{wdC}{dz} = \frac{d}{dx}\ k_x \frac{dC}{dx} + \frac{d}{dy}\ k_y \frac{dC}{dy}$$

$$+ \frac{d}{dz}\ k_z \frac{dC}{dz} + \text{source, sink and transformation terms} \qquad (7)$$

where k_x, k_y and k_z are diffusion coefficients in corresponding cartesian directions (varying in space and time), have previously been used in this context, utilising a fixed co-ordinate approach (also referred to as Eulerian, grid and multibox) and a trajectory approach (also referred to as Lagrangian and moving cell) (Turner, 1979).

Many reviews of these models exist (Eschenroeder, 1975; Dermerjian, 1976; Johnson *et al.*, 1976) which highlight the advantages and disadvantages of these techniques. Lamb and Seinfeld (1973) have described the fundamental mathematics which have recently been developed into a comprehensive modelling system which incorporates recent developments in photochemistry, turbulent diffusion, surface removal processes, objective analysis procedures and numerical solution techniques (McRae *et al.*, 1982). These methods are, of necessity, complex and require long computational time and large computer storage. However, they are very useful in the evaluation of control strategies for photochemical air pollution formation.

Long-range transport models can also utilise solutions of the diffusion equation, similar to those used in photochemical models (Knox, 1974; Maul, 1977). Gaussian plume techniques are not applicable because of the following reasons (Gifford, 1975); there is a paucity of reliable diffusion data for distances greater than 10 km, the effect of wind shear on horizontal diffusion becomes significant, large scale air motions affect plume trajectory and the assumptions of a constant wind speed and homogeneous and stationary turbulence do not hold at these distances.

Gaussian puff models have been used as an alternative, in the case of accidental releases of radioactive material, by assuming source emissions as a series of discrete puffs of material throughout the release period beyond 10 km (ApSimon and Goddard, 1976). Detailed discussion on long range transport of air pollutants can be found elsewhere (Bass et al., 1979; Bass, 1980; Eliassen, 1980).

It is evident from the above that the modelling and monitoring aspects of AQIA are mutually consistent and can be used in conjunction with each other. An orderly approach to the principles and procedures involved in AQIA and the determination of the associated requirements is desirable.

In practice, an AQIA is generally initiated as part of a specific air quality management programme and therefore depends on a clear definition of objectives which such a study would be expected to meet within the framework of the particular programme (Rossano and Thielke, 1976). Once these have been identified, it is then possible to structure the study optimally on the basis of the specific data needs.

A comprehensive AQIA study would encompass the following components (Weber, 1982):

(i) an emissions inventory component (including data on the current and expected emission characteristics for all the relevant sources);

(ii) a meteorological component, providing information on the past and current atmospheric dispersion characteristics, from which future conditions can be inferred;

(iii) a monitoring component providing an assessment of current air quality;

(iv) a data management programme, essential for data acquisition, storage, processing and analysis;

(v) an operating model component, capable of effectively integrating the available information, which can be used to simulate current air quality and to predict changes resulting from alterations in the emission characteristics.

However, the ultimate usefulness and relevance of the individual elements are determined by a number of constraints which include (Rossano and Thielke, 1976):

(i) the specific needs of the potential data users (in terms of quantity, quality, time, etc.);

(ii) existing resources, particularly funds, manpower and existing facilities and developed methods;

(iii) available technology, e.g. equipment, and techniques;

(iv) possible legal requirements, e.g. air quality standards or criteria;

(v) operational criteria, such as cost-effectiveness, performance requirements, etc.: and

(vi) operational responsibility.

Generally, the existing resources, especially in terms of available funds, are found to be the major limiting factor.

Since each situation is characterised by a unique combination of factors, the development of each AQIA will necessarily depend on case-by-case considerations. Thus a systematic approach to AQIA is essential in order to achieve a reasonable compromise between desirable objectives and limiting factors.

The evaluation of proposed future action(s) in terms of overall impacts may well be influenced by considerations other than those derived from AQIA. These include costs expected to result from acceptance or rejection of the proposals or possible alternatives, energy costs and resulting social and other environmental impacts.

1.1 Transport-Related Air Pollution

In a modern society, transport-related sources (aircraft, petrol-engined vehicles, diesel-engined vehicles, railways and coastal and inland shipping) are a major contribution to atmospheric concentrations of CO, HC, NOx, particulates, photochemical oxidants and lead (Cohn and McVoy, 1982).

Table 2 : Summary of estimated UK emission of selected pollutants for 1976 (expressed as percentages) (after Apling et al., 1979)

Source	SO_2	NO_x (as NO_2)	CO	Smoke
Mobile (road)	2.0	25.8	87.5)	23.9
" (rail)	0.4	2.5	0.2)	
Power generation	54.0	44.9	0.6	-
Commercial and Industrial	39.0	23.5	0.6	7.6
Domestic	5.6	2.8	8.4	68.5
Incineration	-	0.2	0.6	-
Agricultural burning	-	0.2	2.2	-
Evaporation	-	-	-	-

Table 3 : General survey of hydrocarbon emissions in the UK from various sources in 1975 (after Brice and Derwent, 1978)

Source	Estimated Annual Emission in 10^3 tons	% of Total
Mobile sources	660	49.8
Stationary sources	40	3.0
Industrial processes		
- petroleum ind.	160	12.1
- general ind.	120	9.1
Evaporation of solvents	310	23.4
Solid waste disposal	35	2.6

Comparisons of selected pollutants emitted from mobile and stationary sources are presented in Tables 2 and 3 which demonstrate the importance of transport-related air pollutants. In addition, the mode of emission of these sources, such as from vehicle exhausts and evapo-

Table 4 : Central London kerbside concentrations of selected pollutants in 1975 (after Apling et al., 1979)

Pollutant	Arithmetic Mean	Percentiles of Distributions of Hourly Means		
		50th	90th	99th
THC (ppm)	3.5	3.1	5.4	9.8
CO (ppm)	2.9	2.5	5.0	8.7
NO (pphm)	6.5	5.2	12.5	26.3
NO_2 (pphm)	4.8	4.5	7.5	10.8

ration, will give rise to greater ground level concentrations than emissions from power generation and industrial processes which are normally discharged at sufficient height for adequate dispersal. Table 4 includes typical kerbside concentrations of total hydrocarbons (THC), CO, nitric oxide (NO) and nitrogen dioxide (NO_2) found in central London in 1975.

An emission inventory of hydrocarbons in the United Kingdom (UK) further demonstrates the importance of petrol-engined vehicles as a source of hydrocarbons in comparison to other transport-related emissions (Table 5) (Brice and Derwent, 1978).

Table 5 : Annual hydrocarbon emissions from mobile sources in 1975 (after Brice and Derwent, 1978)

Mobile Source Category	Annual Emissions in 10^3 tons	Percentage of Total HC Emissions	Notes
Aircraft	6	0.5	Exhaust
Petrol-engined vehicles	490 94	37.0 7.1	Exhaust Evaporative
Diesel-engined vehicles	10	0.7	Exhaust
Railways	10	0.7	Exhaust
Coastal and inland shipping	47	3.5	Exhaust
TOTAL	657	49.5	

Hampton et al. (1982) have identified over 300 different gas phase hydrocarbons, with greater than five carbon atoms, generated by motor vehicles, which fall largely into homologous series of normal and branched alkanes, alkenes, and various alkyl series based on cyclopentane, cyclohexane, benzene, styrene, indane, naphthalene and decalin. Also identified were compounds not associated with homologous series including indene, divinylbenzene, phenylacetylene, benzaldehyde and phenol.

In addition to combustion products from exhausts, evaporative losses and unburnt material can be emitted such as tetra alkyl lead (TAL) compounds (tetra ethyl lead, tetra methyl lead, etc.) and the lead scavengers 1,2-dichloroethane (EDC) and 1,2-dibromethane (EDB). Other high molecular weight hydrocarbons, which are emitted, frequently associate with particulate matter and a list of these polycyclic aromatic hydrocarbons (PAH) is presented in Table 6. In general, PAH from automobiles represent 4-8% of total amount of PAH in the urban environment emitted in respirable form (Rondia et al., 1983).

Table 6 : PAH identified in vehicle exhaust (after United States Environmental Proection Agency, 1972)

anthracene
phenanthrene
fluoranthene
pyrene
alkylpyrene
triphenylene
chrysene
alkylcrysene
benz[a]anthracene*
alkylbenz[a]anthracene
naphthacene
11H-benz[b]fluorene
benz[a]pyrene*
benz[e]pyrene*
benz[k]fluoranthene
perylene
benzo[j]fluoranthrene*
alkylbenz[a]pyrene
11H-benz[b]fluoranthene*
dibenzo[a,h]anthracene*
benzo[ghi]perylene
anthanthrene
inden]1,2,3-cd]fluoranthene
inden[1,2,3-cd]pyrene
dibenz[a,l]naphthacene
dibenz[a,e]pyrene*
dibenz[a,l]pyrene*
coronene
dibenz[b,pqr]perylene
dibenz[b,h]phenanthrene

* indicates that compound is known to be carcinogenic

As mentioned previously, EDC and EDB are added to petrol as scavengers for the lead compounds produced in the combustion system. The predominant particulate lead compounds emitted from exhaust are PbBrCl, $PbBrCl.2NH_4Cl$ and α-$PbBrCl.NH_4Cl$ which are subject to reaction with atmospheric sulphates (Biggins and Harrison, 1979). Other particulates may be emitted as droplets of unburned hydrocarbons, rubber, metal, asbestos from brake shoes and entrained dust (Cohn and McVoy, 1982).

Railways and shipping do not generally contribute any significant impact to air quality (Cohn and McVoy, 1982). However airports are a complex source of air pollution consisting of many individual mobile and stationary sources such as aircraft, service vehicles, motor vehicles, heating plants, fuel storage facilities and engine testing areas. The major pollutants emitted from these sources have been identified as HC-nonmethane (NMHC) and THC, CO, NO_x and particulates (Bastress, 1973).

Aircraft pollutant emissions contribute 1% of HC, NO_x and CO on a national scale (United States Environmental Proection Agency, 1971). Aircraft HC emissions rank as the eleventh highest annual emission contributor in comparison with the top 60 source categories in the United States (United States Environmental Protection Agency, 1977). On a regional scale, airports contribute up to 3% of the total annual emissions in surrounding urban areas (Cirillo et al., 1975; Jordan, 1977) but in rural areas an airport may represent the largest single contributor of total emissions in its area of air quality influence (Yamartino et al., 1980).

1.2 Health Effects, Air Quality Standards and Guidelines for Transport-Related Air Pollutants

Carbon monoxide is a colourless and odourless gas formed through the incomplete combustion of fossil fuels which contain carbon. Carbon monoxide is not particularly toxic to plants or harmful to materials. However, it does combine readily with haemoglobin, the blood protein responsible for oxygen transport within the body. The affinity of haemoglobin for CO is over 2000 times its affinity for oxygen, and carboxyhaemoglobin is a more stable compound than haemoglobin. Thus increasing exposure to CO leads to increasing displacement of oxygen in the blood. Excessive exposure to CO in humans can result in impairment of vision and judgement, cardiovascular changes and in extreme concentrations, death.

The two most important oxides of nitrogen are NO and NO_2. NO_2 has been shown to produce adverse effects on human health which can be classified as effects on:

1. pulmonary function (Shy et al., 1970);
2. incidence of acute respiratory disease (Melia et al., 1980);
3. prevalence of chronic respiratory disease (Yoshida et al., 1976).

NO plays an important role in photochemical reactions that lead to the formation of several reaction products including NO_2. Secondary pollutants, comprised principally of ozone (O_3), peroxyacyl nitrates (PAN), aldehydes, ketones and aerosols, are formed through complex reactions involving HC, NO_x and other chemical species and meteorological factors (temperature, humidity and sunlight) (Dermerjian et al., 1974). Criteria 7 (World Health Organization, 1979) notes that 90% of the total oxidants is in the form of O_3. Evidence from a controlled human exposure study indicates that exposure to O_3 concentrations of 0.1 ppm (200 $\mu g/m^3$) can cause impairment of breathing in healthy human subjects. Other effects of photochemical oxidants are eye irritation and respiratory distress (Goldsmith and Friberg, 1977).

Individual organic species of transport-related air pollutants have specific health effects at high concentrations. However, little data is available on possible health effects due to long term exposure to low concentrations, although this is an area of increasing concern (Singh et al., 1981). Benzene has received a great deal of attention because of its carcinogenic potential (Albert, 1978) and its pathological effects of pancytopenia (decreased levels of one or more of the elements in circulating blood) and chromosomal aberrations. Toluene and xylenes are also suspect, although detailed toxicity studies are not yet complete.

The lead scavengers, EDC and EDB, are bacterial mutagens and suspect carcinogens with EDB expected to have a unit risk 50 times greater than EDC (Singh et al., 1981).

The health effects of mixtures of SO_2 and particulate matter are usually studied because of a general agreement that a synergistic effect occurs when both forms of pollution are present in air. Studies have shown that mortality increases when 24 h average concentrations of combined SO_2 and smoke exceed 2000 μg m^{-3} (World Health Organisation, 1979) and that subjects living in communities with high concentrations of SO_2 (annual average 125-200 μg m^{-3}) and suspended particulate matter (annual average 150-225 μg m^{-3}) show a higher incidence of respiratory complaints than those in communities with low ambient concentrations.

Particulates emitted from vehicle exhausts (petrol and diesel) have been shown to be mutagenic (Pierson et al., 1983) and, although the relationship between mutagenicity and carcinogenicity is not exact, it is a good indication of possible health effects.

Little data is available on possible health effects of trace level exposure to TAL although trialkyl lead metabolic derivations of TAL have been found in brains of deceased humans at concentrations possibly sufficient to inhibit enzyme action (Nielsen et al., 1978; Grandjean and Nielsen, 1979).

Possibly the most contraversial health effect is that of vehicle-related lead. The acute toxic effects of lead are well documented, but sub-clinical lead poisoning as a result of long-term exposure to relatively low doses is not so well defined. Children are more vulnerable to the possible effects of lead because they have a higher intake of lead per unit body weight related to their rapid growth rates. It has been calculated that a 2 year old child absorbs about 50% as much lead through ingestion, and 40% as much through inhalation compared with an adult (McCorry, 1979). Approximately 40% of lead inhaled is absorbed into the blood stream and 5-10% is ingested; although other sources of lead are important such as ingestion from lead in drinking water (Ainsworth et al., 1977; McCorry, 1979). Large particles of lead-contaminated dusts are retained in the upper respiratory tract and either swallowed or discharged in secretion. The absorbed portion circulates via the liver and most is then excreted back into the gut in bile. Lead is excreted in urine, sweat, hair and nails, but a proportion accumulates in the bones and teeth. The concentration of lead in these reservoirs reflects the degree of total exposure while blood-lead levels reflect recent exposure to lead.

Recognition of possible effects in children is difficult because many of the supposed symptoms are behavioural. It has been discovered that lead inhibits glucose metabolism in the brain by interfering with the enzyme adenylcyclase, affecting mitochondrial function, resulting in possible lasting impairment and behaviour changes. Barltrop (1971) found that the enzyme δ-amino laevulinic acid dehydratose (ALA-δ), essential in the synthesis of haem, is inhibited at blood-lead levels that are considered normal, producing symptoms of anaemia.

A number of workers, in particular David et al. (1978), Needleman (1979), Yule and Lansdown (1981), have established that there is an association between hyperactivity, below average IQ and blood-lead levels above 300 μg l^{-1}. The Lawther report (Government of Great Britain, 1980) was critical of previous work on the effects of lead, but did note a positive correlation between blood-lead and health effects. The health effects of lead remain a contraversial issue.

No standards exist in the United Kingdom (UK) for ambient air pollutants except in the case of smoke and SO_2 for which the UK is subject to a European Communities (EC) Directive. Table 7 presents standards promulgated in the United States and the European Communities and guidelines instituted by the Government of Great Britain and the WHO. In the future, the UK will be subject to further EC Directives which are likely to be similar to those introduced in the US (Weaving and Benjamin, 1980).

The US Standard for non-methane hydrocarbons was promulgated for the control of oxidants and not as a health-related standard. Secondary standards do not relate to possible health effects of pollutants.

The US standard for CO is at present under review and is liable to be reduced from 35 ppm to 25 ppm, with no secondary standard and the

Table 7 : Air quality standards and guidelines established by national and international bodies

Pollutant		Averaging Time	Primary Standard Levels	Secondary Standard Levels
Particulate matter	NAAQS	Annual (geometric) mean	75 µgm^{-3}	60 µgm^{-3}
	NAAQS	24 Hours[a]	260 µgm^{-3}	150 µgm^{-3}
	WHO	Annual (arithmetic)	40-60 µgm^{-3}	-
	WHO	24 hours	100-150 µgm^{-3}	-
	EC	Annual (geometric) mean	68 µgm^{-3}	-
Sulphur dioxide	NAAQS	Annual (arithmetic) mean	80 µgm^{-3} (0.03 ppm)	- -
	NAAQS	24 hours[a]	365 µgm^{-3} (0.14 ppm)	-
	NAAQS	3 hours[a]	- (0.5 ppm)	1300 µgm^{-3}
	WHO	Annual (arithmetic) mean	40-60 µgm^{-3} (0.015-0.002 ppm)	-
	WHO	24 hours	100-150 µgm^{-3}	-
Carbon monoxide	NAAQS	8 hours[a]	10[c] mgm^{-3} ppm) (9 ppm)	10 mgm^{-3} (9 ppm)
	NAAQS	1 hour[a]	40 mgm^{-3} (35 ppm)	40 mgm^{-3} (35 ppm)
Nitrogen dioxide	NAAQS	Annual (arithmetic) mean	100 µgm^{-3} (0.05 ppm)	100 µgm^{-3} (0.05 ppm)
	WHO	1 hour[b]	190-320 µgm^{-3} (0.10-0.17 ppm)	-
Ozone	NAAQS	1 hour[a]	235 µgm^{-3} (0.12 ppm)	235 µgm^{-3} (0.12 ppm)
	WHO	1 hour	100-200 µgm^{-3} (0.05-0.1 ppm)	120 µgm^{-3} (0.06 ppm)
Hydrocarbons (non methane)	NAAQS	3 hours[b] (6 to 9 am)	160 µgm^{-3} (0.24 ppm)	160 µgm^{-3} (0.24 ppm)
Lead (particulate)	NAAQS	3 months	1500 ngm^{-3}	-
	DHSS	Annual	2000 ngm^{-3}	-

[a] not to be exceeded more than once a year

[b] not to be exceeded more than once a year

NAAQS = US National Ambient Air Quality Standards - Government of the United States of America (1970)

WHO = World Health Organization Health Criteria - World Health Organization (1977, 1979 a and b)

EC = European Community Directive - Commission of the European Communities (1980)

DHSS = UK Department of Health and Social Sectурity Working Party on Lead in the Environment - Government of Great Britain (1980) number of exceedences per annum allowed to rise from 1 to 5 (Government of the United States of America, 1980). Also under consideration is a short-term NAAQS for NO_2 in the range 0.02-0.05 ppm hourly average (Yamartino _et_ _al._, 1980) and introduction of a NAAQS for benzene (Goldstein, 1983).

1.3 Lead in Petrol

Alkyl lead compounds have been added, as anti-knock agents, to petrol since 1923 in order to increase the octane rating (a general measure of fuel reactivity with regard to preflame conditions). In the United States, stringent gaseous exhaust emission controls by means of noble metal catalysts were introduced because of the prevalence of photochemical smog in ambient air. As a result, unleaded fuel was necessary because such catalysts are intolerant of lead.

In Europe, considerable public and scientific debate over the environmental effects of lead emissions from vehicle exhausts has resulted in increasing pressure on governments to promulgate legislation to limit the alkyl lead content in petrol (Government of Great Britain, 1980). In the United Kingdom the alkyl lead content is to be reduced from 0.4 to 0.15 g l^{-1} by the end of 1985 (Government of Great Britain, 1980), the limit currently adopted in West Germany and Sweden (Associated Octel, 1982). The government is committed to lead-free petrol by the target date of 1990 (Government of Great Britain, 1983).

In order to maintain the octane quality of petrol, the approach that most oil refining companies have adopted is to increase the aromatic content of petrol (Hall _et_ _al._, 1983). The changing situation in Europe with respect to the alkyl lead content of petrol and its associated aromatic content is presented in Table 8. In reducing the alkyl lead content to 0.15 g l^{-1} in 1976, the aromatic content in West Germany was increased by approximatly 20% (Associated Octel, 1976; Associated Octel, 1982) and a similar increase is predicted for other European countries which intend to reduce the lead content in petrol to 0.15 g l^{-1} (Hall _et_ _al._, 1983).

Table 8 Alkyl lead and aromatic hydrocarbon content of European premium petrol (after Associated Octel, 1981; 1982)

Country	Alkyl Lead Content		% Aromatics (v/v)	
	1980	1981	1980	1981
Italy	0.64	0.38	29.0	32.6
France	0.5	0.39	33.1	36.8
UK	0.45	0.38	35.1	34.5
West Germany	0.15	0.14	42.7	43.1

The extra costs in reducing lead in petrol result from higher vehicle fuel consumption, or from higher refinery costs, or a combination of both (Ireland, 1980). The more severe refining process necessary to maintain the octane rating consumes more energy in two ways. The yield of petrol from a barrel of crude oil is reduced, and more energy is consumed in the refining process itself. In West Germany, 690,000 t of oil products are consumed in fulfilling the petrol lead law, corresponding at present prices to several hundred million DM annually (Repenning, 1980).

In Europe, the average premium grade octane quality has increased from a research octane number (RON) of approximately 82 in the early 1950's to approximately 98-99 by the mid-1960's. The improvement in octane quality has been accompanied by a corresponding increase in the compression ratios of engines. The improvement in engine efficiency and its associated fuel consumption benefits has been well documented and is illustrated in Figure 1, where it can be seen that each unit change in compression ratio is associated with a fuel consumption change of *ca* 5% by volume.

The increasing content of aromatics in petrol will result in elevated ambient atmospheric concentrations of aromatic compounds as a consequence of evaporative and vehicle exhaust emissions (Oelert *et al.*, 1974) which are causes for concern.

Aromatic hydrocarbons can undergo photochemcal decomposition in the atmosphere (Hov *et al.*, 1978). The reactivity of each species differs, increasing in the order of benzene < toluene < xylene < trimethylbenzene (Altshuller and Bufalini, 1971).

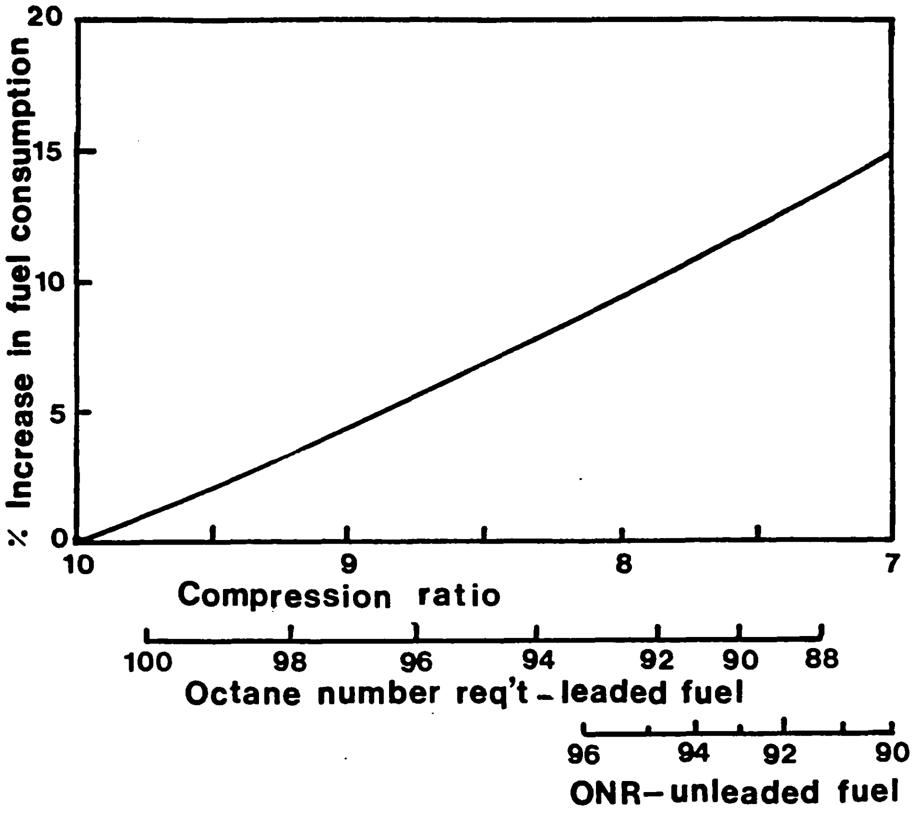


Figure 1 : Association between compression ratio and fuel consumption

The aromatic content of petrol is associated with emissions of PAH either in the gas phase or associated with particulates (Gross, 1973; Candeli et al., 1974). A basic formation mechanism has been proposed in which benzene molecules are attacked by small, unsaturated radical species (Prado and Lahaye, 1983). The necessary conditions for PAH production are the presence of benzene and a high concentration of the radical intermediates which then form stable compounds. Multiple ring systems are autocatalytic and promote further ring condensation. Fuel aromatic content has been shown to influence particle-associated PAH emissions almsost linearly and a 10% increase in aromatics to increase emissions of benzo[a]anthracene, benzo[a]pyrene and benzo[ghi]perylene by approximately 10% (Pedersen et al., 1980). However, the exact relationship between aromatics and PAH is by no means clear at present (Pedersen et al., 1980; Nunnermann, 1983). Indeed, different vehicles operated under the same conditions and fuels emit significantly different amounts of PAH (Egeback and Bertilsson, 1983).

1.4 Air Quality Measurements in the Vicinity of Airports

National and international concern over the effects on ambient air quality of airport- and aircraft-related emissions both inside and outside of airport boundaries has been expressed over a number of years (Parker, 1971; Keddie et al., 1973; Sawada and Nishi, 1974; Naugle and Fox, 1981; Segal and Yamartino, 1981). This concern has been reflected in the United States legislature by introduction of engine emission standards on 17 July, 1973 for Commercial and General Aviation aircraft (Government of the United States of America, 1973) and a Notice of Proposed Rule Making (NPRM) in the Federal Register (Government of the United States of America, 1978) to announce the intention of the Environmental Protection Agency (EPA) to amend the 1973 engine emission regulations. In order to assess the effect of aircraft emissions on ambient air quality, numerous studies involving either modelling and/or measurements have been performed in the United States (Lorang, 1978).

In the UK public concern over the environmental effects of proposed airport developments has also resulted in a number of air quality assessment projects (Parker, 1975; Williams et al., 1980; Nichols et al., 1981). Other studies have also been performed in France and Japan (Delsey et al., 1978; Sawada and Nishi, 1974).

It has been stated that 'studies involving the measurement of ambient air quality in the vicinity of airports are in general the most complex, expensive, time consuming, but also the most persuasive data to explore the impact of aviation on ambient air quality' (Naugle, 1980).

CO is formed during fuel-rich operation of jet engines, for example, during the taxiing and queueing modes of aircraft operation (Naugle and Fox, 1981). However, motor vehicles also produce CO (in the UK motor vehicles account for almost 90% of national CO emissions (Apling et al., 1979)) and this has resulted in difficulties in assessing aircraft emissions.

During monitoring at Los Angeles International Airport (LAX) repeated violations of the NAAQS one-hour CO standard of 35 ppm (Government of the United States, 1970) have been observed at two satellite terminals and ticketing buildings (Los Angeles Air Pollution Control District, 1971). A maximum one hour average of 46 ppm was observed outside a satellite terminal and 141 ppm inside the ticket building. However it was suggested that these excursions were due to aircraft and ground service vehicles combined and that access traffic was responsible for violations at the ticket building. A monitoring site in a residential area, close to the downwind side of a runway at LAX also observed frequent violations of the one-hour standard (United States Environmental Protection Agency, 1972) although a modelling study suggested that the contribution due to aircraft was ca. 20%.

Thayer et al. (1974) documented violation of the one-hour standard and also the eight-hour standard of 9 ppm CO at Washington National Airport (DCA). This occurred at terminals, maintenance areas and, in the case of the eight-hour violation, at runways and areas heavily influenced by access vehicles. A less extensive survey by the Argonne National Laboratory did not observe violations while monitoring in open areas near runways at DCA (Wang et al., 1974), suggesting that CO problems mainly occurred around airport buildings at DCA.

Pollution rose data at Gatwick Airport in the UK also indicated that nearby roads were the major influence on CO concentrations around these airports (Williams et al., 1980). No violations of the one-hour or eight-hour standards were observed at this airport or at Heathrow (Nichols et al., 1981), which also had considerably lower arithmetic mean and ninety-ninth percentile values for CO than London off-street measurements. Similar results were observed at Seattle-Tacoma International Airport utilising a 'roving' monitoring rationale to isolate possible 'hot spots' in CO concentration (Greenberg, 1978). This study also suggested, from monitoring data, a correlation between CO and aircraft activity at the end of a runway where aircraft were queueing and also with the presence of service vehicles.

The problem of queueing and takeoff operations was specifically addressed in a further study at DCA undertaken jointly by the EPA and Federal Aviation Administration (FAA), using CO as a tracer for queueing operations, to permit an unambiguous assessment of the aircraft contribution to nearby pollutant concentrations (Yamartino et al., 1980). Measurement of CO concentrations was performed near an aircraft queueing area for a period of one month. Concentrations at monitoring sites located approximately 150 m from the queueing area were less than 3 ppm for 90% of the time. The one-hour standard was never approached but the eight-hour standard was exceeded by 38% in one single episode, although it has been suggested that airport snowploughs operating intensively in the vicinity of the monitoring sites were responsible. The authors, by extrapolation of the cumulative frequency distribution up to the 99.99% probability level, suggested that a maximum hourly CO concentration of ca. 5 ppm may be expected once a year at approximately 300 m from the queueing area (a distance at which public exposure might be expected). However, it must be pointed out that this study was limited to only one month's data; DCA does not operate between 10 pm and 6 am when meteorological conditions are often stable, resulting in poor pollutant dispersal; nearly all aircraft operations are medium range jets, primarily using the JJ8D-17 engine which has a relatively low CO emission rate (ca. 88 kg h^{-1}) and finally that the runway monitored during the study at DCA is shared between arrivals and takeoffs, resulting in a longer queue time than airports with dedicated departure runways.

The measurement of emissions from queueing aircraft at LAX has also been studied (Segal, 1980) at distances of 220 m and 320 m from the south and north runways respectively. The maximum queue observed was of eight aircraft between 1742 and 1801 hours on 18 April 1979. During this period the hourly mean CO concentration was 1.5 ppm.

This work at LAX is supported by a measurement programme at Boston's Logan Airport which also found CO concentrations to be much lower than standards in queueing areas at the end of runways during a period of high activity (Smith and Heinhold, 1980). Maximum concentrations occurred when winds from nearby urban centres coincided with a strong nocturnal temperature inversion.

The Concorde air quality monitoring and analysis program, conducted at Dulles, provided a unique opportunity to measure CO plumes from taxiing aircraft utilising a three tower array (with thirteen monitoring points) at 65, 116 and 166 m distances from the centre line of the runway (Smith et al., 1977; Segal, 1977; Segal, 1978a). Commercial aircraft types monitored included Concorde, Boeing 707, 727, 737, 747, McDonnel-Douglas DC8, DC9, DC10 and L1011. Peak instantaneous CO concentrations reached 10 ppm at the first tower but maximum aircraft contribution to the hourly average ground level concentration remained below 0.06 ppm per aircraft. Extrapolations to 300 m from the taxiway indicated a maximum hourly concentration of 0.03 ppm CO per aircraft.

The impact of general aviation has been assessed during a major fly-in of 3000 aircraft at Lakeland Airport, Florida (Segal, 1978b). The study, using a three monitor array, assessed various operating modes (take-off, landing, taxi measurements at low and high activity and in one instance queueing). The study concluded that, in areas of possible exposure to the public, CO concentrations were less than 2 ppm for a projected one hour time period.

In order to separate clearly airport and background urban pollution components, a study of airport emissions was carried out at Williams Air Force Base (AFB), Arizona (Daley and Naugle, 1979). The airport contributes approximately 60% of the CO pollution in the vicinity of the base and the level of aircraft activity is comparable to Chicago O'Hare Airport. The CO concentrations monitored were low (arithmetic hourly means varying between 0.108 and 0.363 ppm) with the maximum hourly CO concentration detected at the site which was most heavily influenced by motor vehicles.

NO_x emissions from aircraft consist mainly of NO. Typical emission measurements of Pratt and Whitney JT 3D, JT 8D and JT 9D jet engines have demonstrated that between 92 and 96% of NO_x emissions are accounted for by NO (Pratt and Whitney, 1972). NO is formed when jet engines are operating at high temperatures typically during approach, takeoff and climb-out modes (Jordan and Broderick, 1979).

The conversion of NO to NO_2 is a function of plume dispersion rate and transport time, sunlight intensity and background concentrations of NO, NO_2 and O_3. A typical rate constant for this conversion has been derived by Jordan and Broderick (1979) as 27 $ppm^{-1}min^{-1}$ in a 'typical' urban atmosphere.

Thayer _et_ _al._ (1974) monitored NO_2 at three sites at DCA and the data indicated that the NAAQS annual NO_2 standard (0.05 ppm) was violated at all three sites and the maximum and 98th percentile one-hour average were high enough to indicate repeated violation of any likely short-term NO_2 standard. As in the case of CO, motor vehicles are significant sources of NO_x, accounting for more than 50% of low level emissions of NO_x in the UK (Apling et al., 1979) and consequently the measurement study could not determine what fraction of the concentration was attributable to aircraft. A previous study at DCA (Platt et al., 1971) only measured NO_x (i.e. not differentiating between NO and NO_2) and because of the difficulty of assessing possible violations of NO_2 air quality standards, will not be considered further.

A limited measurement study of NO_x and NO was carried out at Chicago O'Hare Aiport (Rote et al., 1973) and presented data indicating that little of the ambient NO_x was NO at the sites outside the airport (the highest fraction of NO was measured at the terminal area).

Measurement programmes at DCA (Wangen and Conley, 1975), Dulles (Smith et al., 1977), Boston (Smith and Heinhold, 1980), Hartsfield International (Brown et al., 1976) and Williams AFB (Yamartino et al., 1980) presented NO_2 concentration data all in the same 2.5-5.0 pphm range as the potential NO_2 standard.

NO_2 concentrations measured at Gatwick airport (Williams et al., 1980) were in a similar range (1.8-6.9 pphm). Pollution rose data suggested that other sources (such as nearby roads) than the airport were dominant.

In order to resolve airport pollutant sources from non-airport sources, quick-response NO_x monitors were sited near the end of a runway at DCA to assess takeoff/landing emissions (Yamartino et al., 1980). Observed values of background-subtracted and integrated pulse concentrations did not exceed 20 pphm for NO or NO_x and 5 pphm for NO_2. The extrapolation to the 99.99% probability level was 0.3 ppm which is close to a possible hourly air quality standard. However this approach must be treated with some caution, as continuous data were only collected over one month. Further analysis of elevated hourly NO_x concentrations demonstrated that 0.2 ppm was surpassed on more than ten separate occasions, with background concentrations accounting for more than 70% of the mean total NO_x, which underlines the importance of non-airport sources. The authors have also demonstrated the value of observed pulse integrated concentrations regressed against observed departure rates for assessing actual aircraft impact. In the case of DCA this revealed an average aircraft impact of about 0.005 ppm as compared to the annual average 0.05 ppm air quality standard and the observed annual average of 0.03 ppm at DCA.

NMHC are emitted at airports either through evaporative fuel losses, motor vehicle exhausts, or jet engine exhausts, particularly at low power settings i.e. in idling, taxiing or queueing areas (Yamartino et al., 1980). Previous studies at Logan Airport, Boston (Smith and Heinhold, 1980), Williams AFB (Yamartino et al., 1980), Gatwick (Williams et al, 1980) and Heathrow (Nichols et al., 1981) all report relatively high NMHC concentrations in the range of 0.2-10 ppm i.e. well above the air quality standard. In summarising US measurement studies, Yarmartino et al. (1980) concluded that comparison of the wide ranging concentrations among receptor points on and near airports revealed that aircraft do indeed contribute significantly to the elevated NMHC concentrations in the vicinity of airports. Pollution rose data from Gatwick (Williams et al., 1980) supported a similar conclusion. However the US NAAQS, in common with other studies, was exceeded at all sites including the site chosen for the measurement of background concentrations.

The measurement study conducted at Dulles (Yamartino et al., 1980) performed simultaneous measurements of THC and CO from taxiing aircraft and correlated peak concentrations of CO against THC with a coefficient (r) of 0.72 and demonstrated the viability of THC estimation through scaling of CO concentrations (where background concentrations may be separately identified).

A measurement study at Osaka Airport, Japan (Sawada and Nishi, 1974) measured instantaneous concentrations of formaldehyde, acrolein and CO and empirically deduced a linear relationship between them. Formaldehyde and acrolein were measured in the range 15-400 ppb and 1-60 ppb respectively.

A measurement study of aromatic and halogenated hydrocarbons in the vicinity of Gatwick Airport (Tsani-Bazaca et al., 1982) has provided useful data on source identification.

By comparing hydrocarbon profiles of petrol and two commonly-used aviation fuels (Shell Jet and Shell Avgas 100L) with ambient hydrocarbon profiles at six sites around the airport, it was possible to identify tentatively the three sites most influenced by aircraft operations. The ratio between toluene and benzene (C_7/C_6 = 3.19-12.9) at these sties was much higher than those found at an urban site heavily influenced by traffic in London (C_7/C_6 = 2.3-2.8) (Tsani-Bazaca et al., 1981) and two sites at Gatwick Airport (2.05 and 2.48) near road interchanges. The remaining site seems to have been influenced by a source other than aviation or traffic. This technique of source identification, by means of hydrocarbon profiles and ratios, can provide useful data.

A study characterising aircraft turbine engine particulate emissions (Stockham et al., 1978) found the composition of the particles to be essentially carbon and to be less than 0.1 µm in size. Data were also presented on the average geometric mean particle size in idle (0.045 µm) and takeoff (0.097 µm) operating modes of a Pratt and Whitney JT 8D engine.

An earlier study at John F. Kennedy Airport found that ca. 10% of the average total suspended particulate material was organic in nature. Aircraft engines (piston and turbine) have been demonstrated to emit considerable amounts of benzo(a)pyrene (2-10 mg min^{-1}), associated with particulates. Benzo(a)pyrene has been found in soil and vegetation samples in diminishing content with increasing distance from the runway complex (Shabad and Smirnov, 1972). Other particulate-associated PAH are also emitted from aircraft engines (Robertson et al., 1980) and as a class of compounds, represent a source of carcinogenic pollution.

The US primary NAAQS for particulate matter is 75 µgm^{-3} annual geometric mean and 260 µgm^{-3} daily geometric mean (Government of the United States of America, 1970).

The study at John F. Kennedy Airport presented total suspended particulate data for six sites in the vicinity of the airport (Nolan, 1964) and by analysis of parallel samples (northwest and southeast of the airport) concluded that the airport did not contribute significantly to above average particulate pollution levels. Total suspended particulate concentrations measured were in the range of 28-287 μgm^{-3}.

More recent data from the Norfolk Naval Air Station (Virginia) did not exceed the US NAAQS on any occasion (Wood et al., 1978) and the size distribution, which varied between 0.43 and 11.0 µm suggested that aircraft were not the dominant source.

The EC directive on ambient smoke concentrations is 68 μgm^{-3} median of daily means (Commission of the European Communities, 1980). Smoke concentrations at Heathrow (Parker, 1971) and Gatwick (Williams et al., 1980) were similar to smoke measurements at nearby National Survey sites. The directive limit was not exceeded at Gatwick but a maximum daily smoke concentration of 91 μgm^{-3} was measured at Heathrow. However the maximum concentration at the nearest National Survey site (Hayes and Harlington) was 188 μgm^{-3}. These concentrations were not considered to be high by National Survey standards.

No significant difference in particulate pollution, as measured by a soiling index, at sites up and downwind of John F. Kennedy Airport (Nolan, 1964) indicated that airport sources of particulates were not significant when compared to local urban sources.

Particulate lead analysis at Gatwick were similar in range (200 -588 ngm^{-3}) to UK urban sites (McInnes, 1976) and, as jet fuels contain negligible amounts of lead, this emphasizes the importance of motor vehicles as a source of particulate pollution.

Little work has been performed to date on the problem of odour pollution associated with airports. However, an odour survey was carried out as part of the John F. Kennedy study (Nolan, 1964). This study surveyed the major types of odours in the vicinity of the airport, particularly those that can be attributed to aircraft exhaust. The results indicated that odours from combustion and other sources were a problem but these could not be specifically related to jet aircraft emissions, and that sources other than the airport were the main contributors.

A number of air quality measurement studies have also provided information on the dispersion of jet exhaust by examination of concentration time histories which can be incorporated into air quality models.

The study at DCA (Yamartino *et al.*, 1980) examined in detail NO_x concentrations from aircraft during take off and, by comparison between observed and predicted peak concentrations and pulse durations, extrapolated the parameters of initial size ($\sigma_x(0) = 21.1$ m, $\sigma_z(0) = 25.7$ m) and also tail length (L = 52 m).

The measurement program at Dulles provided useful information on plume rise of taxiing aircraft exhausts (Smith *et al.*, 1979; Yamartino *et al.*, 1980). Evidence was presented indicating a 10 s delay in plume rise (due to the momentum of the jet exhaust) and determined plume dimensions ($\sigma_x(0) = 18$ m, $\sigma_z(0) = 8$ m) and plume rise (36 m^2s^1).

Photographic and infra-red imaging studies have also provided useful evidence of plume behaviour in various meteorological conditions suitable for inclusion into air quality simulation studies (Daley and Naugle, 1979; Tank and Hodder, 1978).

The study at Williams AFB demonstrated that ground separation of jet exhaust plumes can occur, generally during unstable atmospheric conditions with low wind speeds (Daley and Naugle, 1979). This can result in the exhaust plume passing over pollutant monitoring stations without detection.

1.5 Analytical Techniques

A variety of suitable analytical techniques are required for the measurement of transport-related air pollutants. A summary of commonly employed methods for the measurement of gaseous air pollutants is presented in Table 9. A further description of selected monitoring instrumentation is given below which is typical of that employed in AQIA.

A schematic diagram of a chromatographic analyser, capable of sequential measurements of CH_4, CO and THC is presented in Figure 2.

Table 9 Summary of commonly employed methods for the measurement of gaseous air pollutants (after Perry and Harrison, 1976)

Pollutant	Measurement Technique	Sample Collection Period	Response Time[a] (continuous techniques)	Minimum Detectable Concentra- ations
Total Hydrocarbons	Non-dispersive infrared spectroscopy (Ndir)		5 s	1 ppm (as hexane)
	Flame ionisation analyser		0.5 s	10 ppb (as methane) 1 ppm
Carbon Monoxide	Ndir		5 s	0.5 ppm
	Catalytic methanation/FID	b		10 ppb
Sulphur Dioxide	Absorption in hydrogen peroxide/ titration/	24 h		2 ppb
	Absorption in hydrogen peroxide/ conducitivity determination		3 min	10 ppb
	Absorption in tetrachloro- mercurate/ spectrophotometry	15 min		10 ppb
	Flame photometric analyser		25 s	0.5 ppb
	Fluorescent analyser		2 min	0.5 ppb
	Coulometric analyser		1.5 min[c]	3.5 ppb
Oxides of Nitrogen	Conversion to nitrite/azo dye formation	30 min		5 ppb
	Chemiluminescent reaction with ozone		1 s	0.5 ppb
Ozone	Oxidation of potassium iodide/ spectrophotometry	30 min		10 ppb
	Oxidation of potassium iodide/ electrolytic cell		30 s[d]	10 ppb
	Chemiluminescent reaction with ethene		3 s	1 ppb
	Uv absorption		30 s	2 ppb

(a) Time taken for a 90 per cent response to an instantaneous concentration change

(b) Instantaneous concentrations measured on a cyclic basis by flushing the contents of a sample loop into the instrument

(c) Time taken for a 63 percent response to an instantaneous concentration change

(d) Time taken for a 75 per cent response to an instantaneous concentration change

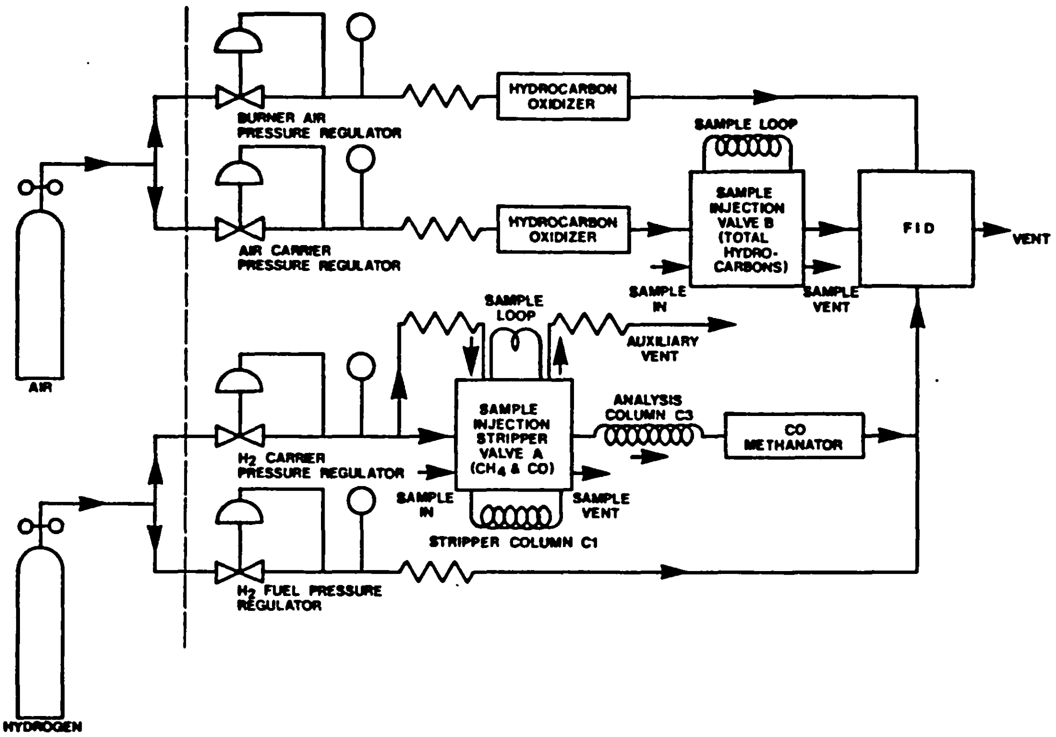


Figure 2 : Schematic diagram of a Beckman 6800 air quality chromatograph for the measurement of CH_4, CO and THC

Hydrogen (H_2) carrier gas flushes a small air sample from a sample loop through a stripper column packed with an adsorbent porous polymer, for sufficient time to allow passage of CH_4 and CO but not the heavier components which are removed by backflushing. A molecular sieve column separates CH_4 and CO which are passed to a flame ionisation detector (FID) via a catalytic methanator. THC are determined by the passage of a 10 ml air sample directly into the FID.

A schematic diagram of a coulometric SO_2 analyser is shown in Figure 3. A sample of ambient air is drawn through the electrolytic cell which contains a solution of potassium bromide (KBr) in dilute sulphuric acid (H_2SO_4), together with a small quantity of free bromine (Br_2). The following chemical reaction takes place.

$$Br_2 + SO_2 + 2H_2O \rightarrow 2Br^- + SO_4^{2-} + 4H^+ \qquad (8)$$

Two reference electrodes in the cell detect the change in the solution as a voltage signal which after amplification is compared to a standard

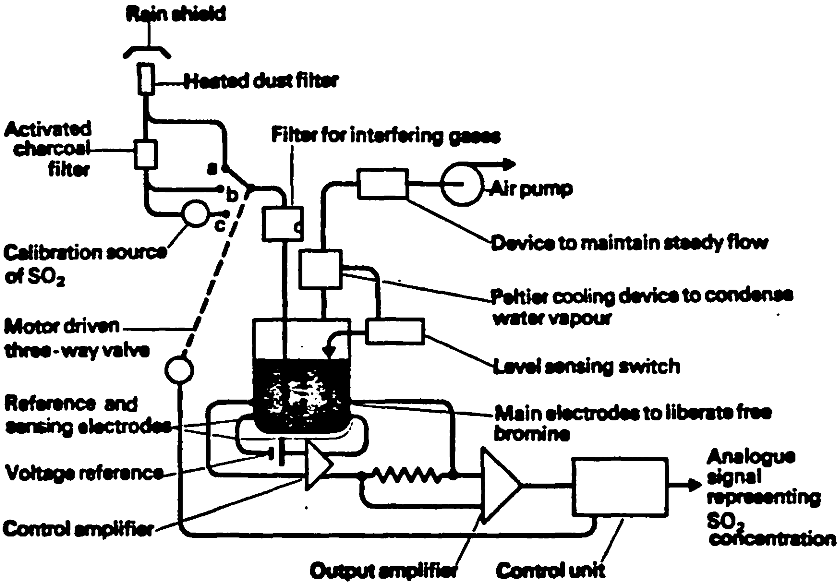


Figure 3 : Schematic diagram of a Philips PW 9700 coulometric SO_2 analyser

reference voltage. A current is then passed between the main electrodes in proportion to the out-of-balance voltage to regenerate free bromine.

$$2Br^- \rightarrow Br_2 + 2e^- \tag{9}$$

A chemiluminescence emission occurs when part of the energy of an exothermic reaction is released as light. NO_x (NO and NO_2) may be measured by using the fast reaction between NO and O_3 which emits light in the 0.6 to 3 µm (600-3000 nm) region with a maximum intensity near 1200 nm (Hodgeson et al., 1973).

$$NO + O_3 \rightarrow NO_2^* + O_2 \tag{10}$$

$$NO_2^* \rightarrow NO_2 + h\nu \tag{11}$$

$$NO_2^* + M \rightarrow NO_2 (M = N_2, O_2, H_2O \text{ etc.}) \tag{12}$$

The light emission (I) is given by

$$I = \text{constant} \times [NO][O_3]/[M] \tag{13}$$

where [M] is proportional to the total pressure.

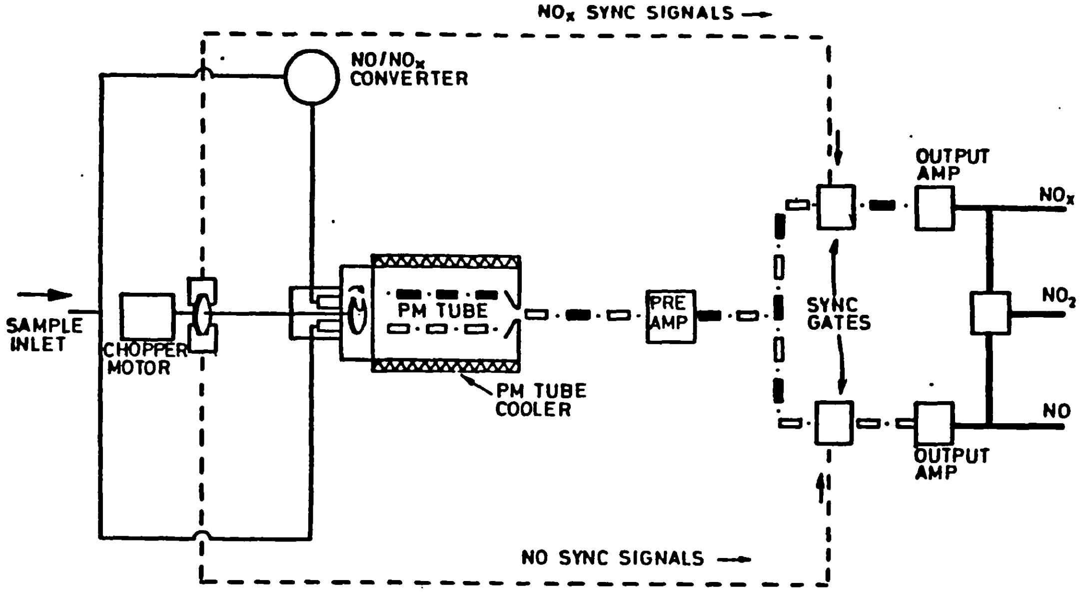


Figure 4 : Schematic diagram of a Thermoelectron 14D chemiluminescent NO_x analyser

In the presence of excess O_3, the light emission varies linearly with the concentration of NO. Figure 4 shows the basic layout of this method. By passing sample gas through a heated stainless steel converter in which NO_2 is decomposed to NO_x the total NO_x ($NO+NO_2$) is subsequently measured and the NO_2 obtained by difference.

The uv absorption of O_3 at 254.7 nm can be employed for monitoring concentrations in the lower atmosphere. Figure 5 presents a schematic diagram of a commercially available instrument. The absorption of uv radiation, from a stabilised miniature low pressure mecurcy arc, is measured through a 70 cm folded path cell which is alternatively filled with sample air and scrubbed (O_3 free) ambient air. The light beam is split, a fraction being directed onto the incident light detector photocell and the remainder passing through the cell to a second detector photocell. The digital photocell outputs are stored, the difference in absorbance being due to the ozone content of the air. It must be noted that this method is not strictly continuous, the digital output being updated every 22 s.

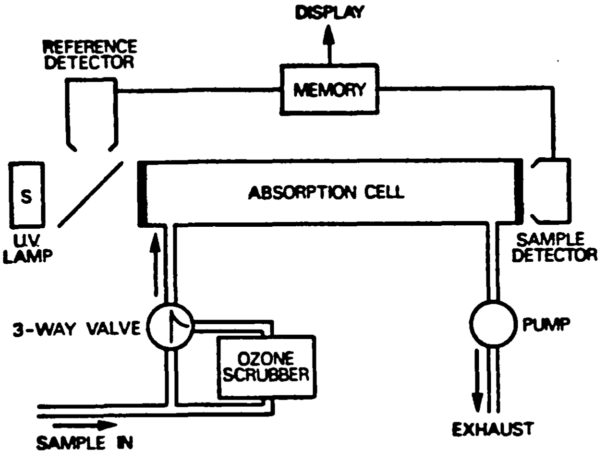


Figure 5 : Schematic diagram of a Dasibi 1003AH O_3 analyser

The most common method of sampling particulate pollution (including 'smoke') is by drawing a sample of contaminated air through a filter. Concentrations of total particulate matter are determined by direct gravimetric methods or by the measurement of the soiling of a filter paper by the diminution of light reflectance.

Collected particulate matter can be readily analysed for lead (Pb) using a variety of techniques which include X-ray fluorescence spectroscopy (Rhodes et al., 1972) (which does not need sample pretreatment), emission spectrography (Seeley and Skogerboe, 1974), polarography (West, 1967), anodic stripping voltammetry (Harrison and Winchester, 1971) and flame and flameless atomic absorption spectrometry (Hwang, 1972). Of these, flameless atomic absorption offers very high sensitivity (2 pg) and is commonly used for the determination of Pb concentrations in ambient air.

Several methods have been developed for the determination of volatile TAL compounds in ambient atmospheres. Filtration of the air sample allows separation from Pb particulates. The method of Hancock and Slater (1975) and Birch et al. (1980) traps TAL compounds in iodine monochloride in HCL solution and converts them to the corresponding diakyl-lead salt. These are extracted from the buffered iodine monochloride solution, after selective complexation by means of addition of several drops of 0.1 m EDTA (to mask any inorganic particulate lead present) with 8×10^{-5} M dithizone in carbon tetrachloride.

Other methods involve cryogenic trapping on empty U-tubes (Cantuti and Cartoni, 1968), glass beads (De Jonghe et al., 1980), porapak N or QS (Nielsen et al., 1981) or other chromatographic adsorbents (Chau et al., 1976) for the determination of individual TAL compounds (TML = tetramethyl lead, TEL = tetraethyl lead, TMEL = trimethylethyl lead, DMDEL = demethyldiethyl lead and MTEL = methyltriethyl lead). Analysis is by gas chromatography/atomic absorption spectrometry (GC/AAS) or gas chromatography/mass spectrometry (GC/MS). Detection limits for GC/AAS reported by De Jonghe et al. (1980) were 40 and 90 pg for TML and TEL respectively as compared to 60 pg and 10 pg for the same compounds by GC/MS (Nielsen et al., 1981).

In common with other trace organics, the concentrations of aromatic hydrocarbons, EDC and EDB in ambient air are relatively low, and therefore a preconcentration step is required when sampling prior to analysis by GC or GC/MS. Concentration procedures frequently include cryogenic trapping on glass beads (Nelson and Quigley, 1982), solvent scrubbing (Wszolek et al., 1973) and adsorption onto a solid surface (Bunn et al., 1975; Cuddeback et al., 1975; Ioffe et al., 1979).

Cryogenic trapping can lead to analytical difficulties because freezing-out of water vapour occurs along with the organic content of air, whereas solvent scrubbing is insufficiently sensitive for the analysis of organics below the ppm range (Lamb et al., 1980). Consequently the use of solid adsorbents such as charcoal, porous polymers (Porapak P, Tenax GC, Chromosorb 102, etc.) and silica gel is more popular when sampling for trace organics in air. Of the adsorbents available, porous polymers have the advantage of direct thermal desorption into a gas chromatograph as opposed to solvent desorption for charcoal and silica gel and, of those most frequently used, Tenax GC has high thermal stability (van Wijk, 1970).

The techniques of mass spectrometry and gas chromatography have the widest applicability to the analysis of organic pollutants in air, especially when interfaced to computerised data systems (Pellizzari, 1977) for identification purposes.

The development of photoionisation detectors (PID) offers the opportunity of measuring specific hydrocarbons in ambient air at ppb levels without preconcentration. The detector is designed to detect species in the effluent from a gas chromatograph. Photoionisation occurs when the absorption of a photon by a molecule leads to ionisation via the reaction:

$$RH + h\nu \rightarrow RH^{+} + e^{-} \qquad (14)$$

where RH is an ionisable molecule and hv is a photon with an energy $\geq$ the ionisation potential of the molecule.

The instruments and techniques described are not necessarily the most suitable for particular measurement studies but they do represent those that are in common use in air quality impact assessments or those that are promising developments with possible widespread use for ambient air quality measurements.

2. OBJECTIVES

Transport-related air pollutants have been identified as major contributors to ground level concentrations. Present concentrations of these pollutants, or indeed future concentrations as a result of emission changes, need to be assessed in order to determine possible detrimental health or welfare effects usually by comparison of measured or predicted concentrations with standards or health criteria.

Air quality impact assessment, as a decision-making tool, is most applicable when some type of emission alteration is involved. At present, a UK airport (Stansted) is being considered for major development to increase its passenger carrying capacity. In addition, the lead content of petrol is to be reduced to 0.15 gl^{-1} by the end of 1985 with subsequent predicted increases in fuel aromaticity in order to maintain octane numbers.

With respect to these examples of emission alteration and the importance of motor vehicle sources of air pollutants, the objectives of this study are as follows:

1. Characterisation of present air quality at Stansted Airport and examination of the importance of the airport and non-airport sources of air pollutants.

2. Evaluation of present air quality at three sites of contrasting degrees of motor vehicle influence.

3. Selection of statistical techniques applied to measured air quality at the three sites in order to determine (i) mathematical relationships between measured air pollutant concentrations and meteorological variables and (ii) the accuracy of prediction of mean and elevated air pollutant concentrations by means of air quality statistical distributions.

4. Development of suitable analytical techniques in order to assess (i) baseline ambient air concentrations of aromatic and halogenated hydrocarbons and (ii) role of varying fuel content and vehicle operating conditions on exhaust emissions of aromatic hydrocarbons.

3. MATERIALS AND METHODS

3.1 General Air Quality Measurements

CO, THC, CH_4 and NMHC (THC-CH_4) were measured by means of a Beckman 6800 air quality chromatograph (Beckman, Peterborough, UK) which operated on a catalytic methanator FID-GC method.

A chemiluminescence oxides of nitrogen analyser (Thermo-Electron 14D) was utilised for the measurement of NO_x, NO and NO_2 (NO_x-NO) (Thermo-Electron, Crawley, UK).

O_3 was measured by means of a Dasibi 1003-AH analyser (Analysis Automation, Oxford, UK) which utilised a uv photometric method.

SO_2 was measured by a Philips PW 9700 analyser (Philips, Cambridge, UK) operating on a coulometric method.

Airborne particulate lead was sampled weekly by passing a known volume of air through a 37 mm type MF (0.8 µm) Millipore filter (Millipore, London, UK). The analytical method for the determination of lead has been described in a nationwide survey of multi-element monitoring (McInnes, 1976), involving acid digestion of filters and analysis by atomic absorption spectrophotometry, and is accurate overall to ±10%.

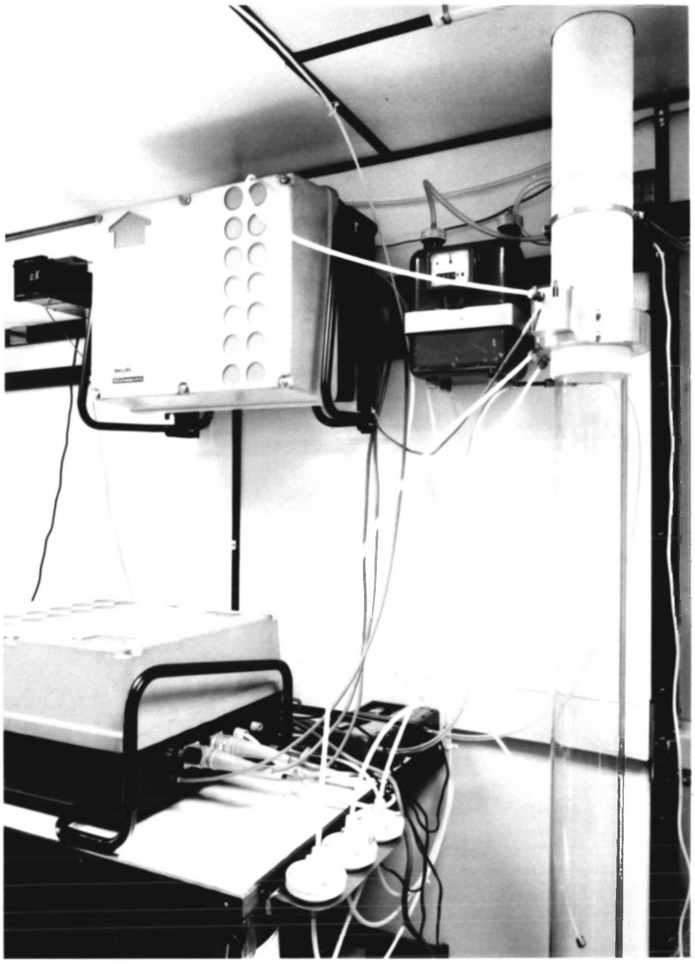
The gaseous pollutant instruments were calibrated and their individual zero values checked once every week using standard gas mixtures (British Oxygen Company, Morden, UK) and an internal source, in the case of the SO_2 analyser.

3.1.1 Mobile Laboratory

The mobile laboratory was equipped for the measurement of the following gaseous pollutants, CO, THC, CH_4, NMHC, NO_x, NO, NO_2, O_3 and SO_2.

Sample air was drawn into the laboratory by means of a centrifugal fan into a Teflon duct (10 cm diameter) (see Plate 1). The inlet of the duct was 4 m above ground level and 1 m above the roof of the

Plate 1	Top	: Teflon duct
	Bottom	: Internal view of mobile laboratory showing the gas chromatographic apparatus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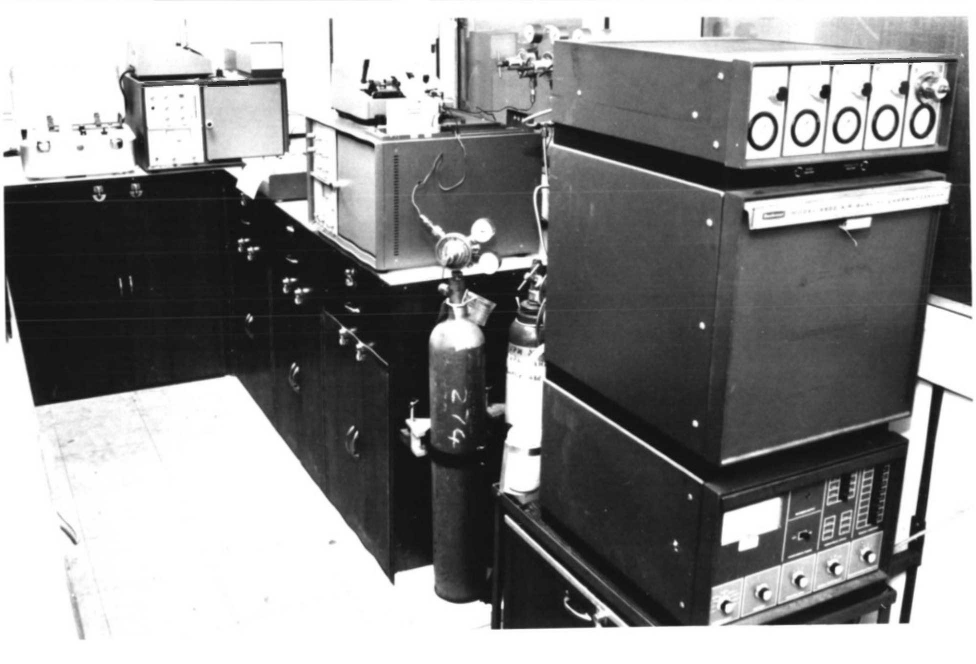
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laboratory. The flow-rate of the fan was sufficient to achieve a residence time in the duct of no more than 5 s for sampled air in order to minimise errors due to degradation, adsorption or contamination. The internal pumps of the instruments drew sample air through glass-lined stainless steel inlet ports and Teflon tubes (6.2 mm o.d.) from the duct.

Airborne particulate lead was sampled weekly, at a height of 4 m. The filter was placed in a weathershield, 1 m above the roof of the mobile laboratory.

Temperature was measured at a height of 4 m by means of a thermocouple housed in an anodised aluminium self-aspirating shield.

Wind speed and direction were measured by a cup-type anemometer and aluminium vane, respectively at a height of 10 m above ground level and 7 m above the laboratory roof.

An external view of the mobile laboratory is presented in Plate 2 which shows the (a) lead particulate sampling head, (b) self-asprirating thermocouple shield, (d) teflon duct and (e) hydraulic mast (not fully elevated) on which the cup anemometer and vane were attached. Also shown is a particular sampling head for smoke measurements (c), but this was not used in this work.

Data from the gaseous air quality instruments and meteorological parameters were recorded utilising 5 min scans on two Solartron 3430 cassette tape data loggers (Solartron, Farnborough, UK). A back-up system of chart recorders was also in operation. This allowed a more detailed analysis of instantaneous pollutant concentrations.

An internal view of the mobile laboratory showing analysers and data recording apparatus is also presented in Plate 2.

3.1.2 Fixed Site

A fixed site (Site A) was equipped for the measurement of the following gaseous air pollutants: NO_x, NO, NO_2, THC, CH_4, NMHC and CO using identical instrumentation to that in the mobile laboratory.

Plate 2 Top : External view of mobile laboratory
Bottom : Internal view of mobile laboratory showing monitoring instruments and data recording equipment


A
B
C
D
E
AIR QUALITY SURVEY
PUBLIC HEALTH ENGINEERING MOBILE LABORATORY
IMPERIAL COLLEGE
2WE

Airborne particulate lead was also measured. Ambient air was sampled through teflon tubes (6.2 mm o.d.) at a height of 4 m (1 m above the roof of the laboratory).

A Solartron DTU paper tape logger was used to record 5 min data scans. In addition, a back-up system of chart recorders was also in operation. Wind speed and direction data were obtained from the airport meteorological station.

3.2 Data Analysis

The five minute data were used to calculate hourly mean, maximum and minimum pollutant concentrations. Summaries of the distribution of data were calculated as selected percentiles for all sites. An nth percentile of x ppm is defined as when n% of all the data are less than or equal to x ppm (Nehls and Akland, 1973). Data from Site A were used to calculate diurnal averages and pollution roses.

A series of computer programs was developed which enabled the calculation of detailed pollution roses (showing maxima, quartile concentrations and arithmetic mean concentrations), total/weekday/weekend diurnal averages, estimation of the relative frequency of occurrence of the different wind direction sectors with hour of day and and the frequency of occurrence of different wind velocity classes.

Further analyses were performed on specific data sets, to examine the relative performance of the normal, 2-parameter lognormal (LN2) and the 3-parameter censored lognormal (LN3C) distributions using the least squares criterion.

The LN2 distribution is completely characterised by two parameters: the geometric mean (m_g) of measured pollutant concentrations and the standard geometric deviation (s_g) given by

$$m_g = \mathrm{EXP}(m_{\log}) \tag{15}$$

and

$$s_g = \mathrm{EXP}(s_{\log}) \tag{16}$$

where m_{log} = the mean of the natural logarithms of the pollutant concentrations and

s_{log} = the standard deviation of the logarithms of the pollutant concentrations

EXP indicates that e is to be taken to the power that follows in parenthesis.

The LN3C distribution is also characterised by these parameters and also a constant (k) which may be positive or negative, and is subtracted from every concentration value. An iterative process was used to define the optimum magnitude of k.

The concentration expected for any frequency, for a given averaging time was calculated from

$$c = k + m_g s_g^{\,z} \qquad (17)$$

for the LN3C distribution, where z is the standardised normal deviate (the number of standard geometric deviations from the median). Values of z for a specific level of confidence can be found in standard statistical tables.

The method, described by Hale (1972) has been used to determine the sample size necessary to obtain, with a fixed probability, upper and lower bounds for the geometric mean of a lognormal distribution:

$$n = \frac{Z^2 S_{log}^2 N}{N \ln^2(P+1) + Z^2 S_{log}^2} \qquad (18)$$

where n = sample size

z = normal deviate corresponding to the upper percentage point for a specified level of confidence. For a 95 per cent level z = 1.96.

S_{log} = standard deviation of the logarithms of the original observations

N = population size

P = fraction of the observed geometric mean by which it can differ from the true geometric with specified probability.

Correlation and multiple regression analysis were undertaken, in an attempt to define the relative importance of meteorological variables in determining the observed pollutant concentrations. Dispersion equations suggest the adoption of a multiple regression equation (Keddie *et al.*, 1979; Benarie, 1980) of the form:

$$\ln c = a + b_1 \ln U + b_2 \ln T \qquad (19)$$

where c = the ambient pollutant concentration

U = the wind speed

T = the ambient temperature

The constants a, b_1 and b_2 are the regression coefficients.

Persistence in emissions and meteorological variables was evaluated by the multiple regression equation

$$\ln c = a + b_1 \ln u + b_2 \ln T + b_3 \ln c' \qquad (20)$$

where c' = the previous hourly concentration (lagged concentration)

For these latter analyses the statistical computer package "MINITAB" was used.

3.3 Sampling and Measurement Techniques for Aromatic and Halogenated Hydrocarbons in Ambient Air and Vehicle Exhausts

3.3.1 Adsorption Tube Sampling Method

Tenax GC sampling tubes were employed because of the high thermal stability of the porous polymer adsorbent (van Wijk, 1970). The compounds utilized in this study have been selected as representative of vehicle-related aromatic and halogenated hydrocarbon emissions (Tsani-Bazaca *et al.*, 1982).

Stainless steel sampling tubes (74 mm × 4.5 mm i.d.), cleaned by ultra-sonication in Decon 90 (B.D.H., Chadwell Heath, UK), were packed with 0.13 g of Tenax GC, 35-60 mesh (Chrompack, London, UK). This had previously been purified by soxhlet extraction with 'Aristar' grade methanol (B.D.H., Chadwell Heath, UK) for 18 h and preconditioned at 280°C with oxygen-free nitrogen (OFN) carrier gas at a flow-rate of

20 ml min^{-1} for 8 h to avoid heat shrinkage of the Tenax GC. The adsorbent was held in place by clean silanised glass wool and after packing was re-conditioned as described above.

Sampling tubes were thermally desorbed at 250°C in a Bendix flasher unit (Bendix, Milton Keynes, UK) interfaced with either an electron capture (EC) or flame ionisation detector (FID) equipped Hewlett Packard 5700 A gas chromatograph (Hewlett Packard, Winnersh, UK).

The efficiency of desorption was examined by comparing direct column injections of standards of the individual compounds made up in hexane to similarly spiked sampling tubes which were thermally desorbed into the gas chromatograph.

Chromatographic separation of halogenated hydrocarbons was achieved on a 2 m × 3.1 mm o.d. stainless steel column packed with 5% Carbowax 1500 on Chromosorb W HP (80-100 mesh) operated isothermally at 70°C. The (EC) detector temperature was 250°C with a carrier gas flow-rate of 35 ml min^{-1} argon/methane (95%/5%). Aromatic hydrocarbons were separated on a 2 m × 3.1 mm o.d. stainless steel column packed with 10% TCEP on Chromosorb P HP (100-120 mesh) operated isothermally at 70°C. The FID detector temperature was 250°C with a carrier gas flow rate of 40 ml min^{-1} OFN. Both columns were supplied by Phase Separations (Queensferry, UK).

It is desirable that the calibration method should reflect actual sampling procedures as closely as possible. Therefore, a permeation tube oven coupled to an exponential dilution flask (Bruner _et_ _al._, 1973) was adopted for the introduction of a known mass of organic vapour onto the sampling tubes, which on subsequent analysis provided values for construction of calibration graphs. A constant-flow sampling pump Model P-4000 (Du Pont, Stevenage, UK) was used to draw clean air through the permeation oven and into the exponential dilution flask until the atmosphere in the flask was saturated with the vapour of the calibration compound. The pump was then used to draw clean air through the flask and onto sampling tubes for known periods of time. The concentration of organic vapour decayed in the flask according to the equation,

$$C = C_o e^{-Ft/V} \qquad (21)$$

where C = the concentration at time t (min)

C_o = the initial concentration

F = dilution flow-rate (ml min^{-1})

V = volume of the dilution flask (ml)

The vapour concentration in the flask was verified at intervals during the calibration procedure by direct injection of aliquots (0.05-1 ml) into the gas chromatograph. Wall losses were evaluated similarly by direct injection of identical aliquots over a period of time with no dilution taking place. The accuracy of exponential dilution was verified by comparison with standard atmospheres built up in a glass flask by static dilution of headspace vapours of the pure compound. A worked example of the static dilution procedure is given in Appendix A.

Equal amounts of benzene and toluene were introduced, by the exponential dilution method, onto a representative number of tubes which were then capped and stored at 4°C for periods varying between 1 and 21 days in order to evaluate the effects of storage time on analysis.

3.3.2 Method for the Evaluation of Sampling Parameters

A sampling tube was connected into the gas chromatograph oven with the outlet connected directly to the FID. Two forms of analysis were performed (frontal and elution), differing primarily in their manner of sample introduction.

Organic vapour was introduced continuously during frontal analysis by diverting carrier gas through a permeation oven, containing either benzene or EDC permeation tubes and then into the inlet of the sampling tube. The time taken for the concentration of determinand in the effluent carrier gas stream from the tube to equilibrate (monitored by the FID) and the shape of the breakthrough curve provided chromatographic data on retention volumes and the number of theoretical plates for these components.

In elution analysis, small quantities (0.01-0.5 ml) of organic vapour from a static dilution flask were injected by gas syringe onto the sampling tube. The time taken to obtain peak maxima and the peak shapes were recorded for various operating temperatures. In this way data on retention volumes and the numbers of theoretical plates were obtained, thus permitting an evaluation of the effects of sampling conditions of adsorbate concentration, humidity and flow-rate.

The retention volume (V_g), in both frontal and elution analysis, corresponds to 50% breakthrough (Gallent et al., 1978; Senum, 1981) i.e. the volume at peak maxima in elution analysis and the volume at which 50% of the inlet absorbate concentration (C) is detected in the effluent carrier gas stream from the sampling tube in frontal analysis.

Retention volumes for the compounds of interest were determined by elution analysis at a flow-rate of 50 ml min^{-1} by operating the sampling tubes at temperatures above ambient and extrapolating the log retention volumes against reciprocal absolute temperature using least squares regression i.e.

$$\log V_g = AT - B \qquad (22)$$

where T = reciprocal of absolute temperature (1/K)
and A and B are the regression constants.

The number of theoretical plates (N) was determined by frontal analysis from the slope of the line at the 50% breakthrough volume from the equation

$$\text{slope} = C(N/2\pi)^{\frac{1}{2}}/V_g \qquad (23)$$

N was determined by elution analysis using the equation

$$N = (4t/w)^2 \qquad (24)$$

where t is the elution time (or volume) and w is the distance between the points of intersection of the tangents to the inflection points of the peak (Van Deemter et al., 1956).

High adsorbate concentrations of benzene, toluene and EDC were prepared in a flask and single aliquots of the sample atmospheres were injected onto the sample tubes (at an OFN carrier gas flow-rate of 50 ml min^{-1}). The sample tubes were operated at 120, 190 and 116°C for benzene, toluene and EDC respectively, in order to measure the retention volumes at different concentrations.

The constant-flow pump was used to draw clean air (activated charcoal filtered ambient air) through an exponential dilution flask containing a high concentration (1-20 ppm) of aromatic hydrocarbons for 10 min. This frontal analysis technique was compared with the elution analysis described above.

The effect of humidity on the sampling efficiency of Tenax GC was evaluated by introducing a humidifier into the carrier gas flow and measuring the retention volumes of the compounds of interest by elution analysis. The humidifier consisted of a stainless steel cartridge (200mm × 50mm i.d.) filled with water and glass beads (3 mm diameter) and with this large surface area of water it was assumed that the carrier gas was saturated at room temperature.

3.3.3 Analysis of Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry

A Bendix flasher unit was interfaced with a Carlo Erba Fractovap 4200 GC (Erba Science, Swindon, UK). This necessitated modification of the flasher unit to bypass the internal flow controller and the use of a pressure regulator installed on the GC. The GC was equipped with a capillary column interfaced with a Jeol JMS-D300 double focussing mass spectrometer (MS) with a JMA-2000H data processing system (Jeol, Tokyo, Japan).

Sampling tubes were desorbed, at a temperature of 250°C with a helium carrier gas flow-rate of 2 ml min^{-1}, onto the capillary column. The initial 30 cm of the column were immersed in liquid nitrogen (-180°C) during tube desorption in order to obtain a small plug of desorbed material. After desorption and subsequent cryogenic trapping, the GC oven was temperature programmed as follows: 30°C for 4 min, 10°C min^{-1} to 80°C, then 20°C min^{-1} to 220°C held for 5 min. The column was connected directly to the ion source of the MS in order to optimise resolution and sensitivity. The MS was operated under the following conditions.

Accelerating voltage	3.0 KV
Mass range	40-500 m/z
Ionising voltage	70 eV
Ionising current	300 µA
Ion source temperature	250° C
GC/MS transfer line	250°C
Electron multiplier	1.3 KV
Resolution	1000

The MS was scanned once a second under data system control and the mass spectra were stored on magnetic disc cartridge. Reconstructed ion chromatograms (RIC), mass spectra of component peaks and mass chromatograms were then retrieved from the stored data.

Positive identification of desorbed compounds was achieved by computer comparisons of sample and library mass spectra. Quantification of desorbed compounds was achieved by introduction of a known amount of deuterated toluene (δ8) (Aldrich Chemicals, Gillingham, UK) onto sample tubes. Response factors between δ8 and identified compounds were calculated. The GC/MS system was then calibrated by direct injection of δ8 standards of varying concentrations.

3.3.4 Photoionisation Detector/Gas Chromatograph

A Photovac 10A10 PID/GC (Photovac, Thornton, Ontario, Canada) is shown in Plate 1. The instrument was fitted with flexible teflon columns (1.5 m × 3.1 mm o.d.) packed with either 1.5% OV17+1.95% QFI on Supelcoport 100/120 or 5% SE30 on Chromosorb G 100/120. Hydrocarbon-free air (Air Products, Bracknell, UK) was used as carrier gas at a flow-rate of 15 ml min^{-1}. The instrument was operated at ambient temperature. Chromatographic traces were recorded on a strip-chart recorder.

Standard atmospheres of various concentrations (0-100 ppb) of benzene, toluene, o-, m- and p-xylene and ethylbenzene were established in glass flasks by static dilution of headspace vapour of the pure compounds. Sample air was directly injected into the PID/GC by means of a 1 ml gas-tight syringe. The detection limits of these compounds were defined as 2.5 times the noise signal. Exponential dilution of the flasks with clean air provided a secondary method of producing standard atmospheres and provided a method of comparison with the Tenax GC sampling tube method.

Standard atmospheres of high concentrations of aromatic hydrocarbons (1-100 ppm) were prepared in glass flasks. Sample air was injected into the PID/GC in 1, 0.5 or 0.05 ml aliquots by means of appropriate gas-tight syringes.

3.4 Ambient Air Measurements of Aromatic and Halogenated Hydrocarbons, Organic and Particulate Lead

Two constant-flow pumps were used to draw sample air from the duct in the mobile laboratory through glass-lined stainless steel inlet ports and through two stainless steel sampling tubes (74 × 4 mm i.d.) packed with Tenax GC (0.13 g, 35/60 mesh) at a flow-rate of 100 ml min^{-1} for 20 min. The mobile laboratory was equipped with the thermal desorption-gas chromatographic apparatus (Plate 1) and the general air quality instruments described in Section 3.1.1.

Tube desorption, chromatographic separation and analysis was performed as previously described (see Section 3.3.1). Calibration for aromatic and halogenated hydrocarbons was achieved by direct injection of standard atmospheres of various concentrations in glass flasks, established by static dilution of headspace vapour of the pure compounds. Chromatograms from the aromatic and halogenated hydrocarbon analyses were recorded on strip-charts.

In addition, 24 h or 48 h measurements of particulate and organic lead in ambient air were carried out at a height of 4 m, utilising the method developed by Birch *et al.* (1980).

3.5 Dynamometer Studies

A regularly serviced test car (Ford Cortina, MK IV, 1.6 l engine with manual transmission) was used in this study on a twin roller chassis dynamometer (Consine Dynamics, Chesterfield, UK) with a proportional cooling fan. The dynamometer load controls were adjusted to reproduce conditions experienced by the test car when running on a level road.

The car was operated on three test fuels of similar Research Octane number and benzene content. The lead and aromatic content of test fuels was varied during ECE 15 test cycles (Economic Commission for Europe, 1982) and 90 kmh^{-1} constant speed tests. The ECE 15 test driving cycle is illustrated in Figure 6.

For each test run, the car was filled with approximately 0.5 l of fuel and conditioned for 5 min at 70 kmh^{-1}. Three replicates of each test were performed. After completion of each run, the fuel tank was drained and the test car operated until the remaining fuel in the fuel lines and carburettor had been used up.

The test car exhaust was diluted by a constant volume sampling system (G. Gussons, Worthing, UK) and then collected in a preconditioned Tedlar bag (1580×832 mm). The sample entry point was at the geometric centre of the bag fitted with an exhaust gas spreader (6.4 mm o.d. Teflon perforated tube).

Aliquots of 1 ml were then taken out of the bag, via a septum-capped sampling point and injected into the PID/GC fitted with a 2 m × 3.1 mm o.d. Teflon column packed with 1.5% OV17 + 1.95% QFI on Supelcoport 100/120.

Calibration of samples was by preparation of standard atmospheres by static dilution of headspace vapour of the pure compounds.

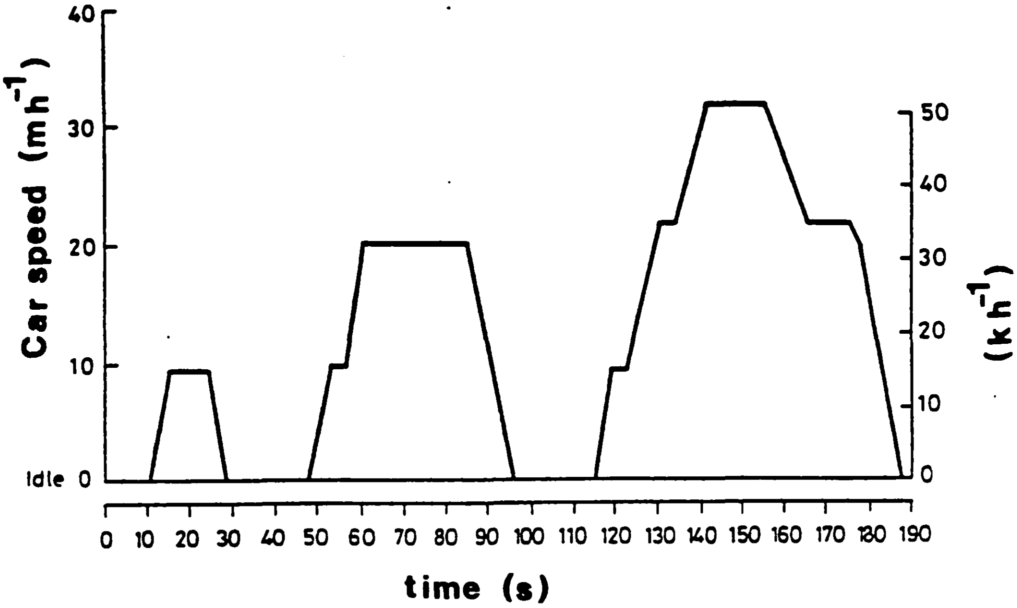


Figure 6 : ECE-15 test cycle

4. RESULTS

4.1 An Investigation of the Impact of Various Transport-Generated Air Pollutants on Air Quality

Although most transport systems generate air pollution, concern appears to be greatest about road and air transport. The impact of these sources is strongly influenced by the type and mode of operation of the engine in use. In order to assess the air quality impact of transport-related air pollutants, a number of monitoring surveys have been performed.

The effect of aircraft and airport-related air pollutant emissions were evaluated at a UK airport (Stansted). An urban site was chosen which was adjacent to a slow-moving heavily trafficked road in order to assess the impact of motor vehicles on air quality. In addition, a motorway location was selected as representative of high traffic density and constant high speed operation as compared to the driving modes prevalent in urban areas. A rural site was chosen as a control. At this site, transport-related air pollutant sources were minimal.

4.1.1 Stansted Airport

In order to provide a reasonable description of current air quality and to assess the air quality impact of aircraft and airport-related air pollutants, a monitoring survey was performed at Stansted Airport.

A total of seven monitoring sites were chosen, in the vicinity of Stansted Airport. Site A was located on the eastern side of the runway, while Sites B-G were located in a ring around the airport. A map, indicating the locations of the sites is presented in Figure 7. Sites B, D and C were in the immediate vicinity of the airport. Site E was chosen as a control site in order to assess background concentrations of air pollutants. Site F was located at a busy road interchange between the A120 and the M11 motorway and Site G was located in the nearby town of Sawbridgeworth as a comparison with the airport.

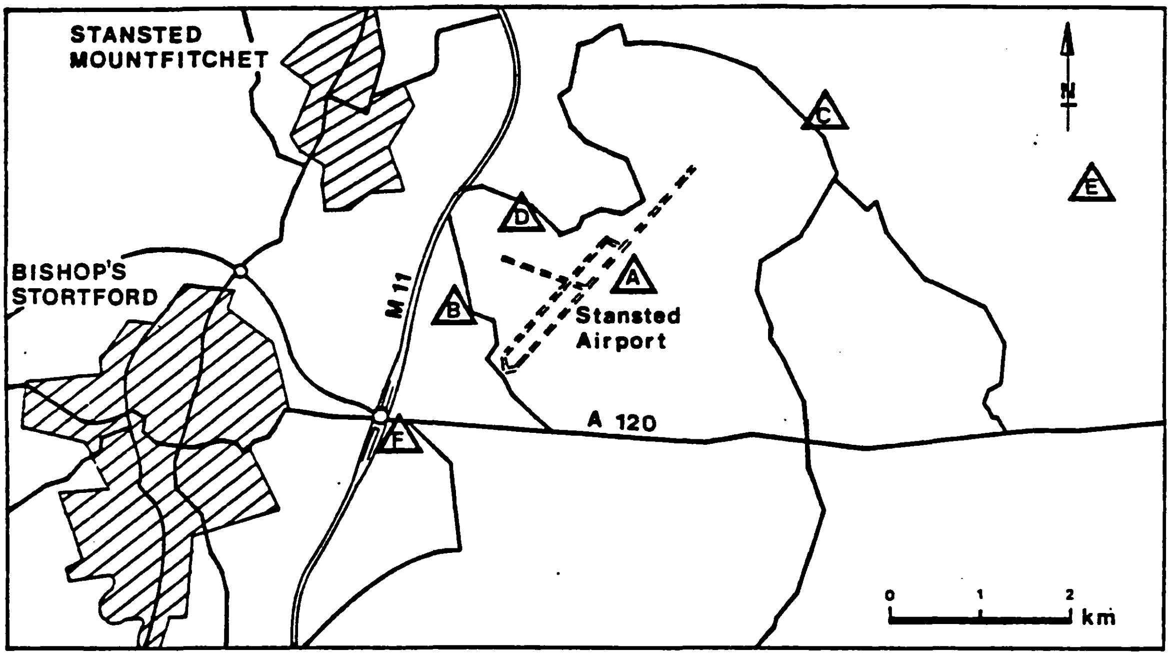


Figure 7 : Location of monitoring sites in the vicinity of Stansted Airport (Site A)

The mobile laboratory (see Section 3.1.1) was employed for the measurements at Sites B-G. The sampling took place between 19 May and 31 December 1980, maintaining three week measurement periods at each site (except for 1 week periods at Site G) in both summer and winter conditions. Site A (fixed site) was operated continuously between 19 May and 31 December 1980 (see Section 3.1.1).

A summary of hourly gaseous air quality measurements is presented in Table 10 this includes THC, NMHC, CO, NO and NO_2.

Concentrations of THC measured at all the sites were similar up to 99th percentile with arithmetic means varying between 1.9 ppm at Sites D and E to 2.2 ppm at Site A. NMHC measured at Sites A-G varied between 0.1 ppm at Site E to 0.4 ppm at Site A (arithmetic mean).

The results of the CO measurement data demonstrated the influence of local motor vehicle sources. Sites F and G, which were adjacent to a motorway/trunk road interchange and a car park respectively, and these exhibited higher concentrations of CO (0.49 ppm at Site F and 0.53 ppm at Site G arithmetic means) than the other sites which varied between 0.21 and 0.28 ppm.

Table 10 : Summary of hourly gaseous air quality measurements in the vicinity of Stansted Airport

Site		THC ppm	NMHC ppm	CO ppm	NO pphm	NO_2 pphm
A	arithmetic mean	2.2	0.4	0.22	0.7	0.8
	50th percentile	2.1	0.2	0.07	0.4	0.5
	90th percentile	2.5	0.6	0.29	0.9	1.6
	99th percentile	3.2	1.3	1.1	3.3	3.5
B	arithmetic mean	2.0	0.2	0.28	0.9	1.7
	50th percentile	1.9	0.1	0.14	0.4	1.4
	90th percentile	2.3	0.3	0.45	1.9	3.0
	99th percentile	2.9	0.6	1.0	7.5	4.9
C	arithmetic mean	2.1	0.2	0.27	0.6	1.6
	50th percentile	1.9	0.1	0.14	0.3	1.4
	90th percentile	2.2	0.3	0.43	1.0	2.5
	99th percentile	3.1	0.5	1.1	4.2	4.0
D	arithmetic mean	1.9	0.2	0.23	0.6	1.3
	50th percentile	1.8	0.1	0.08	0.2	1.1
	90th percentile	2.1	0.2	0.37	1.1	2.2
	99th percentile	2.5	0.6	1.4	5.2	3.5
E	arithmetic mean	1.9	0.1	0.21	0.3	1.0
	50th percentile	1.7	0.1	0.09	0.1	0.7
	90th percentile	2.0	0.2	0.29	0.5	2.0
	99th percentile	2.3	0.4	0.57	3.0	2.9
F	arithmetic mean	2.0	0.2	0.49	2.8	1.7
	50th percentile	1.8	0.1	0.26	1.4	1.4
	90th percentile	2.2	0.4	0.93	6.9	2.6
	99th percentile	3.0	0.9	2.0	17.2	6.0
G	arithmetic mean	2.1	0.3	0.53	1.3	1.2
	50th percentile	1.8	0.1	0.29	1.3	0.9
	90th percentile	2.7	0.5	1.0	3.1	2.3
	99th percentile	3.5	0.9	2.7	12.7	3.6

A similar pattern to CO was observed in the case of NO where Sites F and G demonstrated higher concentrations (2.8 and 1.3 pphm arithmetic means respectively) compared to 0.3 pphm at Site E which was located away from any major roads. Arithmetic mean concentrations of NO_2 at Sites A-G varied between 0.8 pphm (Site A) to 1.7 pphm (Sites B and F). The 99th percentile concentrations at Sites B and F (corresponding to 10 h for a sampling period of 6 weeks at each site) were 4.9 and 6.0 pphm respectively. On analysis of the hourly and five minute data at Site F, the elevated concentrations all occurred between the 20-27

August with four occasions when the hourly mean was greater than 10 pphm and in each case occurring between 4 and 5 pm. On one occasion the hourly mean was 3-5 times higher than the daily average. The peaks were of relatively short duration (20-25 min) with no discernible associated peaks of other pollutants nor did they occur on the same, or similar wind directions. Of the four peaks > 10 pphm, two occurred on broadly 270° (southwesterly) wind directions and one each on broadly 90° (easterly) and 180° (southerly). The peaks in NO_2 did not coincide with low wind speeds.

Pollutant roses for CO, NO, NO_2 and NMHC were obtained by averaging all the hourly mean concentrations recorded when the wind was from each of the twelve 30° sectors centred on 0° (due north) at Site A and are presented in Figures 8 and 9. The CO rose indicated that the highest average concentrations appeared from wind directions 120°-210° which broadly corresponded with bearings of the major emission areas for CO, namely the nearby roads, the A120, and the small industrial area to the east-south-east of Site A.

The NO rose exhibited a slightly more westerly bias than the CO rose with highest average concentrations in the 120-270° arc. This behaviour also broadly reflected the pattern of major source areas around the site. The NO_2 rose illustrated a similar pattern to the NO rose but had a pronounced bias in the southerly sectors (150°-210°). In general, the proportion of NO_2 in an air mass containing NO and NO_2 increases with time, so that the concentration from the south east and west, where NO_2 > NO, would appear to arise from more distant sources than those in the north-eastern section where NO > NO_2.

The NMHC rose exhibited the highest average concentrations from the 210°-240° and 330° sectors. These were directions such that the Airport could contribute to concentrations at Site A, although it was not possible to quantify the proportional contribution of the Airport and other sources in these directions from measured data alone.

Diurnal averages obtained by averaging all the concentrations of a particular pollutant for each hour of the day are presented in Figures 10 and 11.

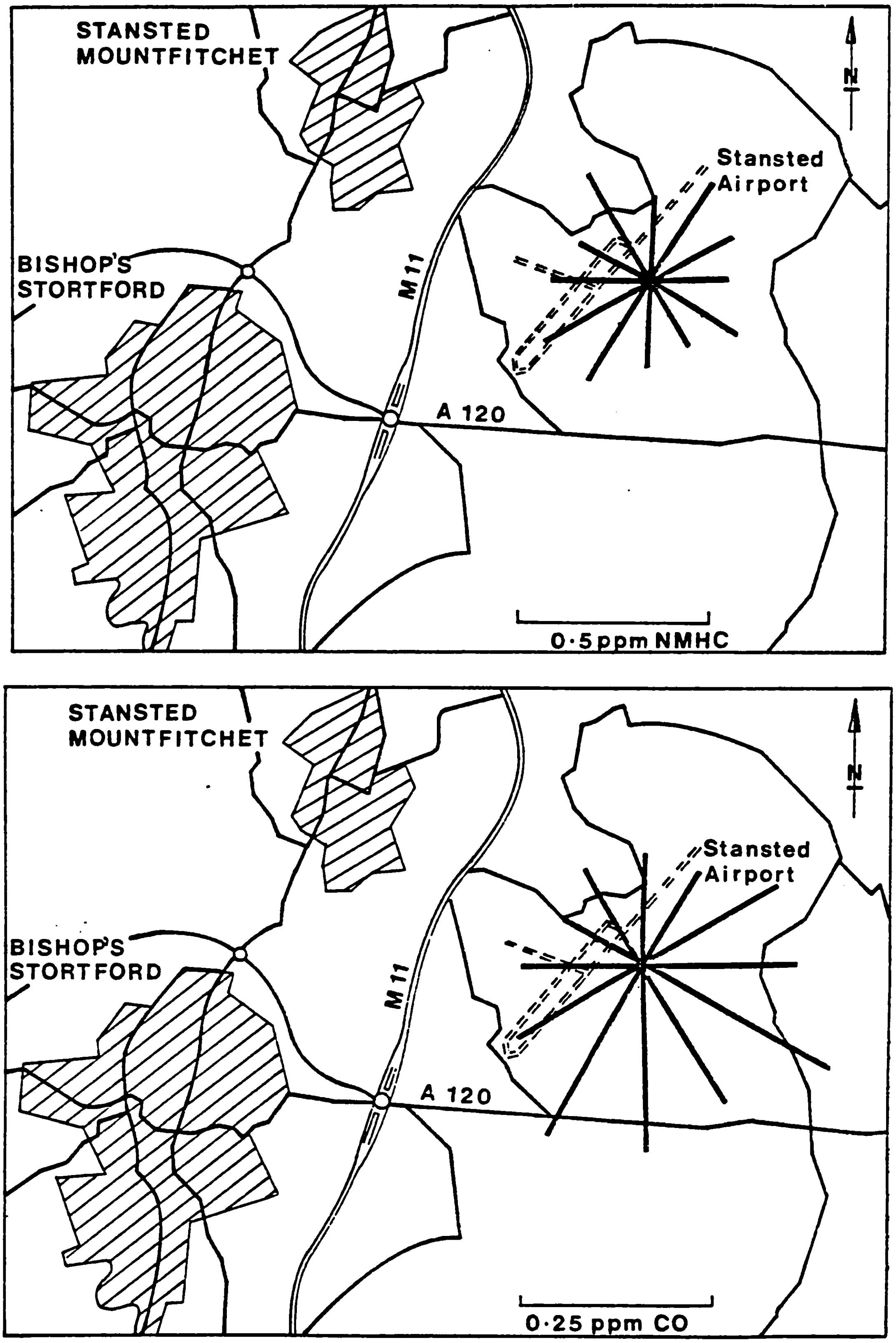


Figure 8 : Pollution roses for NMHC and CO at Stansted Airport

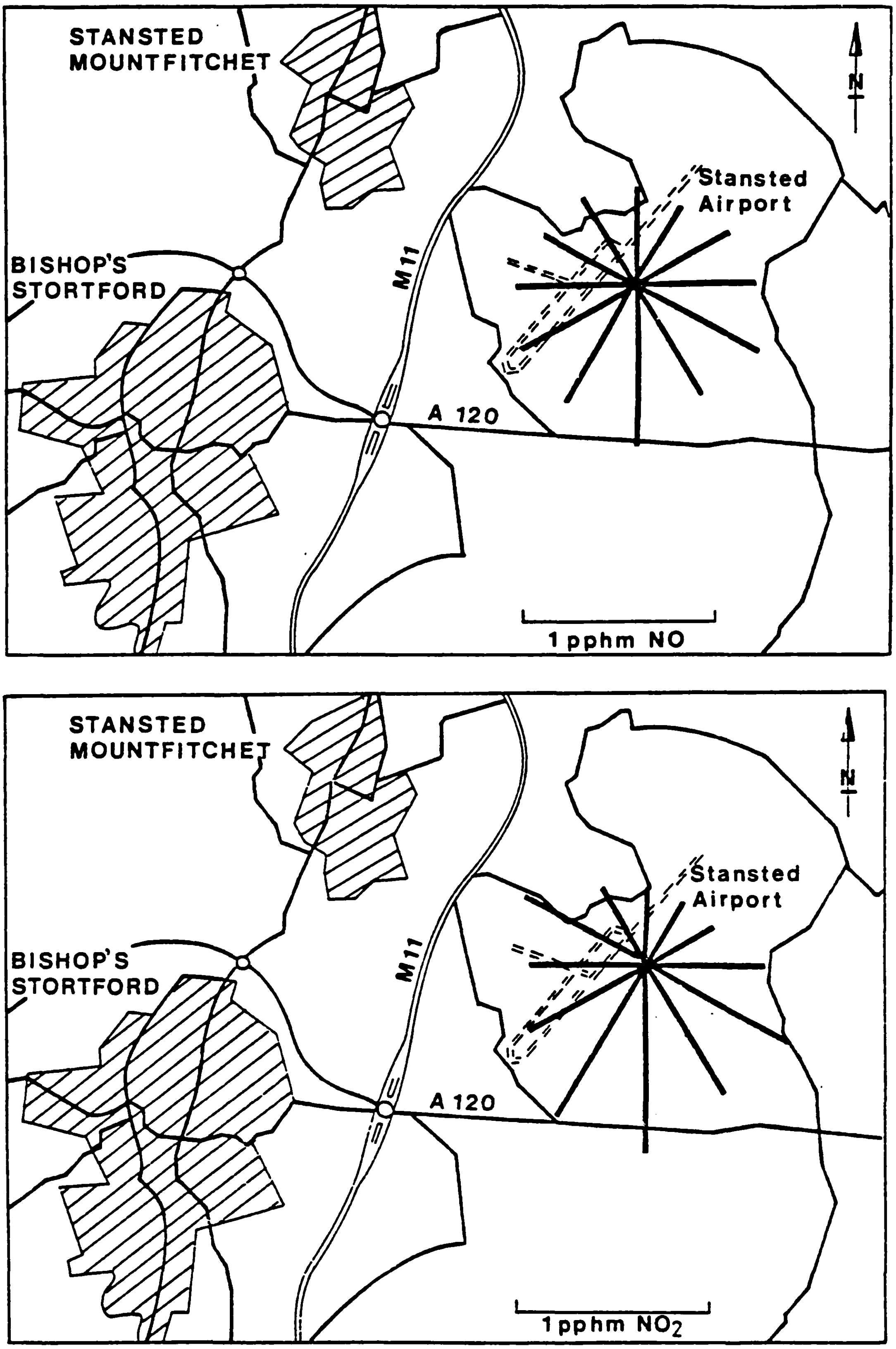


Figure 9 : Pollution roses for NO and NO_2 at Stansted Airport

The CH_4 concentrations arise primarily from natural sources of approximately constant source strength.

The diurnal variation in CH_4 concentrations arose from the variation in the dispersive properties of the atmosphere. Concentrations were approximately inversely proportional to wind speed and mixing height. The diurnal patterns of these two variables were similar, each displaying a low value overnight increasing to a maximum around midday and slowly declining in the evening. The CH_4 (and THC) diurnal patterns were consistent with this behaviour.

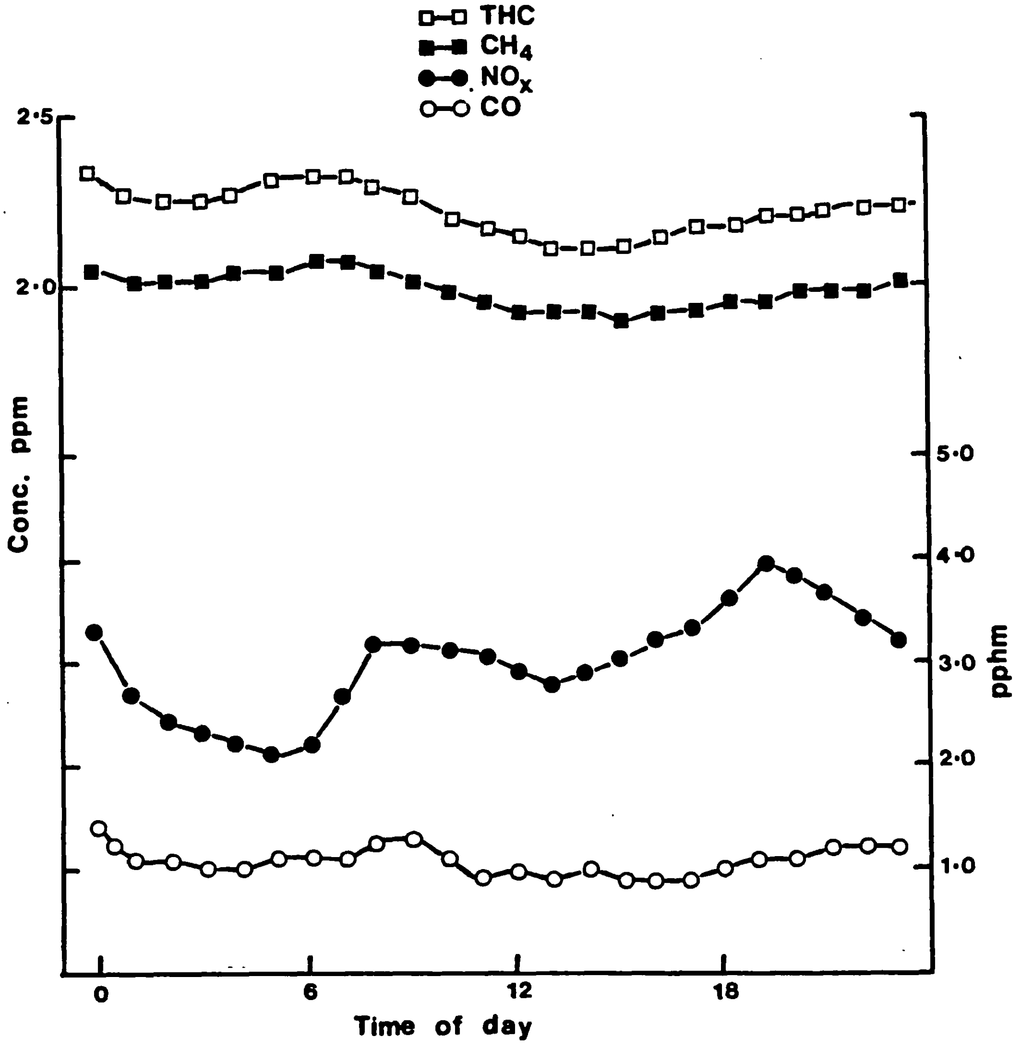


Figure 10 : Diurnal averages of THC, CH_4, NO_x and CO concentrations at Stansted Airport (Site A)

Combustion sources of NO_x tend to increase from 6 am to a peak around 9 am (particularly motor vehicles) then decline for the rest of the day. The observed NO_x peak from 7-10 am occurred when an increase in emissions from both local and more distant sources coincided with lower wind speeds. The evening NO_x peak was less straightforward to interpret and a breakdown of the NO and NO_2 components is of interest. The NO_2/NO ratio is a broad indicator of the remoteness of the NO_x source area. In the morning this was slightly greater than 1, which suggested that more distant sources as well as local emissions were significant, while for the evening peak the ratio was 1.4 which is consistent with more distant sources being the major contributor. Nearby towns such as Bishop's Stortford and Stansted Mountfichet, as well as more distant urban areas such as Harlow and the Greater London conurbation were also possible source areas.

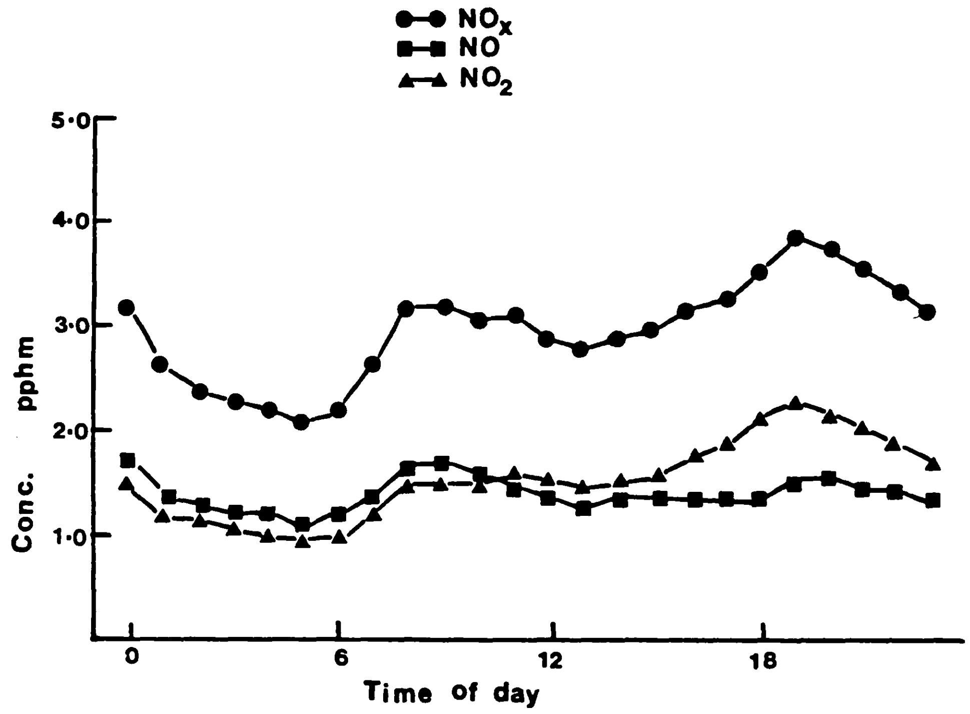


Figure 11 : Diurnal averages of NO_x, NO_2 and NO concentrations at Stansted Airport (Site A)

The results of the particulate lead measurements at the Stansted sites are presented in Table 11. The concentrations varied between 185 and 609 ngm^{-3}. The degree of influence of petrol-driven vehicles, noted in the gaseous pollutant results, is also apparent in the lead results where Site F exhibited the highest concentration. Aviation fuel (AVGAS) contains no lead although piston-engined aircraft utilize fuel containing lead. The particulate lead results for Site A suggest that the concentrations of ambient particulate lead were negligible from this source.

Table 11 : Particulate lead concentrations, Sites A-G at Stansted Airport

Site	Lead Concentration* ngm^{-3}
A	185
B	358
C	227
D	282
E	285
F	609
G	357

* Arithmetic average over period of monitoring at each site

In general, the monitoring survey indicated that motor vehicle pollution had a significant influence on air quality in the vicinity of Stansted Airport. However, it was not possible to quantify the precise contributions of the various sources from the measurements undertaken at these essentially similar sites.

4.1.2.1 Urban Site - Exhibition Road, London

In order to examine the relationship between air quality and traffic-related pollution, two monitoring surveys were performed at an urban site in London during the summers of 1982 and 1983. The mobile laboratory was situated approximately 10 m from the kerb at Exhibition Road, SW7. The site was considered representative in terms of traffic density, mode of vehicle operation and also in terms of its 'street canyon' morphology. The sampling periods were approximately four weeks from 6 June to 11 July 1982 and from 15 May to 11 June 1983.

Summary tables of the hourly air quality characteristics during the monitoring periods in 1982 and 1983 are presented in Tables 12 and 13. Arithmetic mean concentrations and NMHC were high during the 1983 survey in both arithmetic mean (0.36 ppm compared to 0.24 ppm in 1982) and distribution (0.8 ppm 99th percentile compared to 1.09 ppm). The percentage of NMHC to THC also varied from 13.1% in 1982 to 18.6% in 1983.

Carbon monoxide measured concentrations during 1982 and 1983 were similar (1.66 and 1.77 ppm arithmetic mean, respectively) and were similarly distributed (5.82 and 6.15 ppm 99th percentiles, respectively).

Table 12 : General air quality characteristics at the urban site, 1982

	CH_4 ppm	THC ppm	NMHC ppm	CO ppm	SO_2 ppb	Ozone ppb
Arithmetic Mean	1.59	1.83	0.24	1.66	17.6	0.96
Minimum	1.20	1.20	0	0.01	10.37	0
25th percentile	1.45	1.64	0.05	0.59	14.30	0.02
50th percentile	1.55	1.82	0.19	1.44	16.19	0.29
75th percentile	1.69	1.99	0.39	3.37	19.80	1.06
90th percentile	1.83	2.19	0.56	3.36	23.89	2.64
95th percentile	1.94	2.33	0.67	4.24	27.14	4.57
99th percentile	2.18	2.59	0.85	5.82	33.13	7.54
Maximum	2.69	3.25	1.04	8.41	48.47	29.33
Standard Deviation	0.19	0.28	0.22	1.29	4.74	2.04
Variability*	12.27	15.58	90.71	77.76	36.93	210.45

* variability is defined as (standard deviation/arithmetic mean) × 100

Table 13 : General air quality characteristics at the urban site, 1983

	CH_4 ppm	THC ppm	NMHC ppm	CO ppm	SO_2 ppb	Ozone ppb	NO pphm	NO_x pphm	NO_2 pphm
Arithmetic Mean	1.93	2.27	0.36	1.76	20.8	4.97	4.10	9.77	5.69
Minimum	1.30	1.35	0	0	14.46	0	0	0.08	0.08
25th percentile	1.74	2.03	0.17	0.7	18.6	0.65	0.63	4.96	3.60
50th percentile	1.87	2.23	0.34	1.51	19.8	2.59	2.96	9.43	5.72
75th percentile	2.02	2.50	0.50	2.44	21.94	6.42	6.31	13.15	7.80
90th percentile	2.44	2.77	0.66	3.5	25.58	13.38	10.00	17.68	9.29
95th percentile	2.67	3.09	0.75	4.13	28.24	17.48	12.08	21.02	10.04
99th percentile	3.16	3.52	1.09	6.15	33.04	28.47	16.95	25.24	11.56
Maximum	3.42	3.69	1.38	8.39	35.86	56.45	23.77	31.42	14.62
Standard Deviation	0.39	0.45	0.24	1.32	3.54	6.99	4.12	5.90	2.78
Variability*	20.17	19.79	66.60	74.73	16.99	139.03	100.62	60.40	48.89

* variability is defined as (standard deviation/arithmetic mean) × 100

Figure 12 : Pollution roses for NMHC and CO at the urban site, 1982

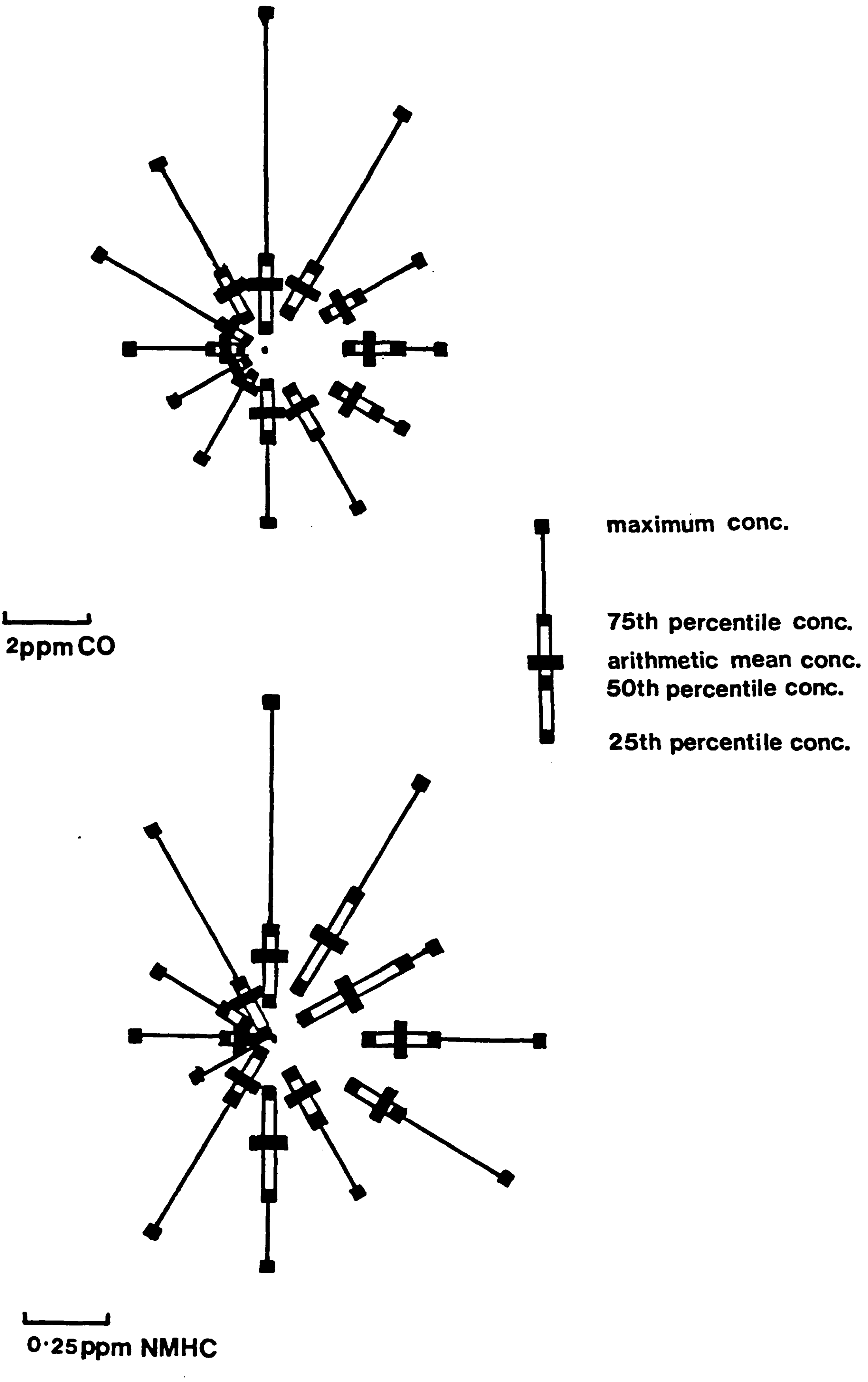


Figure 13 : Pollution roses for SO_2 and O_3 at the urban site, 1982

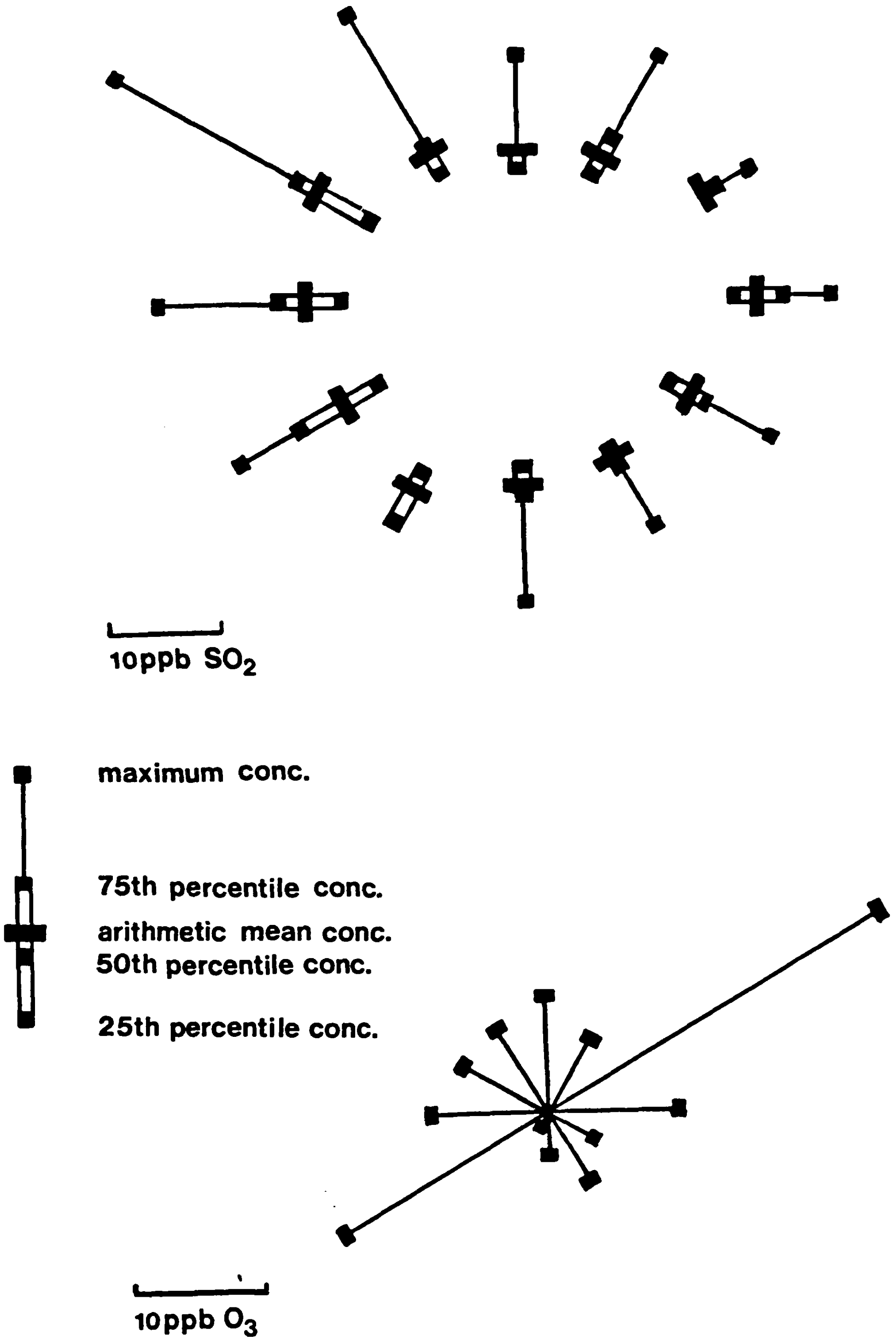
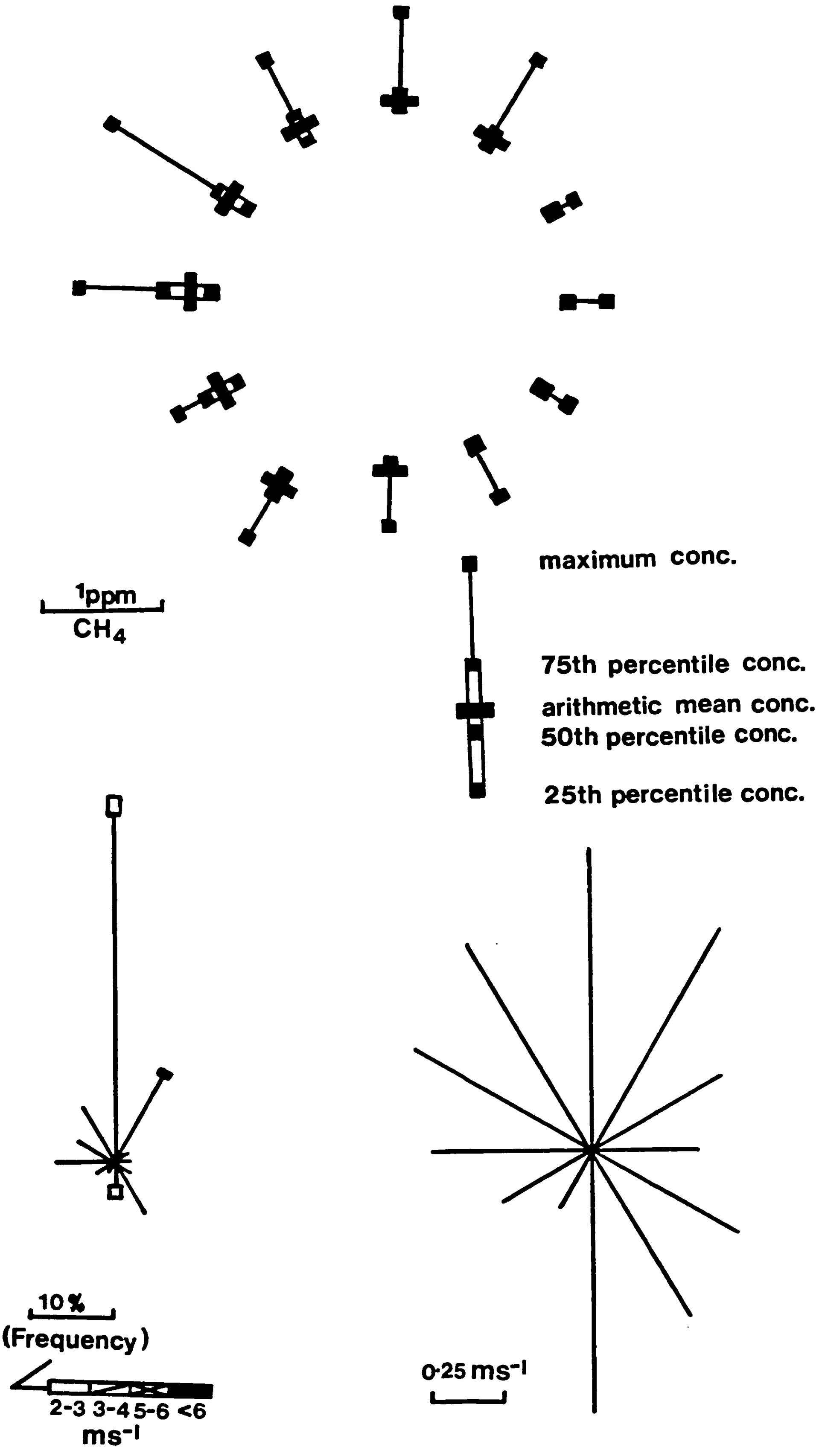


Figure 14 : Pollution rose for CH_4, composite wind rose, magnitude of mean wind velocity per sector at the urban site, 1982



Composite wind rose

Mean wind velocity

Sulphur dioxide, although not strictly a transport-related pollutant, was measured as a comparison with the other pollutants. Measured SO_2 concentrations were similar during the 1982 and 1983 surveys (17.6 and 20.8 ppb arithmetic mean, respectively). Ozone, a secondary pollutant, is a product of photochemical reactions with other transport-related pollutants and was therefore included in the monitoring survey. Arithmetic mean O_3 concentrations were comparatively low in 1982 and 1983 (1 and 5 ppb, respectively) but both periods demonstrated a high variability with maxima of 48.5 and 56.4 ppb, respectively).

Measured concentrations of NO and NO_2 in 1983 had arithmetic means of 4.1 pphm and 5.7 pphm. The 95th percentile concentration of NO_2 was greater than 10 pphm, corresponding to 36 h for a sampling period of 30 days.

Pollution roses for NMHC, CO, SO_2 and O_3 during the 1982 survey are presented in Figures 12 and 13. The CH_4 pollution rose is presented in Figure 14 along with the composite wind rose (frequency of occurrence of wind in a particular sector, and of the wind velocity classes recorded in that sector) and the magnitude of the mean wind velocity per sector.

The CH_4 rose demonstrated no strong directional bias, reflecting the approximate constant emission from natural sources. The NMHC and CO roses displayed a strong directional bias of the arithmetic mean concentrations, which indicated the importance of traffic-related emissions from the road. The NMHC and CO maxima concentrations occurred mainly in the 330-30° arc in which the frequency of wind occurrence was also the greatest.

The pollution rose for SO_2, like CH_4, exhibited insignificant directional bias which demonstrated that no single dominant point source contributed to SO_2 concentrations at this site. Only maxima concentrations have been presented in the O_3 pollution rose, since minima, mean and quartile values were comparatively low. Highest concentrations occurred in the 60° and 210° sections, directions in which low wind speeds occurred.

Figure 15 : Pollution rose for NMHC and CO at the urban site, 1982

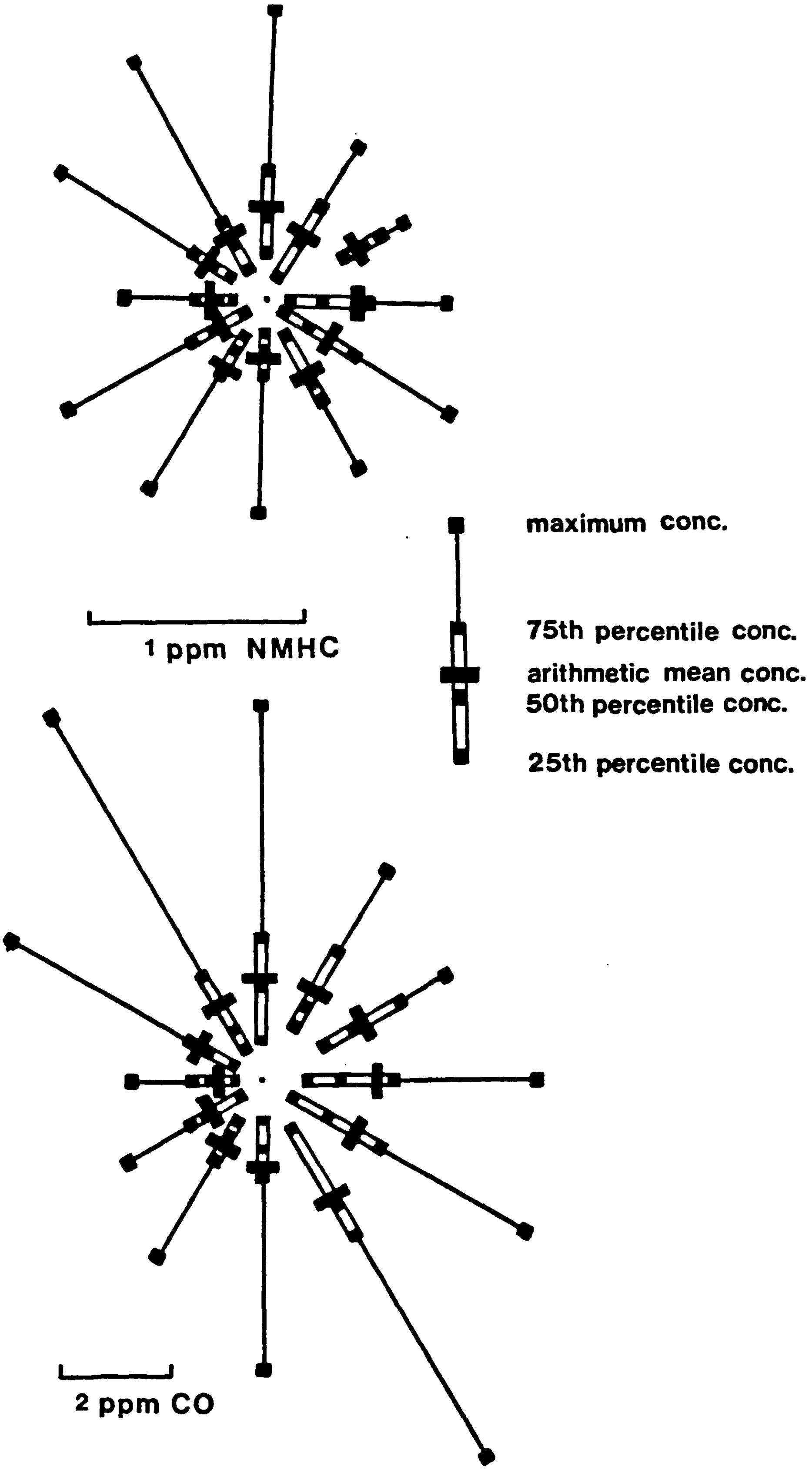
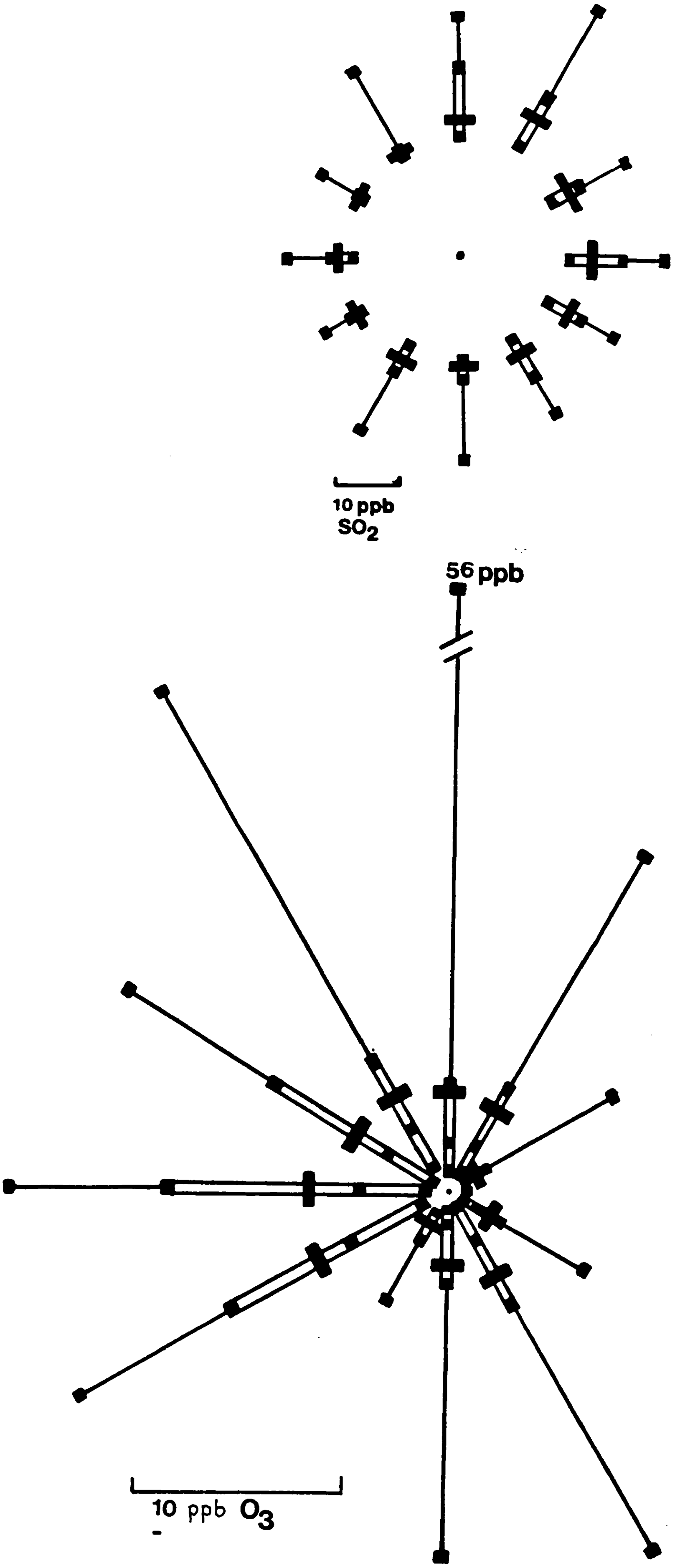


Figure 16 : Pollution rose for SO_2 and O_3 at the urban site, 1983



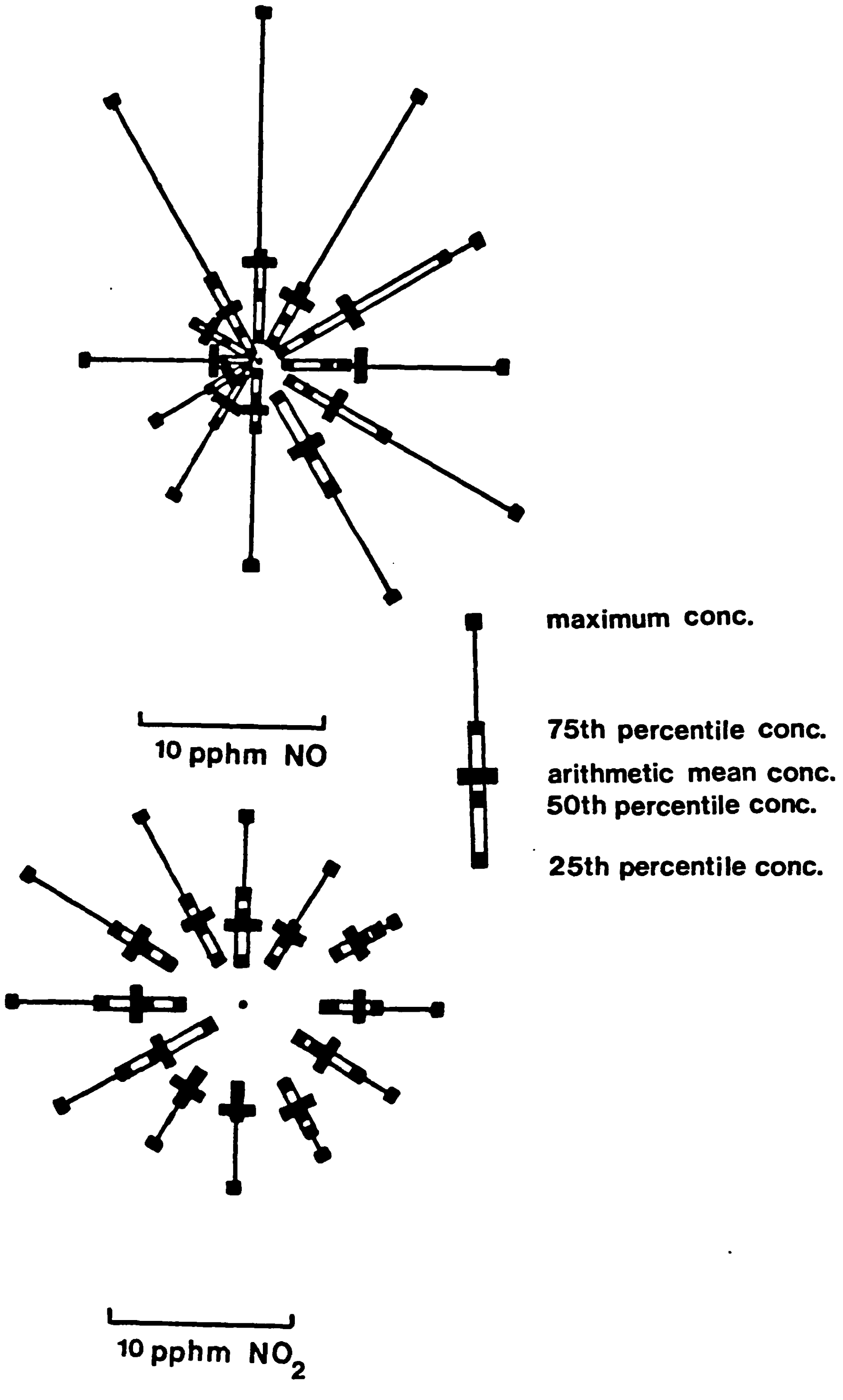
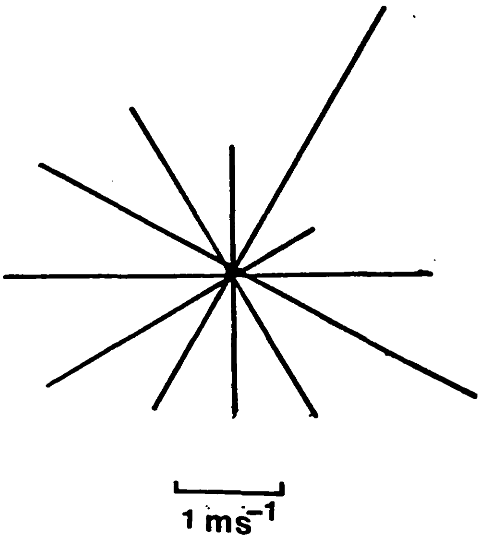
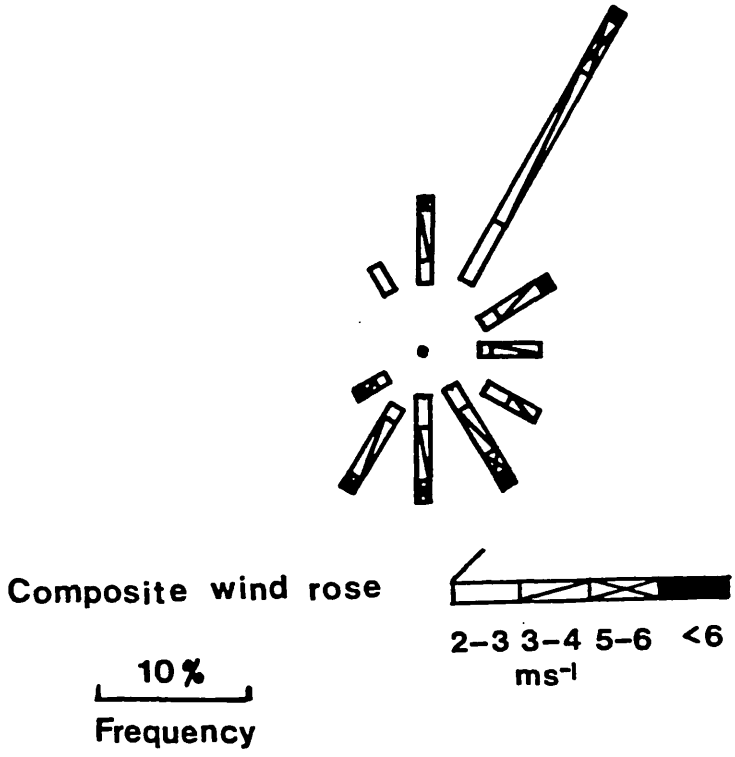


Figure 17 : Pollution rose for NO and NO_2 at the urban site, 1983

Figure 18 : Composite wind rose and the magnitude of mean wind velocity per sector



Mean wind velocity



Pollution roses for NMHC, CO, SO_2, O_3, NO and NO_2 are presented in Figures 15, 16 and 17. The composite wind rose and the magnitude of mean wind velocity per sector is presented in Figure 18.

An easterly bias was also present in the 1983 pollution roses for NMHC and CO arithmetic mean concentrations (Figure 15). The CO and NMHC maxima occurred in sectors (0°, 150° and 330°) with the highest frequencies during periods of low wind velocity (< 2 ms^{-1}).

The SO_2 pollution rose demonstrated no significant directional dependence and was similar to that obtained in the 1982 survey (Figure 13). The O_3 pollution rose displayed a directional bias in the 240-30° arc with a maxima of 56.4 ppb occurring in the 0° sector.

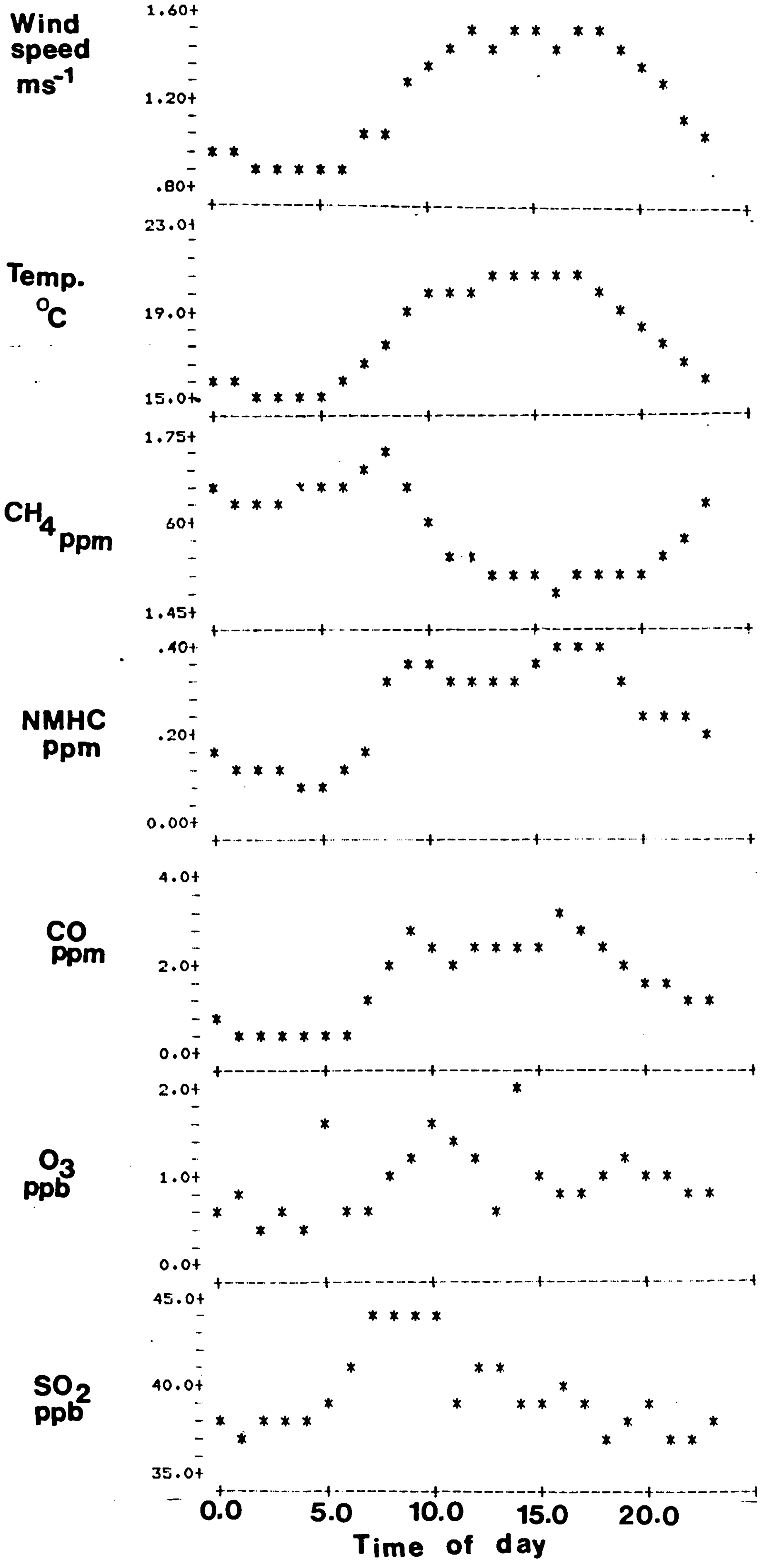
The NO pollution rose followed the same pattern as CO and NMHC, with a strong easterly directional dependence indicating the importance of localised traffic sources. Nitrogen dioxide, formed by the oxidation of NO, exhibited no such directional dependence.

Diurnal variations in wind speed, temperature, CH_4, NMHC, CO, O_3 and SO_2 obtained from the 1982 survey are presented in Figure 19. The typical diurnal pattern of wind speed and temperature broadly corresponds to the dispersive properties of the atmosphere. The diurnal variation of CH_4 reflected these conditions with a minimum concentration occurring in the afternoon. Figure 20 illustrates the total traffic flow, as measured throughout the day. Traffic peaks occurred at approximately 0800 hours and 1700 hours. The CO and NMHC diurnal variations closely followed this pattern.

The diurnal variation in O_3 is difficult to interpret as measured concentrations were low and no distinct pattern was observed. The SO_2 concentrations exhibited a morning peak, followed by fluctuations during the rest of the day, presumably reflecting different source strengths and atmospheric dispersion.

Weekday-weekend differences in diurnal variation of O_3, CO and NMHC concentrations are presented in Figure 21. Non-methane hydrocarbons and CO at weekends displayed a significantly different pattern with concentrations rising more slowly than weekdays to a peak around

Figure 19 : Diurnal variations in wind speed, temperature, CH_4, NMHC, CO, O_3 and SO_2 at the urban site, 1982



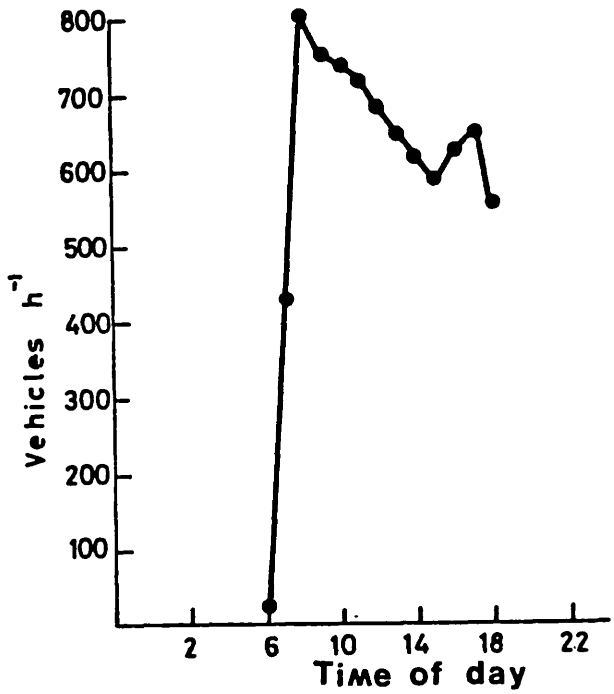


Figure 20 : Diurnal variation in traffic flow at the urban site, 1982

1200-1400 hours with additional peaks appearing at later hours (1700 and 2000-2200 hours) reflecting a different vehicle usage pattern at weekends. The weekend diurnal variation in O_3 is difficult to interpret. Generally, concentrations of O_3, CO and NMHC were lower than those occurring during weekdays.

Diurnal variations in windspeed, temperature, NMHC, CO, SO_2, O_3, NO and NO_2 observed during the 1983 survey are presented in Figure 22.

Similar patterns to the 1982 survey were obtained for windspeed, temperature, NMHC and CO. Sulphur dioxide concentrations demonstrated minimal variation except for a peak between 1700 and 2100 hours.

Ozone exhibited a distinct diurnal pattern with maxima occurring at approximately 0300 hours and 1100 hours and the minimum occurring at 0800 hours. The early morning peak coincided with the minimum windspeed and temperature values and thus with minimum atmospheric dispersion. The second maximum occurred in the morning between 1 and 2 hours after the maximum values of NMHC and CO, NO and NO_2.

Figure 21 : Weekday-weekend differences in diurnal variation of NMHC, CO and O_3 at the urban site, 1982

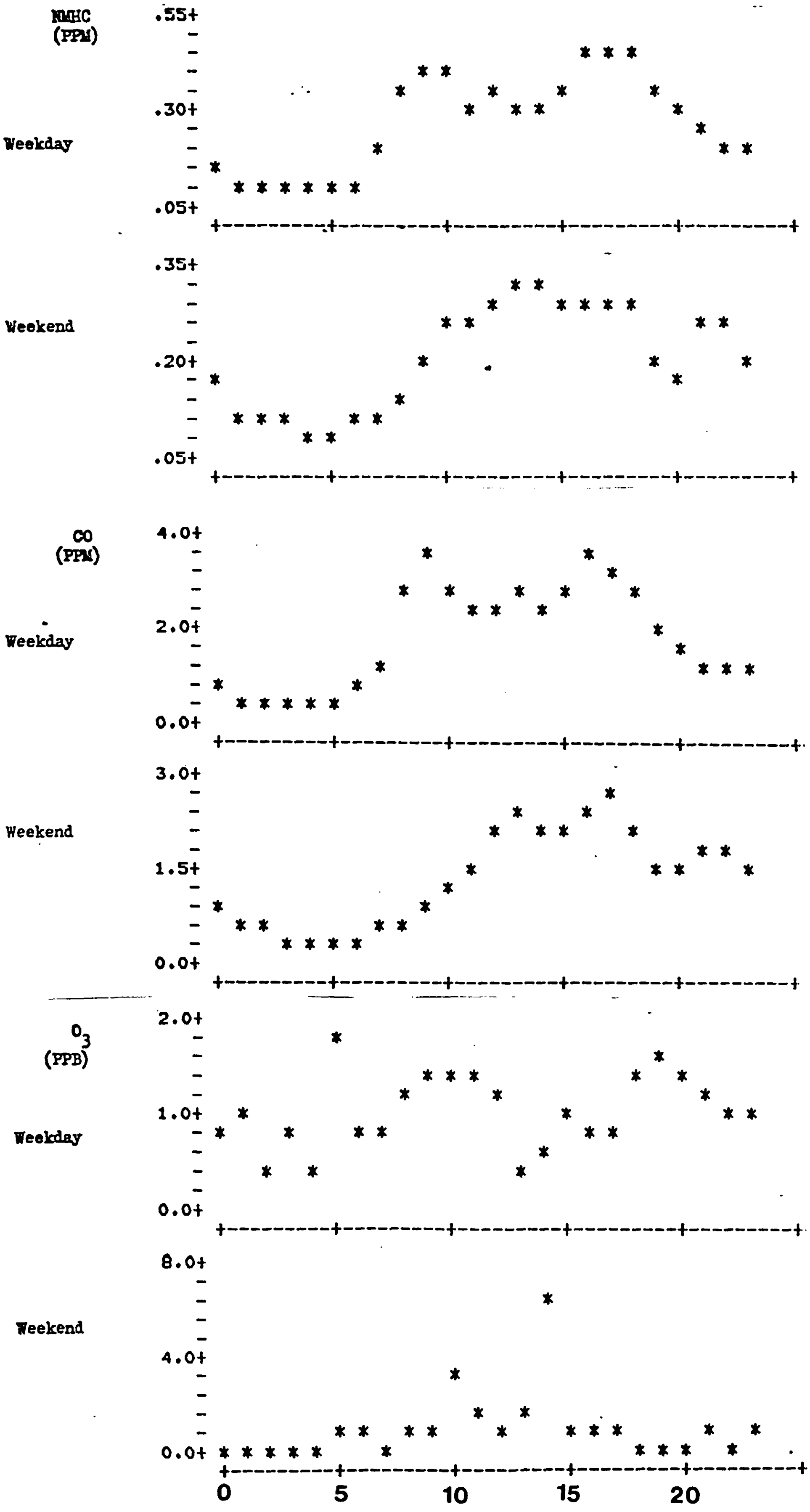


Figure 22 : Diurnal variations in wind speed, temperature, NMHC, CO, SO_2, O_3, NO and NO_2 at the urban site, 1983

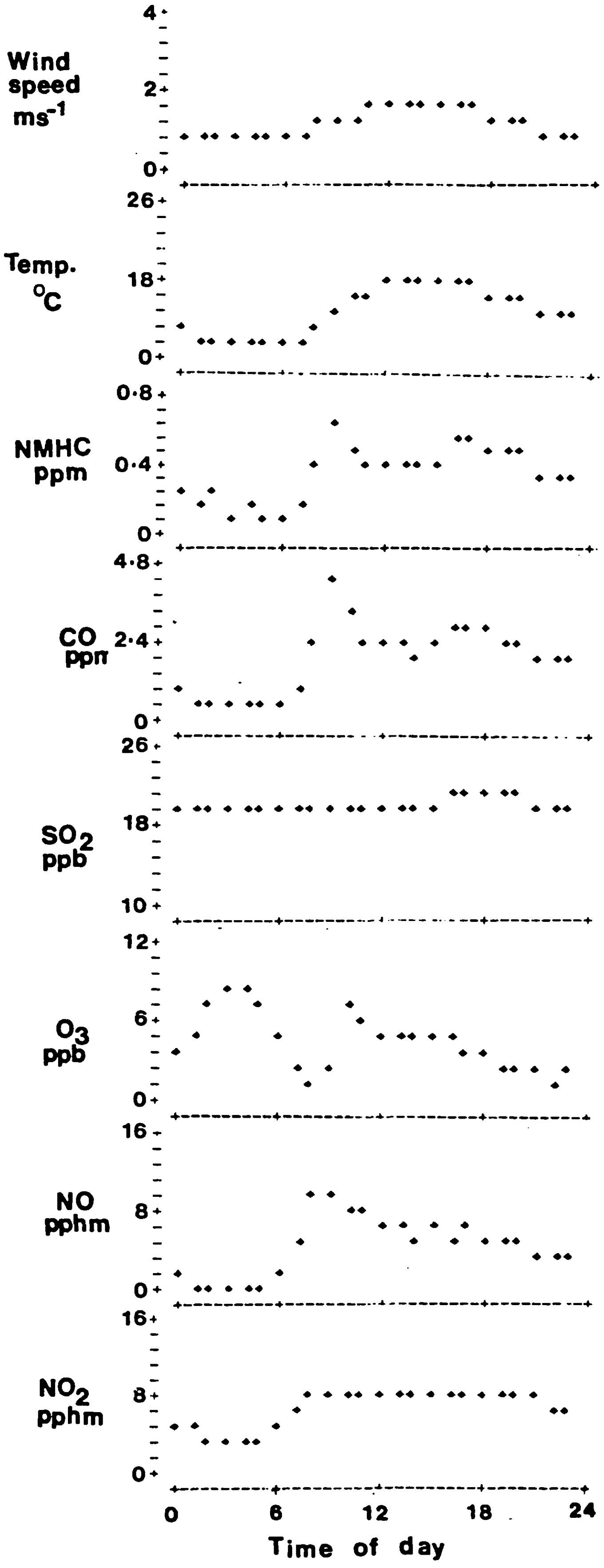


Figure 23 : Weekday-weekend differences in diurnal variation of NMHC, CO and O_3 at the urban site, 1983

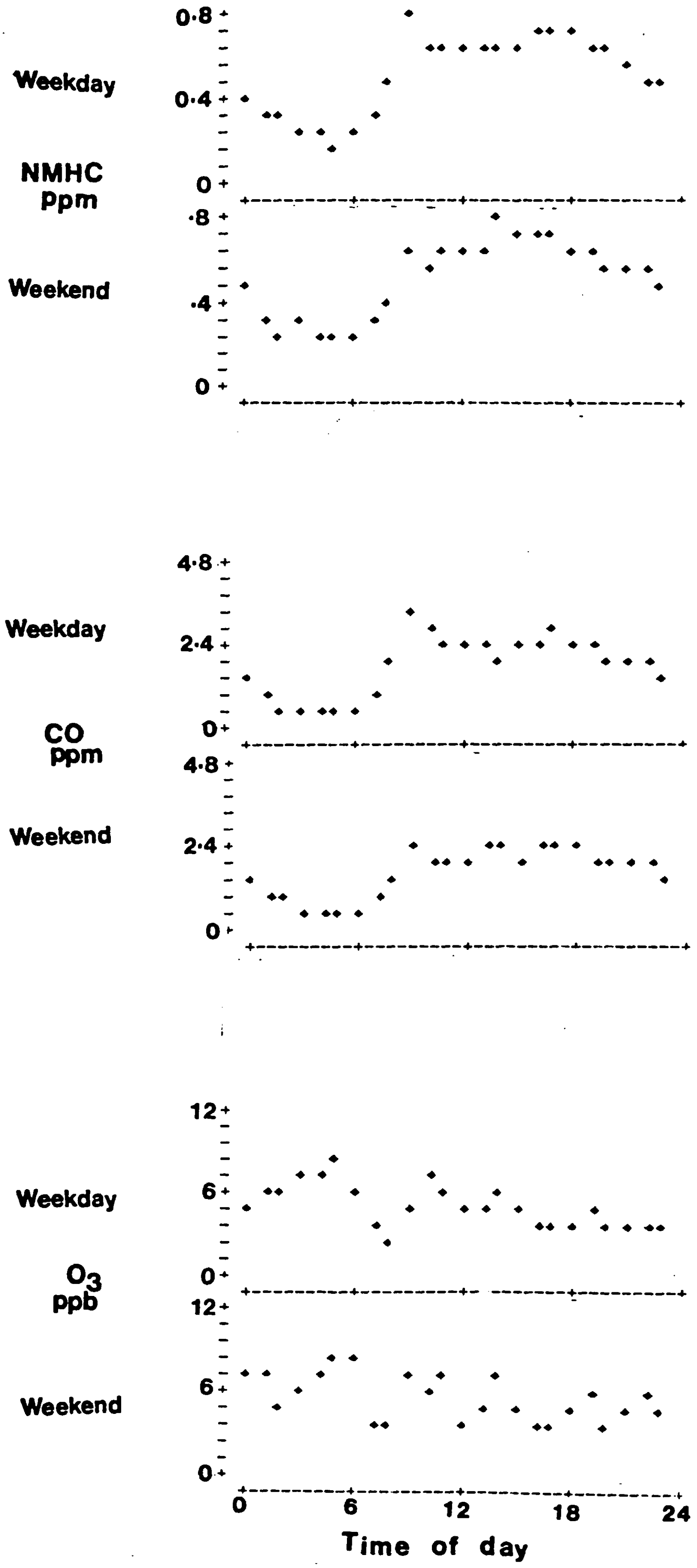
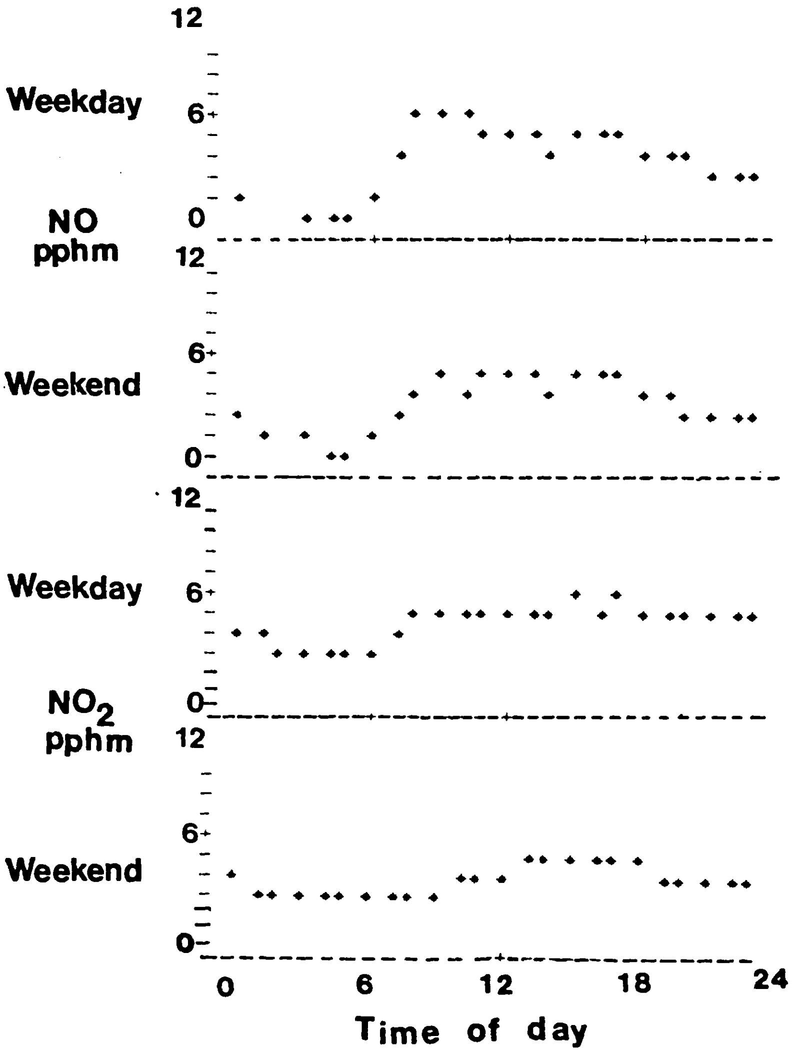


Figure 24 : Weekday-weekend differences in diurnal variation of NO and NO_2 at the urban site, 1983



The weekday-weekend differences in diurnal variation of NMHC, CO and O_3, presented in Figure 23, were not as distinct as those occurring in the 1982 survey. The NO and NO_2 weekday-weekend diurnal variations are presented in Figure 24. The morning peak in NO was more pronounced during weekdays than at weekends. Additionally, elevated NO_2 concentrations occurred between 0800 and 2000 hours on weekdays as opposed to between 1300 and 1800 hours at weekends.

The diurnal variation of the NO_2/NO ratio is presented in Figure 25. The ratio, between 0000 and 0600 hours in the morning (>3), broadly indicates that distant sources were responsible for measured concentrations. However, the ratio rapidly decreased to approximately 1, coinciding with the morning build-up in traffic, indicating that local emissions were the major influence on measured concentrations.

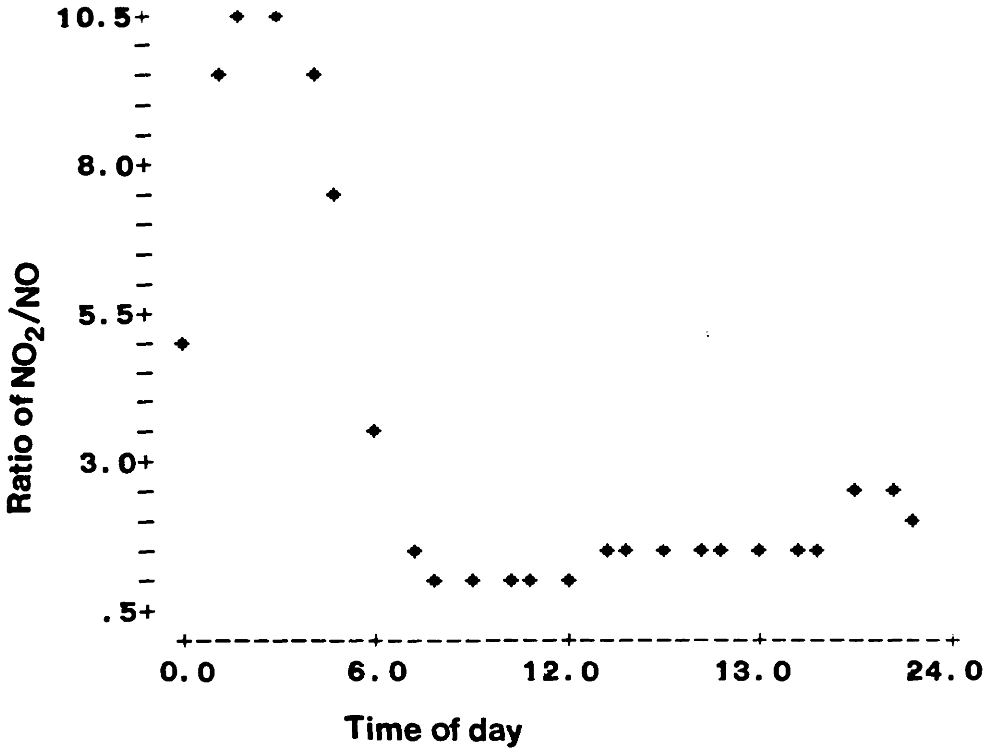


Figure 25 : Diurnal variation of the NO_2/NO ratio at the urban site, 1983

In general, these surveys at this site demonstrated the importance of the traffc-related pollutants (CO, NMHC, NO_x and O_3) in defining overall air quality in the urban environment. The pollution roses and diurnal averages describe the spatial and temporal distributions of the pollutants. However, they provide little information on the role of vehicle operating mode on air quality.

4.1.2.2 Motorway Site - Toddington, M1

The effect of a different vehicle operating mode on air quality was evaluated by two monitoring surveys at the southbound side of the M1 motorway, Toddington, Bedfordshire (see Figure 26) during the summers of 1982 and 1983. At this location, traffic density was high and vehicles were travelling at a constant high speed.

The mobile laboratory was employed for measurements (see Section 3.1.1) and was situated approximately 10 m from the hard shoulder. The sampling periods were from 8 August to 5 September 1982 and from 12 June to 10 July 1983.

Summary tables of the air quality characteristics during the monitoring periods in 1982 and 1983 are presented in Tables 14 and 15.

Similar arithmetic mean concentrations of NMHC were found during 1982 and 1983 (0.21 and 0.25 ppm, respectively). However, data distributions for the two periods were distinct. In 1982, the 99th percentile was 0.89 compared to 1.41 ppm in 1983. The maximum concentration found in 1983 was 4.31 ppm. The percentage of NMHC to THC varied between 13.5% in 1982 and 12.1% in 1983.

Methane concentrations in 1983 were unusually distributed. A maximum hourly concentration of 6.34 ppm was recorded with a 4.06 ppm 99th percentile.

Carbon monoxide arithmetic mean concentrations were 0.73 and 0.84 ppm in 1982 and 1983 respectively. However, a higher 99th percentile value of 7.8 ppm was found than the value of 2.57 ppm at this site in 1982. Measured SO_2 arithmetic mean concentrations were similar in both 1982 and 1983 (17.5 ppb and 17.0 ppb, respectively).

Ozone arithmetic mean concentrations and percentile values were more elevated during the 1983 survey (mean of 7.9 ppb) than in 1982

Figure 26 : Location of the motorway site, Toddington, Bedfordshire

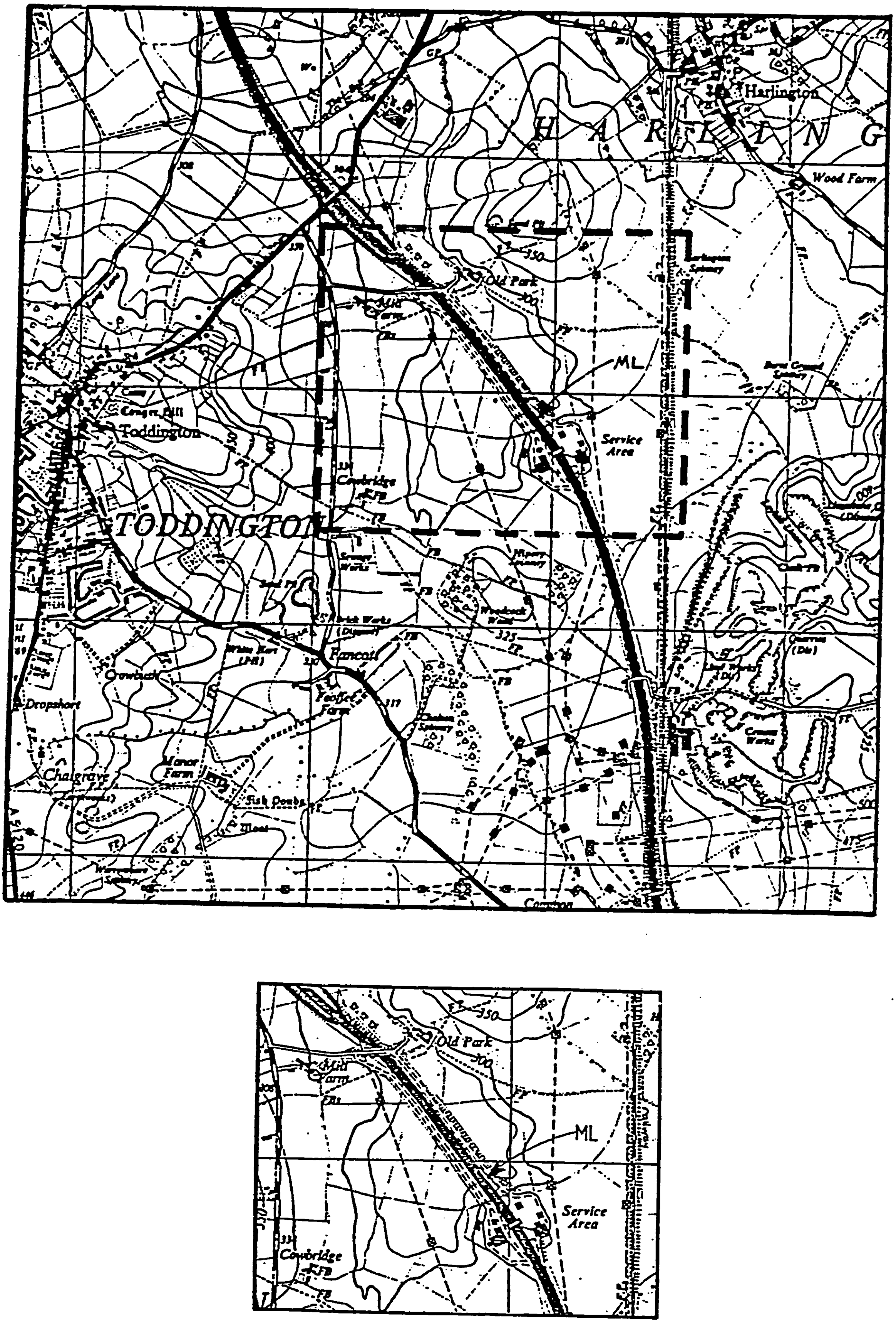


Table 14 : General air quality characteristics at the motorway site, 1982

	CH_4 ppm	THC ppm	NMHC ppm	CO ppm	SO_2 ppb	Ozone ppb
Arithmetic Mean	1.39	1.55	0.21	0.75	17.52	0.35
Minimum	1.07	1.22	0	0.06	12.8	0
25th percentile	1.25	1.38	0.07	0.40	15.52	0
50th percentile	1.42	1.49	0.17	0.67	17.09	0
75th percentile	1.54	1.70	0.28	0.97	19.03	0.23
90th percentile	1.61	1.85	0.51	1.38	21.16	0.8
95th percentile	1.63	1.93	0.6	1.69	22.31	1.95
99th percentile	1.66	2.15	0.73	2.57	25.49	4.69
Maximum	2.08	2.33	0.81	2.96	28.32	20.13
Standard Deviation	0.17	0.21	0.18	0.49	25.8	1.13
Variability*	12.17	13.69	88.34	64.53	14.75	328.32

* variability is defined as (the standard deviation/arithmetic mean) × 100

Table 15 : General air quality characteristics at the motorway site, 1983

	CH_4 ppm	THC ppm	NMHC ppm	CO ppm	SO_2 ppb	Ozone ppb	NO pphm	NO_x pphm	NO_2 pphm
Arithmetic Mean	1.83	2.07	0.25	0.84	16.98	7.93	9.17	12.11	2.99
Minimum	1.32	1.38	0	0.12	12.6	0	0	0.14	0.12
25th percentile	1.55	1.64	0.07	0.31	15.47	0.24	0.17	0.93	0.76
50th percentile	1.65	1.81	0.14	0.57	16.67	2.58	3.06	5.94	2.50
75th percentile	1.84	2.16	0.38	1.07	18.03	9.76	15.52	20.92	4.69
90th percentile	2.35	2.77	0.49	1.60	20.05	25.13	25.36	31.23	6.15
95th percentile	3.07	3.64	0.7	2.15	21.77	38.12	30.48	35.35	7.33
99th percentile	4.06	5.17	1.41	5.95	23.67	50.92	52.21	53.99	11.57
Maximum	6.34	8.43	4.31	7.80	30.26	71.06	57.49	60.65	13.62
Standard Deviation	0.58	0.81	0.33	0.93	2.31	12.16	11.66	13.27	3.50
Variability*	31.82	39.01	131.22	110.48	13.63	153.33	127.19	109.62	83.69

* variability is defined as (the standard deviation/arithmetic mean) × 100

Figure 27 : Pollution rose for NMHC and CO at the motorway site, 1982

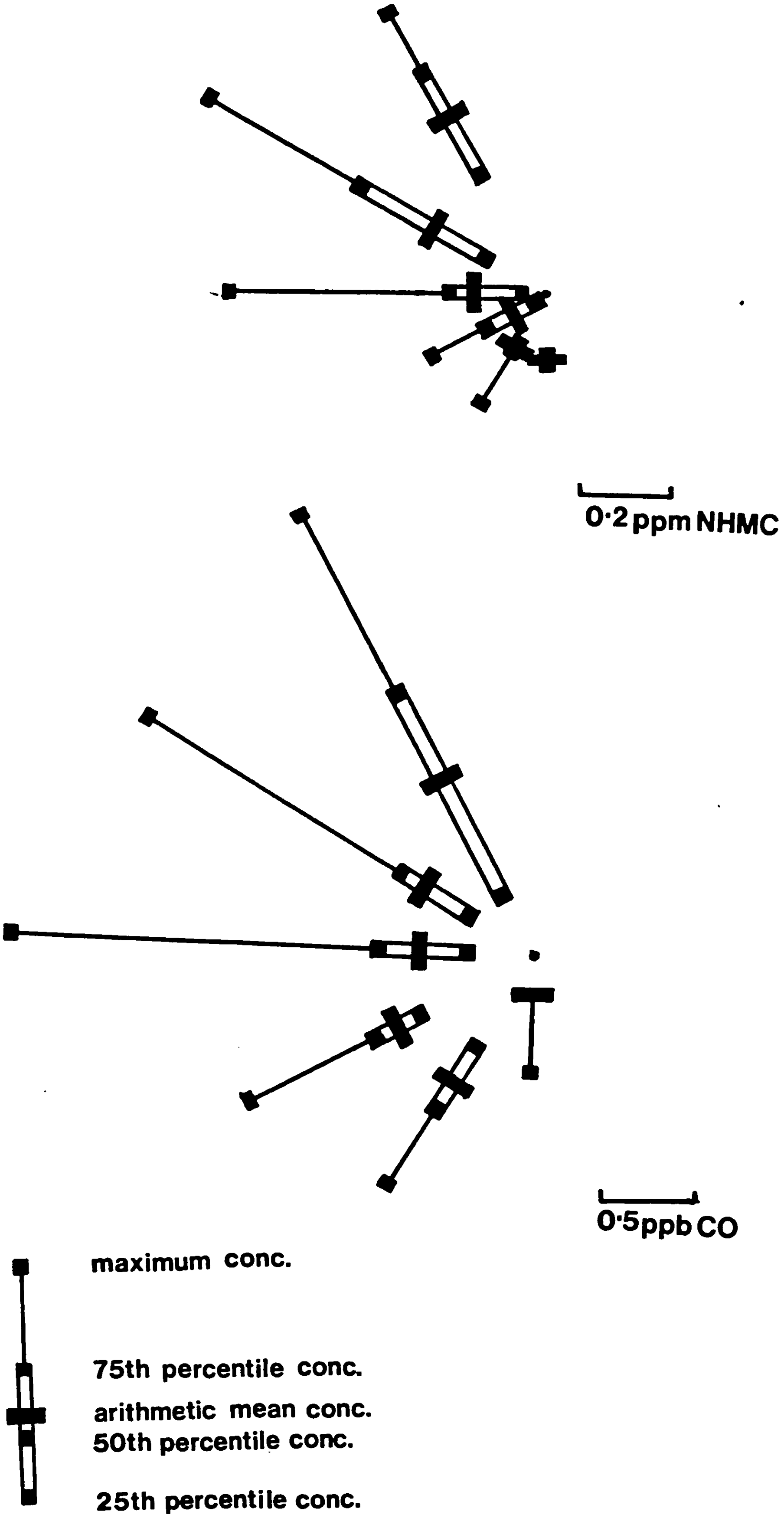


Figure 28 : Pollution rose for SO_2 and O_3 at the motorway site, 1982

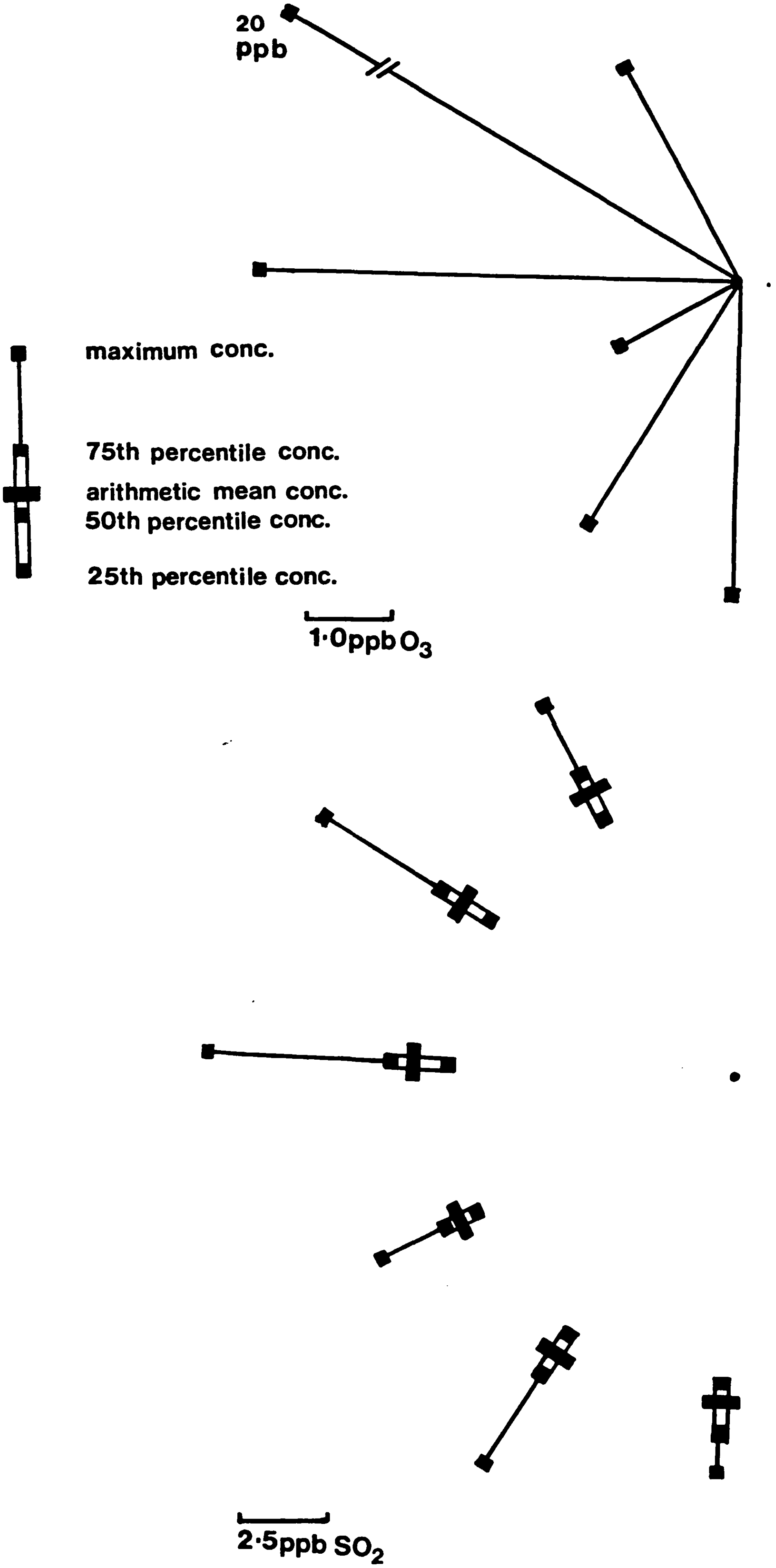
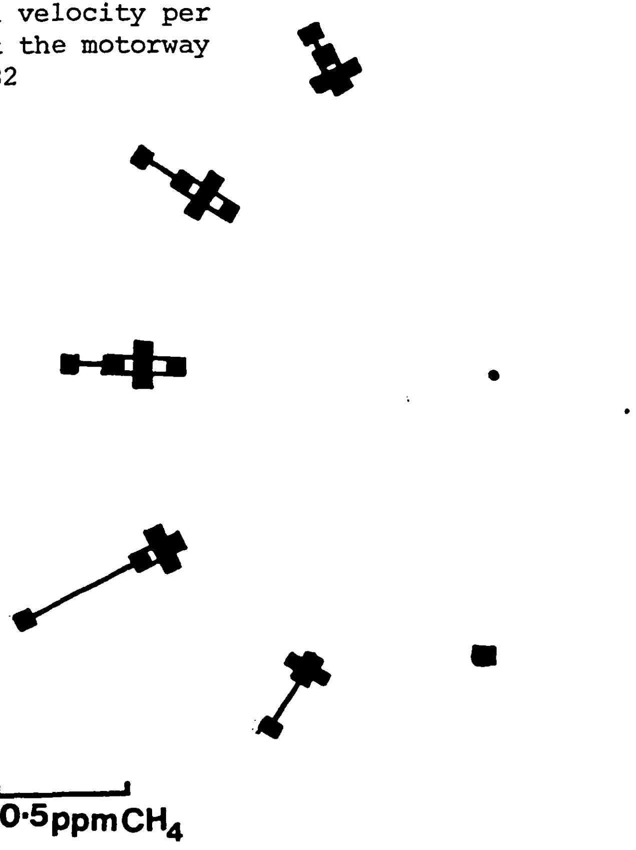
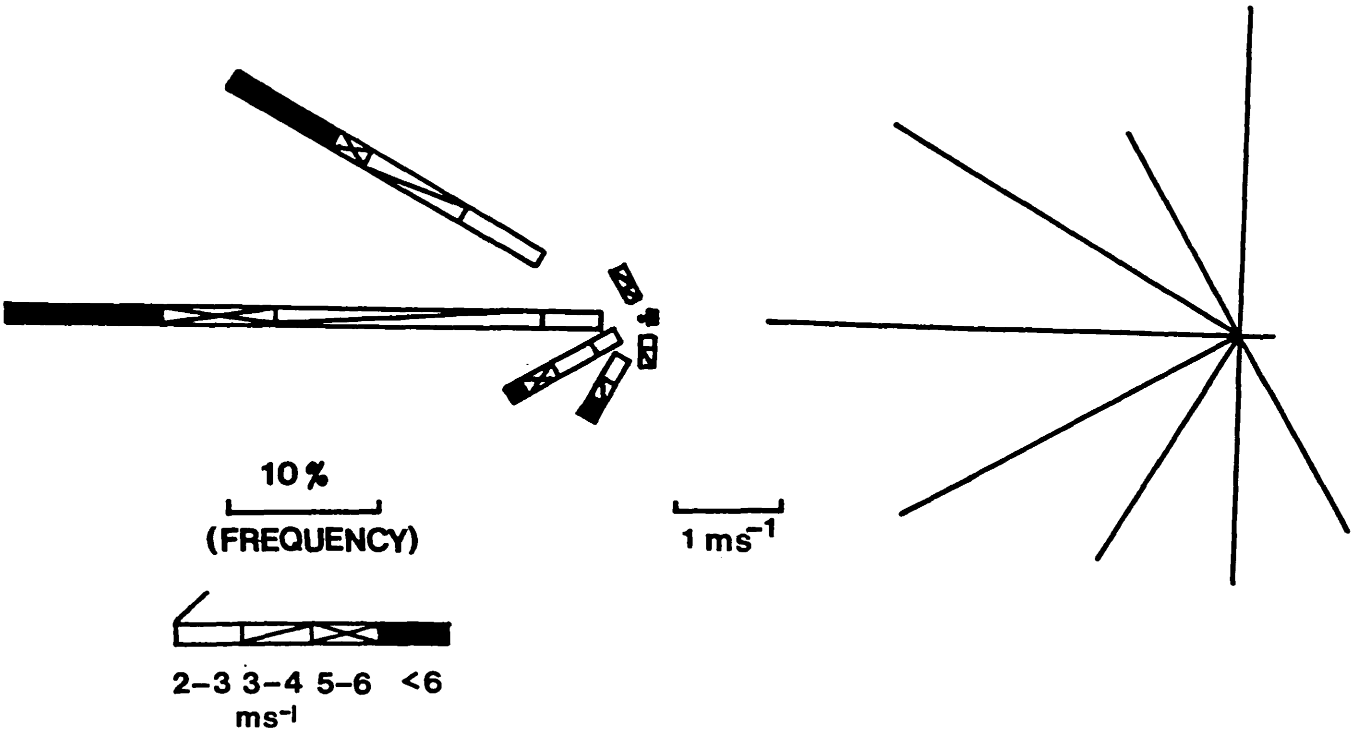


Figure 29 : Pollution rose for CH_4, composite wind rose, magnitude of mean wind velocity per sector at the motorway site, 1982





Composite wind rose

Mean wind velocity

(mean of 0.3 ppb). Arithmetic mean concentrations of NO and NO_2 were 9.2 pphm and 3.0 pphm, respectively. A more elevated 99th percentile value was also observed for NO (52.2 pphm) than NO_2 (11.6 pphm). The ratio between arithmetic mean NO_2 and NO concentrations was 0.32 which indicated that local emissions of NO predominated at the motorway site.

Pollution roses for NMHC, CO, SO_2 and O_3 during the 1982 survey are presented in Figures 27, 28 and the CH_4 pollution rose along with the composite wind rose and the magnitude of mean wind velocity per sector presented in Figure 29.

The composite wind rose (Figure 29) demonstrated that the wind was predominantly from the 270° and 300° sectors i.e. blowing across and parallel to the motorway. The maximum CH_4 result arose in the 240° sector. Figure 30 shows the presence of a sewage works, 1.75 km away, on a 230° bearing from the mobile laboratory. It is reasonable to assume that this was the source of the CH_4 maximum.

The NMHC and CO pollution roses exhibit similar patterns, with the highest arithmetic means arising in the 330° sector which is parallel to the motorway. Maxima concentrations arose from the 300° sector for NMHC and from the 270-330° arc for CO.

The SO_2 pollution rose showed no directional dependence which is similar to the SO_2 rose derived from the urban surveys. Only the maxima ozone rose is presented in Figure 28, as measured concentrations were low. The highest concentration occurring was 40.3 ppb which arose from the 300° sector. The greatest frequency of wind velocity also arose from this sector.

Pollution roses for NMHC, CO, SO_2, O_3, NO and NO_2 during the 1983 survey are presented in Figures 30, 31, 32 and the CH_4 pollution rose along with the composite wind rose and the magnitude of mean wind velocity per sector is presented in Figure 33. The wind predominantly arose in the arc between 90° and 150° with major contributions from other sectors except 0°, 30° and 60°.

The CH_4 rose demonstrated the ubiquitous nature of CH_4 sources with maxima concentrations mainly occurring from the 150° and 240°

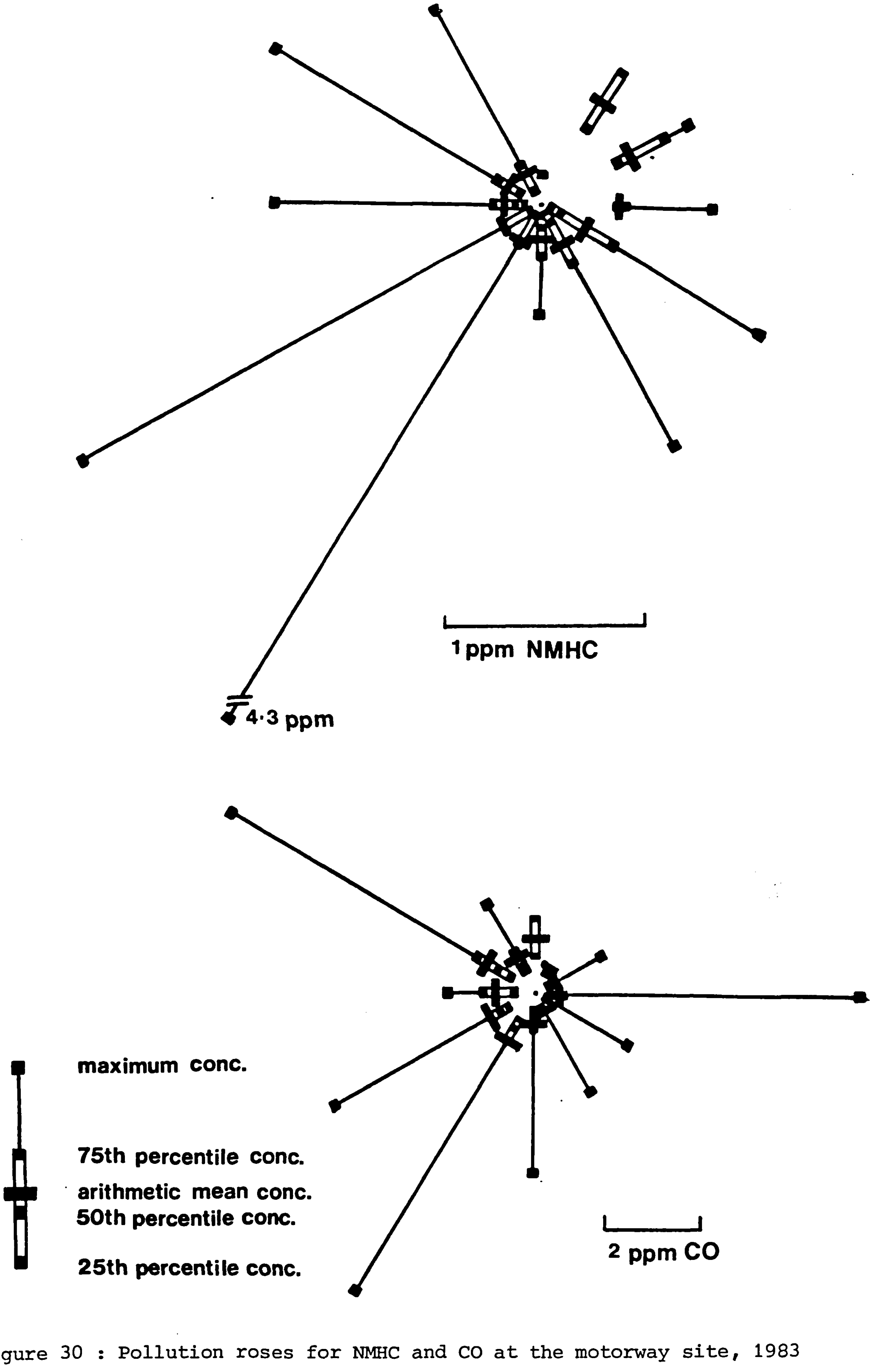


Figure 30 : Pollution roses for NMHC and CO at the motorway site, 1983

Figure 31 : Pollution roses for SO_2 and O_3 at the motorway site, 1983

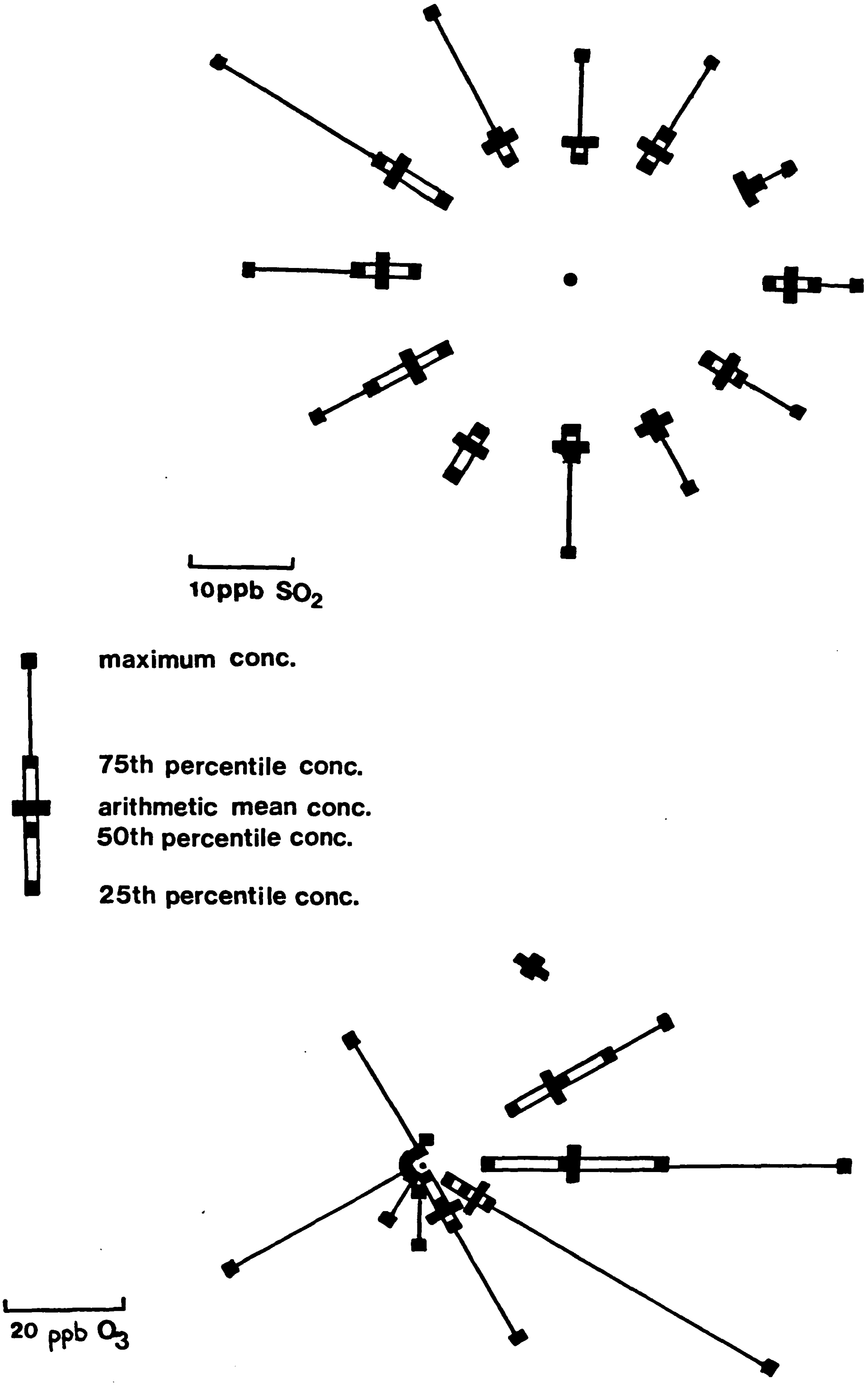
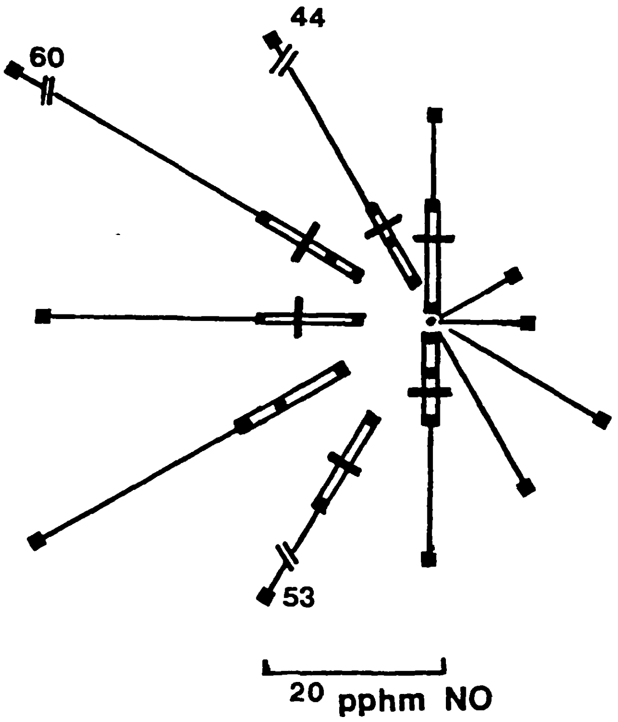
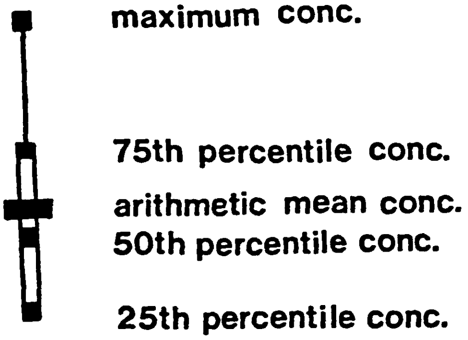


Figure 32 : Pollution roses for NMHC and CO at the motorway site, 1983





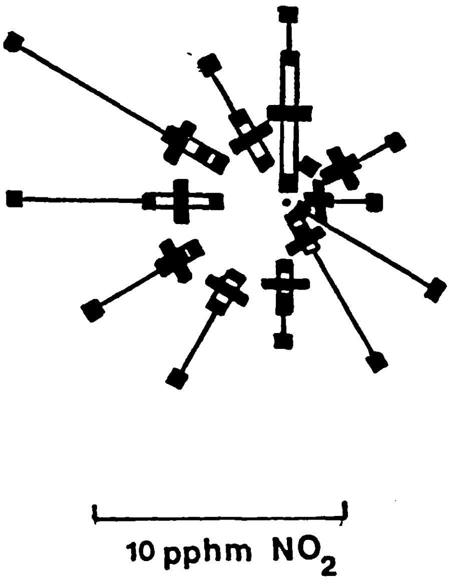
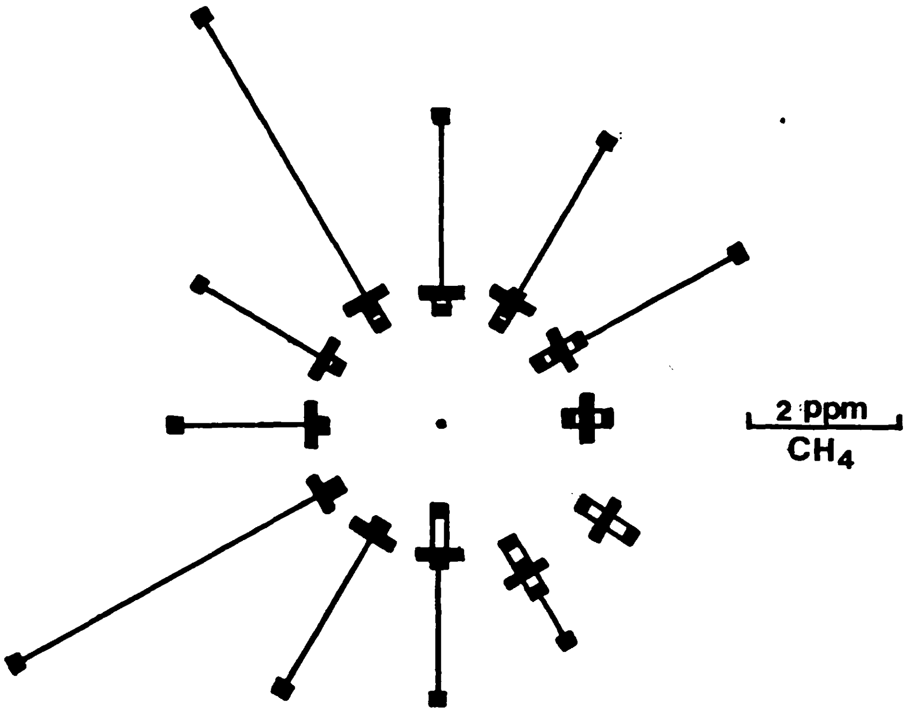
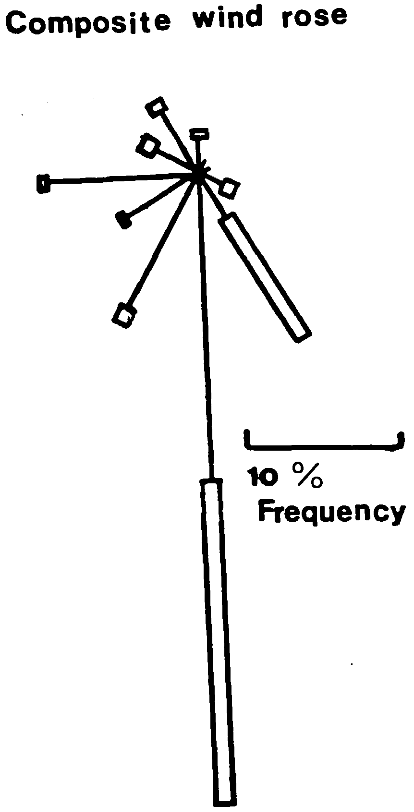


Figure 33 : Pollution rose for CH_4, composite wind rose, magnitude of mean wind velocity per sector at the motorway site, 1983





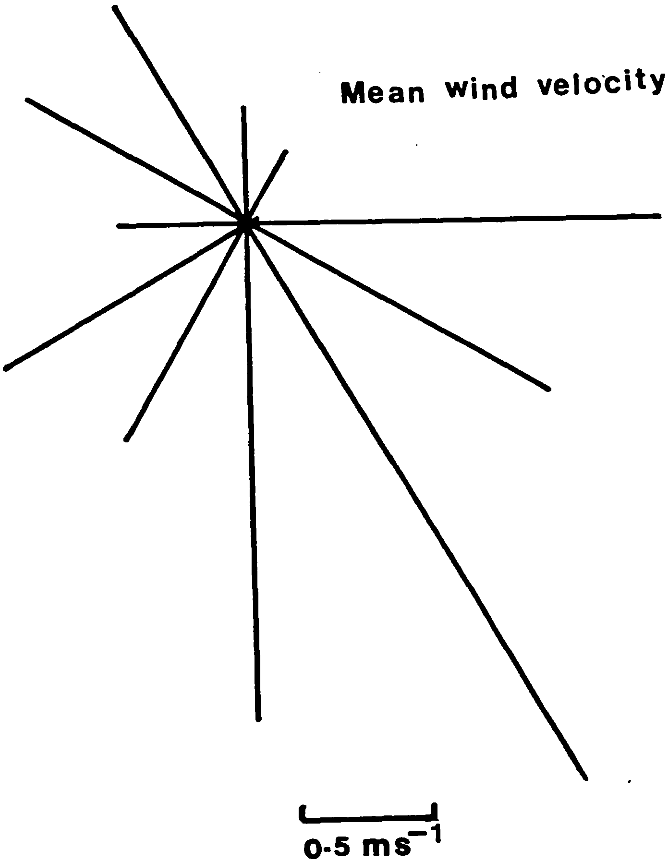
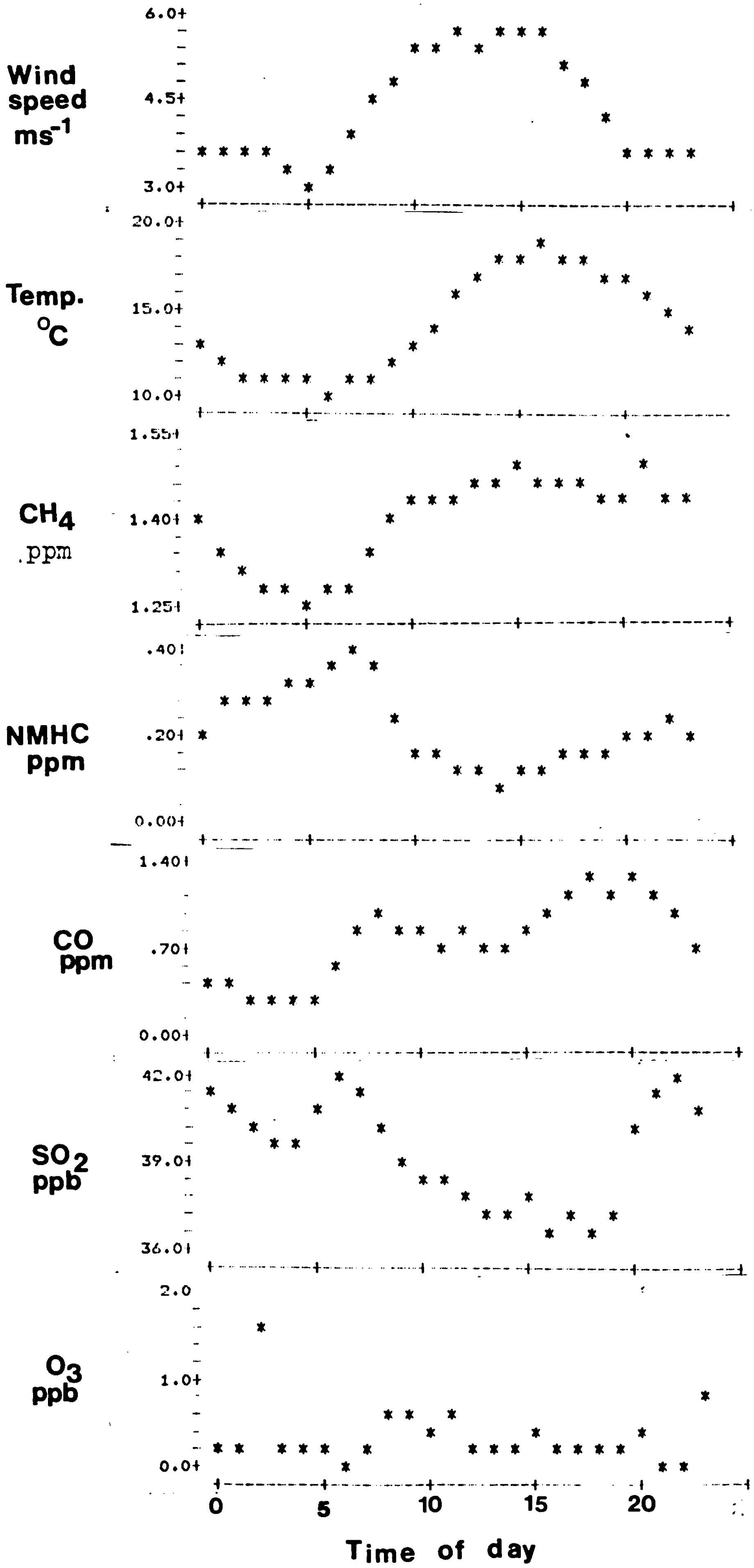


Figure 34 : Diurnal variations in wind speed, temperature, CH_4, NMHC, CO, O_3 and SO_2 at the motorway site, 1982



sectors. The nearby sewage works is on a 230° bearing from the laboratory and was probably the source of the maxima in the 240° sector.

The NMHC rose is atypical in that the highest arithmetic mean concentration was derived from the 30° sector which is away from the motorway. In addition, a maximum concentration of 4.31 ppm was recorded from the 120° sector. This may be due to the petrol filling stations present at the nearby (0.25 km) service areas on both sides of the motorway.

The CO rose was similar to that derived from the 1982 survey. The arithmetic mean concentrations demonstrated a westerly directional dependence. The highest maxima occurred in the 300°, 120° and 90° arc. The latter was probably due to the nearby service road (20 m from mobile laboratory).

The O_3 rose exhibits a directional dependence with the highest arithmetic mean occurring from the 30° sector and the highest maxima occurring in the 90° sector. Again the maxima occurred in the sector with the highest frequency of low wind velocity. The SO_2 rose, as in the 1982 survey, showed no strong directional dependence.

The importance of traffic-related emissions is best illustrated by the NO rose, Figure 32, with the highest arithmetic mean and maxima occurring in the 120°-330° arc, the direction of the motorway. The NO_2 rose is similar except in scale and demonstrated the mechanism of oxidation of NO by O_3, as the minimum concentration of ozone occurred from the directions in which the highest arithmetic mean and maxima concentrations of NO_2 were derived.

Diurnal variations in wind speed, temperature, CH_4, NMHC, CO, O_3 and SO_2 obtained from the 1982 survey are presented in Figure 34. Methane did not follow the diurnal pattern demonstrated at the urban site in that concentrations increased from 0600 hours and peaked at 2200 hours suggesting the presence of a source other than natural production from decaying vegetation.

Concentrations of NMHC reached a peak at approximately 0700 hours which coincided with the peak southbound traffic-flow (presented in

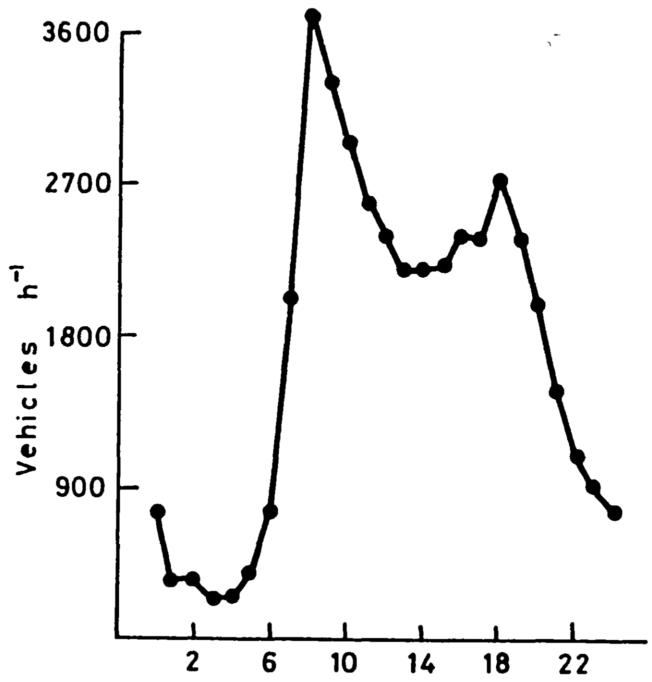


Figure 35 : Diurnal variation in southbound traffic flow at the motorway site, 1982

Figure 35). However, concentrations decayed throughout the day in line with increased temperature and windspeed. The CO concentrations reached a similar peak to NMHC in the morning and a second peak between 1800 and 2000 hours, the evening rush hours.

Measured O_3 concentrations were low and did not demonstrate any significant diurnal variation. Measured SO_2 concentrations decayed as atmospheric turbulence increased suggesting that an approximately constant emission rate of SO_2 exists from local and distant sources.

Weekday-weekend differences in diurnal variation of CO, NMHC and O_3 concentrations are presented in Figure 36. Concentrations of NMHC and O_3 did not show any significant differences. However, weekend peaks in CO occurred at later hours (1200 and 2000-2200 hours, respectively), although the concentrations were not significantly lower than those occurring on weekdays.

Figure 36 : Weekday-weekend differences in diurnal variation of NMHC, CO and O_3 at the motorway site, 1982

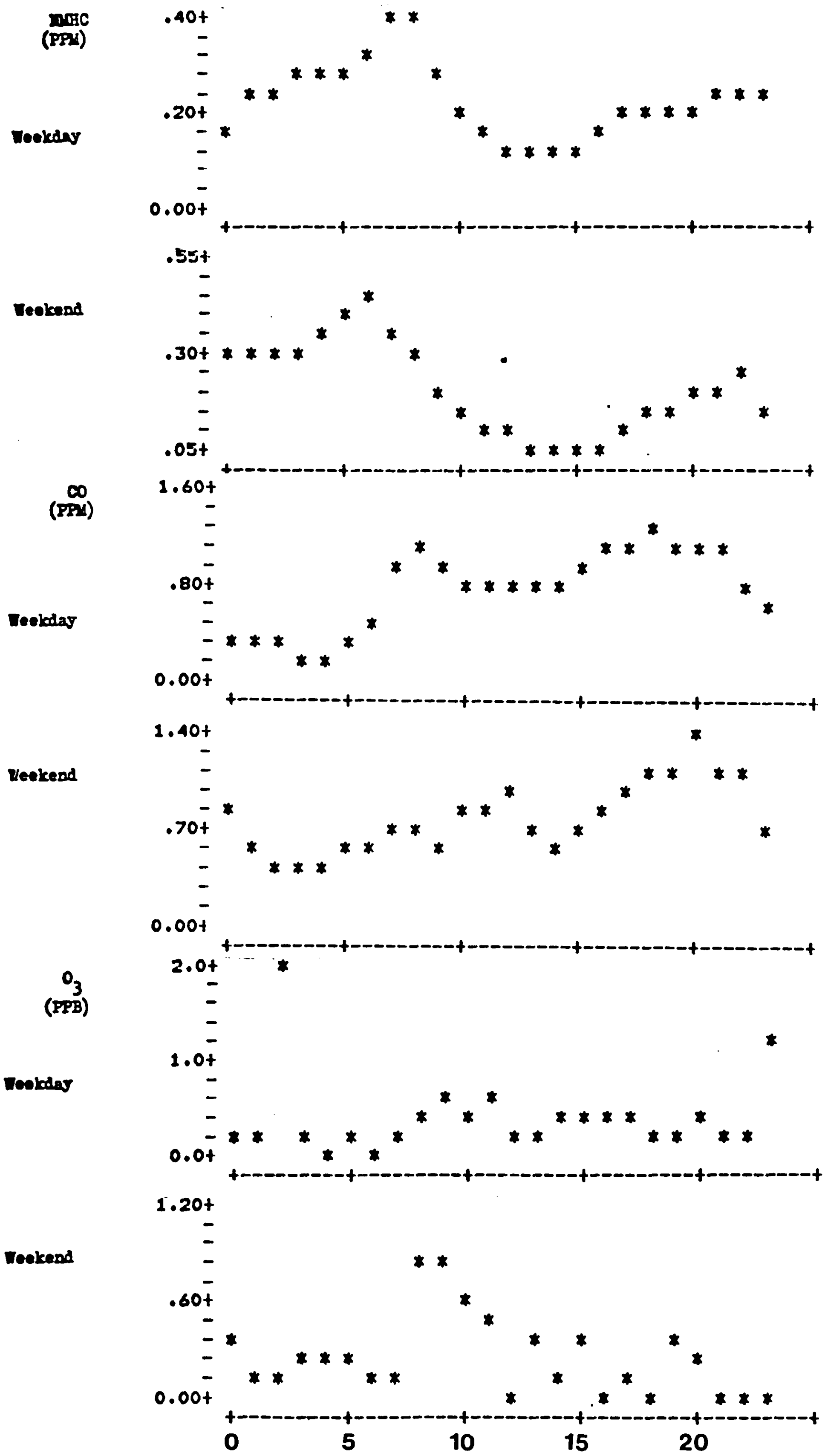


Figure 37 : Diurnal variations in wind speed, temperature, NMHC, CO, SO_2, O_3, NO and NO_2 at the motorway site, 1983

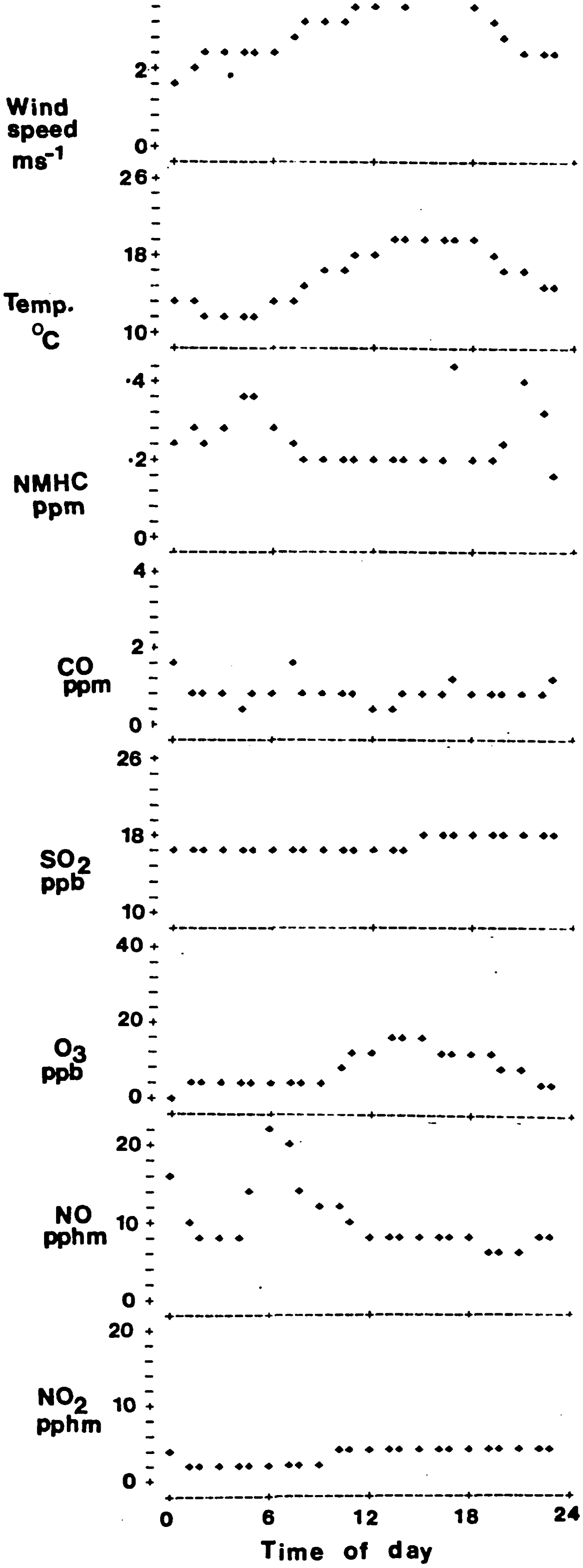


Figure 39 : Weekday-weekend differences in diurnal variation of NMHC, CO and O_3 at the motorway site, 1983

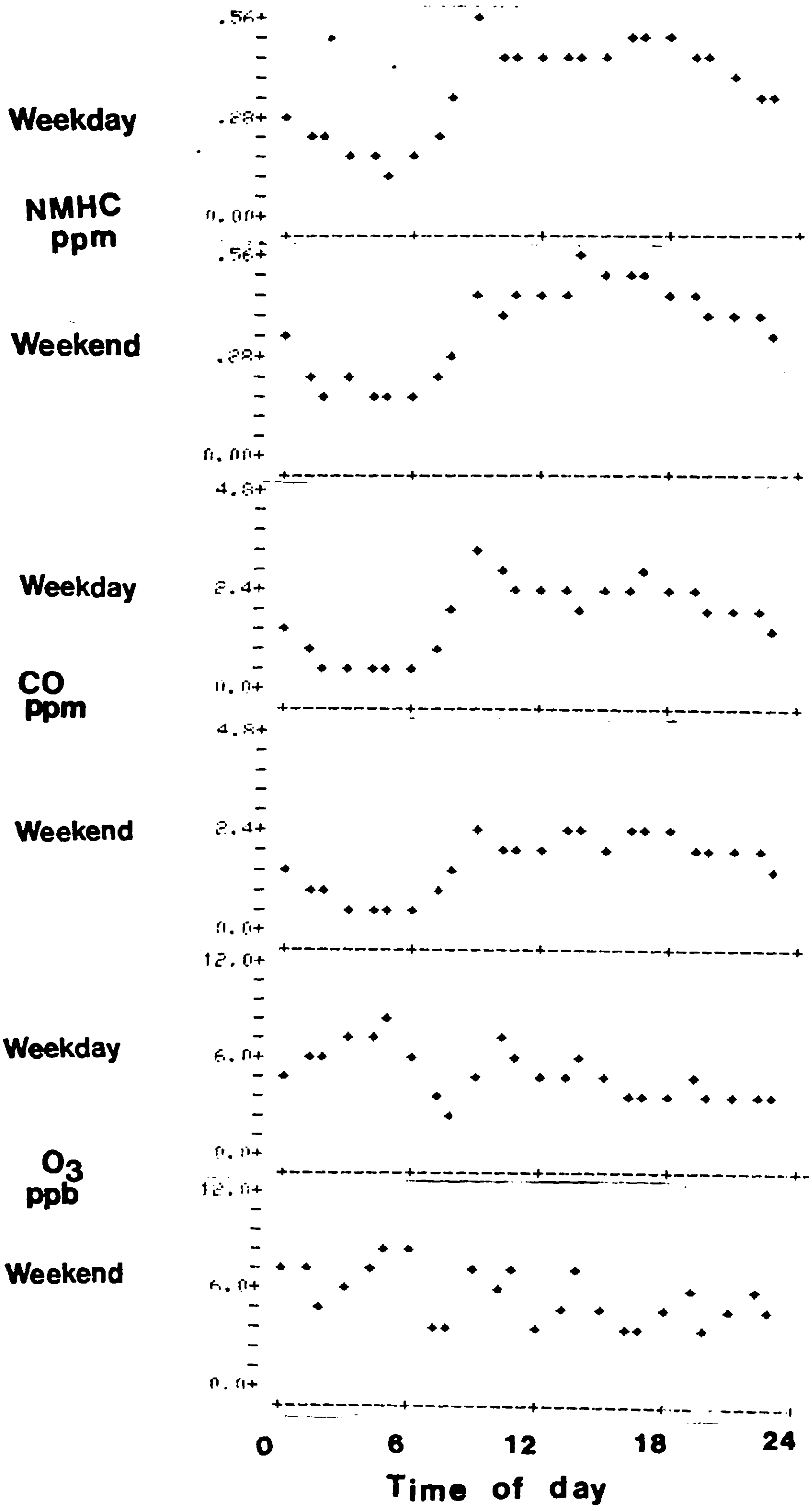
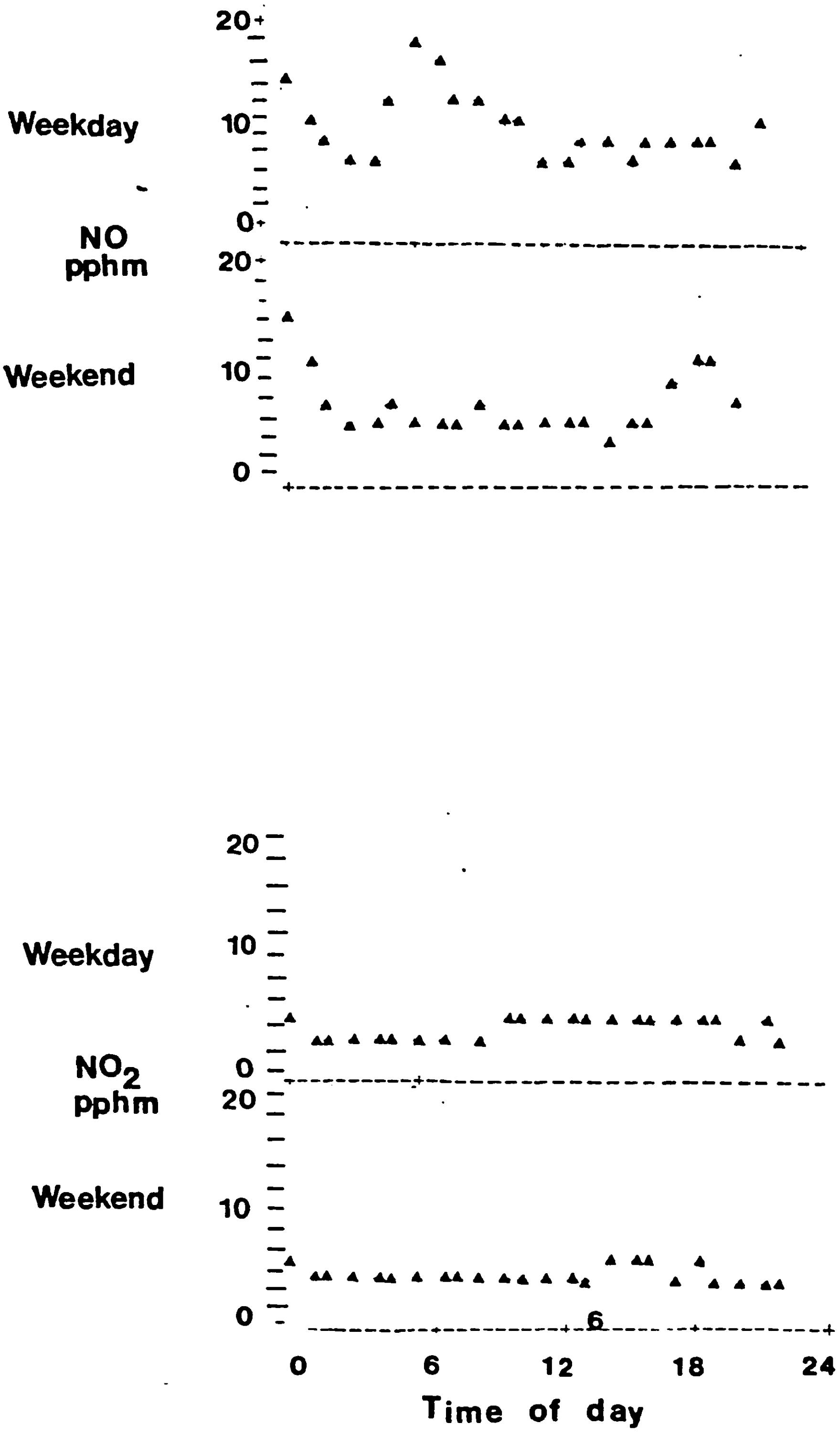


Figure 40 Weekday-weekend differences in diurnal variation of NO and NO_2 at the motorway site, 1983



Diurnal variations during the 1983 survey of wind speed, temperature, NMHC, CO, SO_2, O_3, NO and NO_2 are presented in Figure 37. The NMHC concentration reached a peak at approximately 0400 hours. At this time the wind was mainly from the 330° and 0° sectors i.e. blowing parallel to the motorway. Wind speeds of approximately 2 ms^{-1} and low nocturnal temperatures (~11°C) would have resulted in little atmospheric turbulence at this time. A secondary peak in NMHC concentrations occurred at approximately 1700 hours coinciding with the evening rush hour (diurnal variation in southbound traffic is presented in Figure 38). The diurnal variation in CO concentrations also reflected traffic conditions with peaks at 0700 and 1700 hours. A third peak occurred overnight.

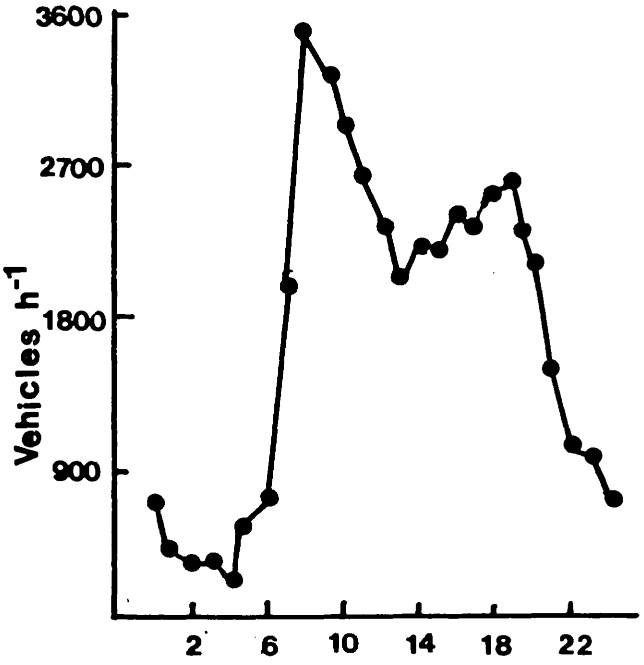


Figure 38 : Diurnal variations in southbound traffic flow at the motorway site, 1983

Diurnal variations in SO_2 concentrations were not pronounced. Ozone concentrations, however, rose steadily from mid-morning, reaching a peak towards 1300-1500 hours.

Diurnal variation of NO was also pronounced exhibiting a large early morning (0600 hours) rise which did not reoccur in the evening rush hour. Nitrogen dioxide concentrations demonstrated a different pattern and increased in line with O_3.

Weekday-weekend differences in diurnal variations of NMHC, CO and O_3, presented in Figure 39, displayed typical peaks correlating with traffic variations in a more distinct fashion than at weekends although measured concentrations were similar. No significant variation was present for O_3. The NO and NO_2 weekday-weekend differences in diurnal variation are presented in Figure 40. The variation in NO and NO_2 was similar but the morning rise in concentrations was slower than during weekdays.

The ratio of NO_2 to NO diurnal variations, presented in Figure 45, did not rise above 0.6, indicating that NO_x sources were localized. The minimum occurred at 0600 hours and the maximum at 1600 hours, the time of maximum O_3 concentrations.

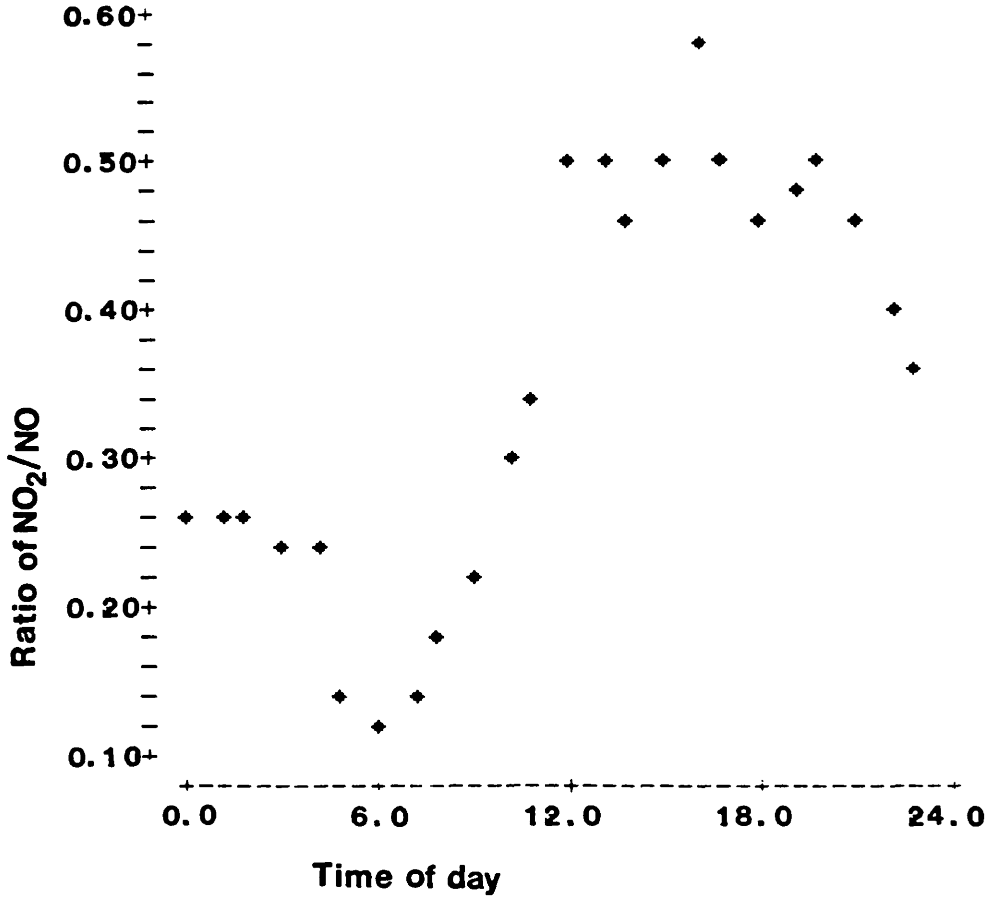


Figure 41 : Diurnal variation of the NO_2/NO ratio at the motorway site, 1983

The results of the motorway surveys demonstrated the significance of a motorway as a line source of traffic-related air pollutants. However, the effect on air quality of the vehicle operating mode typical of motorway traffic was not fully described by the general, spatial and temporal analyses performed.

4.1.2.3 Rural Site - Silwood Park, Berkshire

The mobile laboratory was employed for measurements (see Section 2.1.1) at a control site. This site was situated in a rural area at Silwood Park, near Ascot, Berkshire (Figure 42). Measurements took place between 12 July and 8 August 1982 and 11 July and 7 August 1983.

Summararies of the air quality characteristics during the monitoring periods in 1982 and 1983 are presented in Tables 16 and 17.

Similar arithmetic mean concentrations of NMHC were found in 1982 and 1983 (0.08 and 0.11 ppm, respectively). The 99th percentile concentration value in 1982 was 0.3 ppm and in 1983, 0.9 ppm. Arithmetic mean concentrations of CO were 0.28 ppm and 0.48 ppm in 1982 and 1983, respectively. The SO_2 arithmetic mean concentrations were 17.7 and 18.0 ppb in 1982 and 1983, respectively.

Ozone concentrations were elevated during the 1983 survey in comparison to the 1982 survey. The arithmetic mean concentration was 22.2 ppb with a maximum measured hourly concentration of 144.4 ppb. The NO_x arithmetic mean concentrations were low (0.5 pphm NO and 2.16 pphm NO_2). The ratio of NO_2 to NO was 4.32 which indicated that distant sources were responsible for measured concentrations at this site.

Pollution roses for NMHC, CO, SO_2 and O_3 during the 1982 survey are presented in Figures 43 and 44. The CH_4 rose along with the composite wind rose and the magnitude of mean wind velocity per sector is presented in Figure 45.

The wind was predominantly from the north over the monitoring periods and wind speeds were generally low.

Figure 42 : Location of the rural site, Silwood Park, Berkshire

Table 16 : General air quality characteristics at the rural site, 1982

	CH_4 ppm	THC ppm	NMHC ppm	CO ppm	SO_2 ppb	Ozone ppb
Arithmetic Mean	1.37	1.45	0.08	0.28	17.7	1.34
Minimum	1.14	1.25	0	0	10.25	0
25th percentile	1.30	1.35	0.02	0.11	14.85	0
50th percentile	1.34	1.41	0.06	0.21	16.69	0.07
75th percentile	1.41	1.51	0.12	0.36	18.93	0.59
90th percentile	1.50	1.65	0.18	0.65	21.10	2.11
95th percentile	1.57	1.70	0.22	0.79	24.00	3.99
99th percentile	1.74	1.87	0.30	1.27	28.21	37.82
Maximum	2.25	2.47	0.33	1.53	39.18	58.84
Standard Deviation	0.11	0.14	0.67	0.25	3.55	5.73
Variability*	8.18	9.18	88.34	89.20	20.57	427.57

* variability is defined as (standard deviation/arithmetic mean) × 100

Table 17 : General air quality characteristics at the rural site, 1983

	CH_4 ppm	THC ppm	NMHC ppm	CO ppm	SO_2 ppb	Ozone ppb	NO pphm	NO_x pphm	NO_2 pphm
Arithmetic Mean	1.51	1.63	0.11	0.48	18.01	22.19	0.50	2.68	2.16
Minimum	1.32	1.38	0	0	0	0	0	0	0
25th percentile	1.40	1.50	0	0.3	14.48	5.20	0.10	1.60	1.30
50th percentile	1.50	1.60	0.1	0.4	15.88	15.70	0.20	2.20	1.90
75th percentile	1.60	1.80	0.1	0.6	20.46	32.10	0.40	3.30	2.70
90th percentile	1.80	1.90	0.2	0.8	27.26	55.80	1.10	4.50	3.80
95th percentile	1.90	2.00	0.3	1.10	30.86	66.90	2.70	5.40	4.90
99th percentile	2.20	2.60	0.9	1.60	39.23	80.40	3.00	8.90	6.20
Maximum	2.50	2.90	1.10	2.10	48.17	144.40	34.50	32.50	7.20
Standard Deviation	0.29	0.33	0.15	0.32	6.51	21.55	1.80	2.16	1.25
Variability*	19.36	19.95	144.57	66.57	36.15	97.11	363.82	80.52	57.87

* variability is defined as (standard deviation/arithmetic mean) × 100

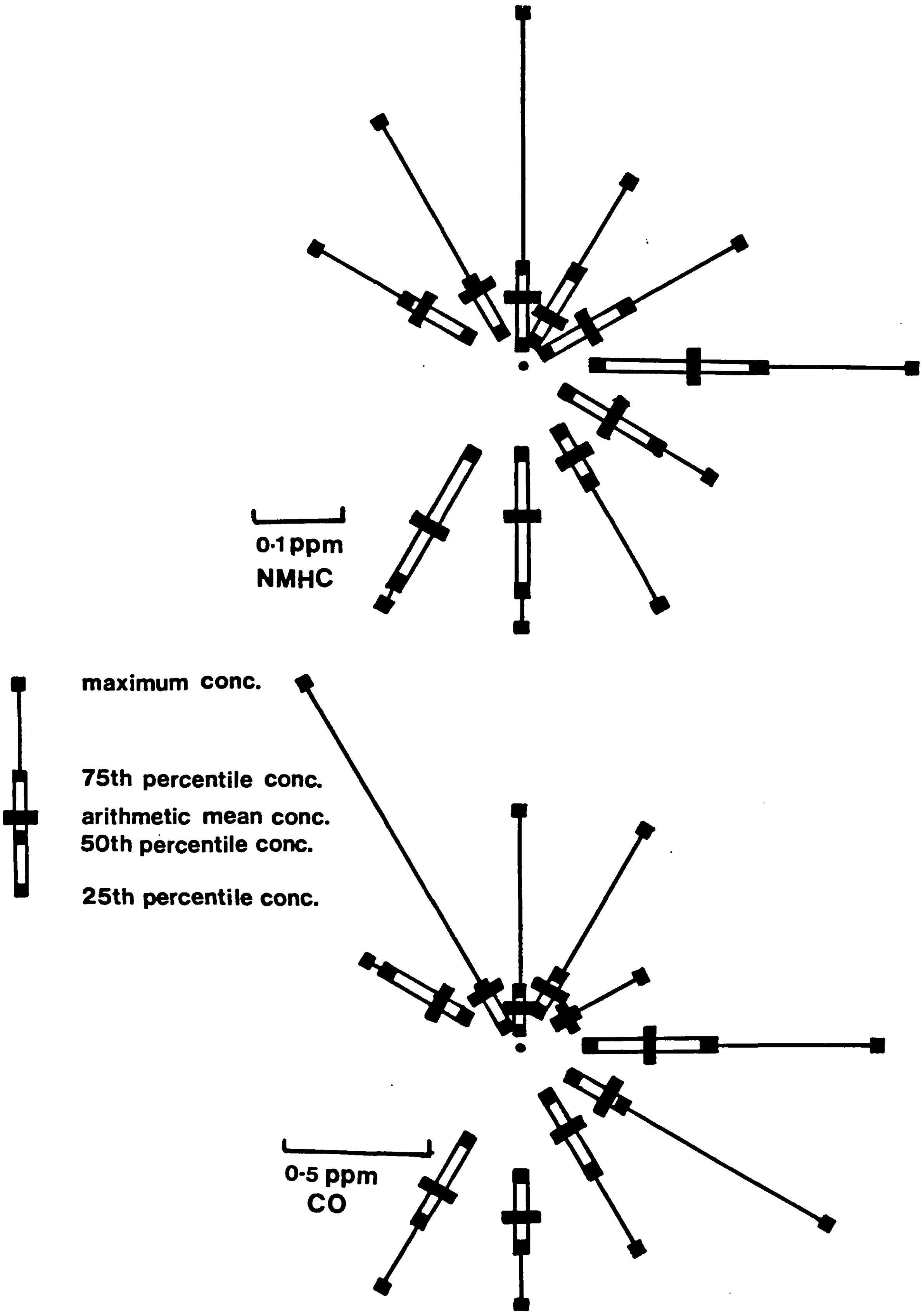
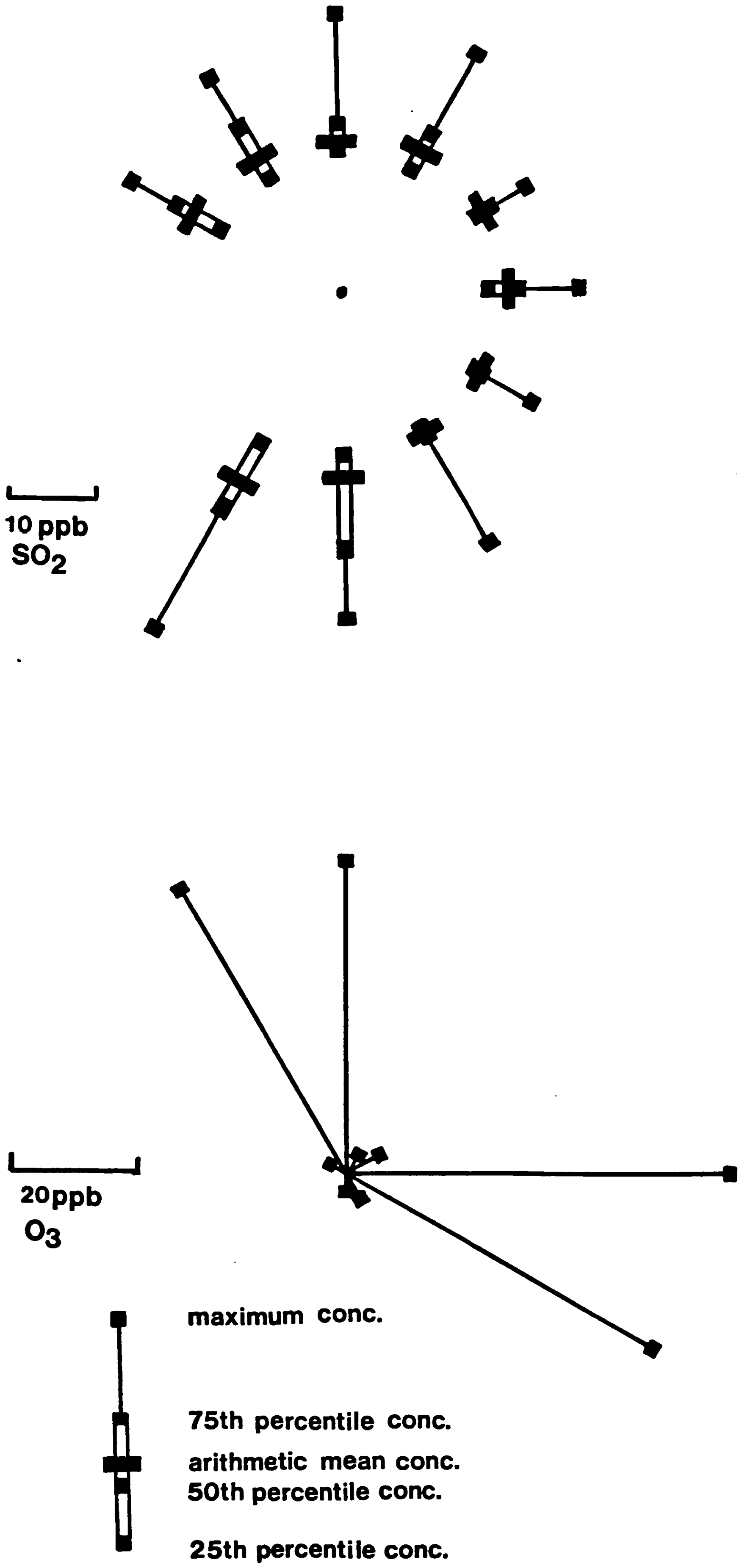


Figure 43 : Pollution roses for NMHC and CO at the rural site, 1982

Figure 44 : Pollution roses for SO_2 and O_3 at the rural site, 1982



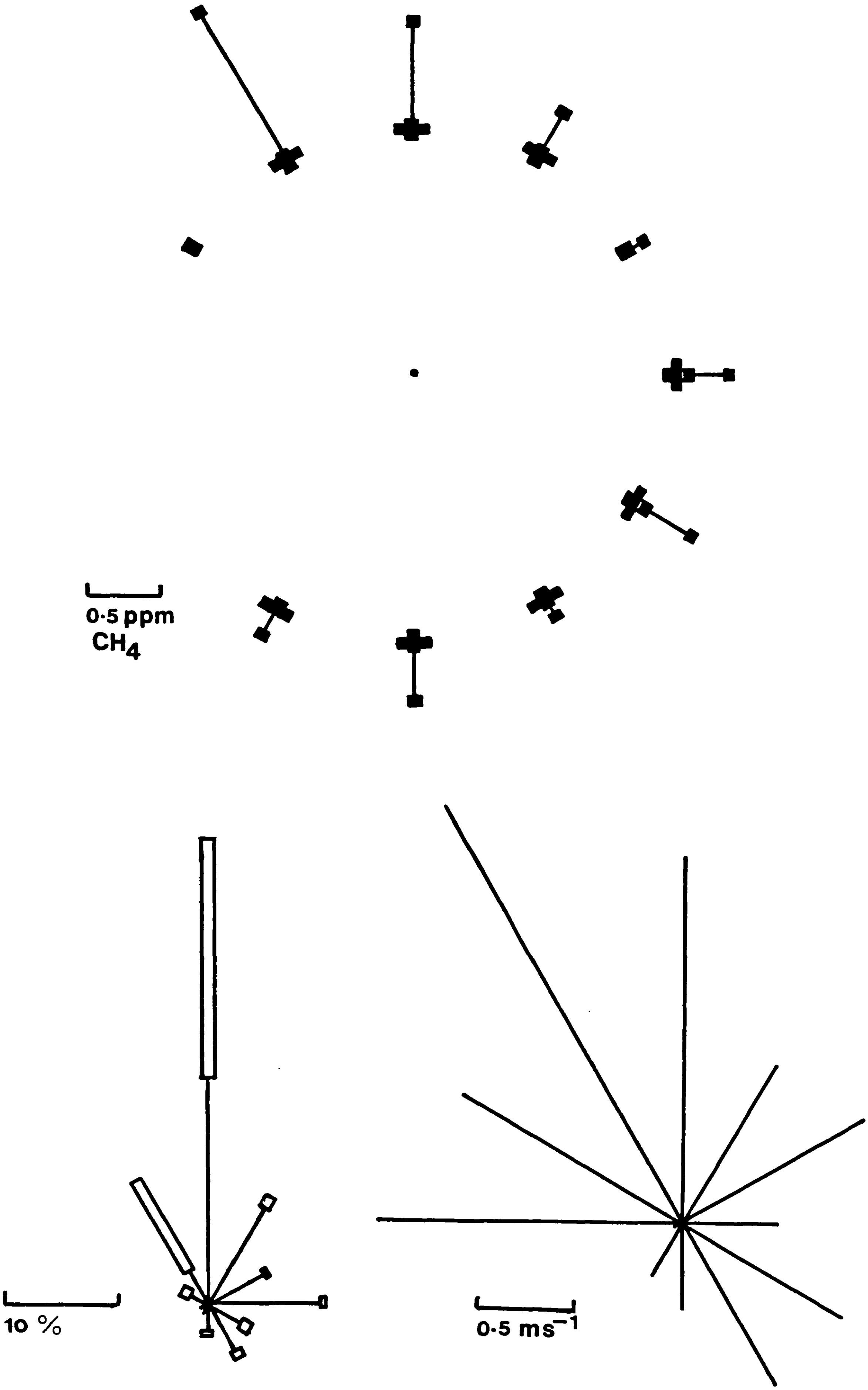


Figure 45 : Pollution rose for CH_4, composite wind rose, magnitude of wind velocity per sector at the rural site, 1982

Figure 46 : Pollution roses for NMHC and CO at the rural site, 1983

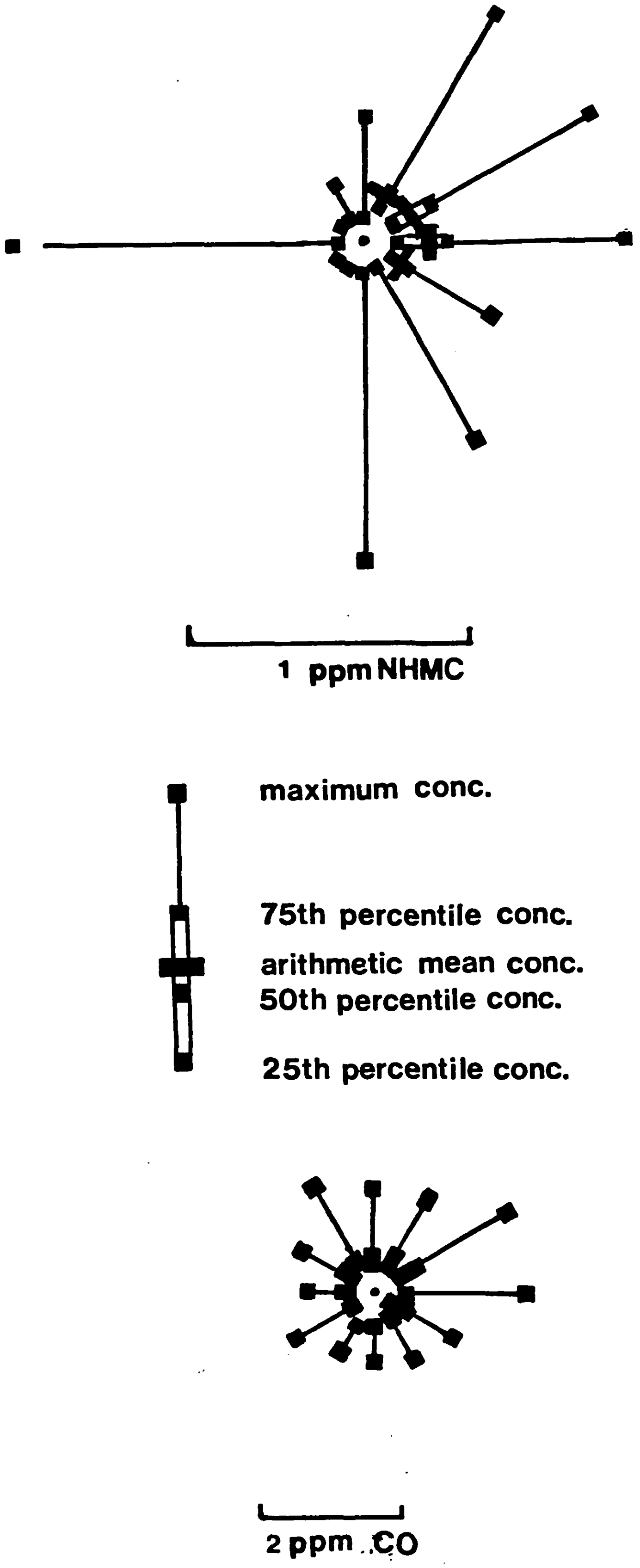


Figure 47 : Pollution roses for SO_2 and O_3 at the rural site, 1983

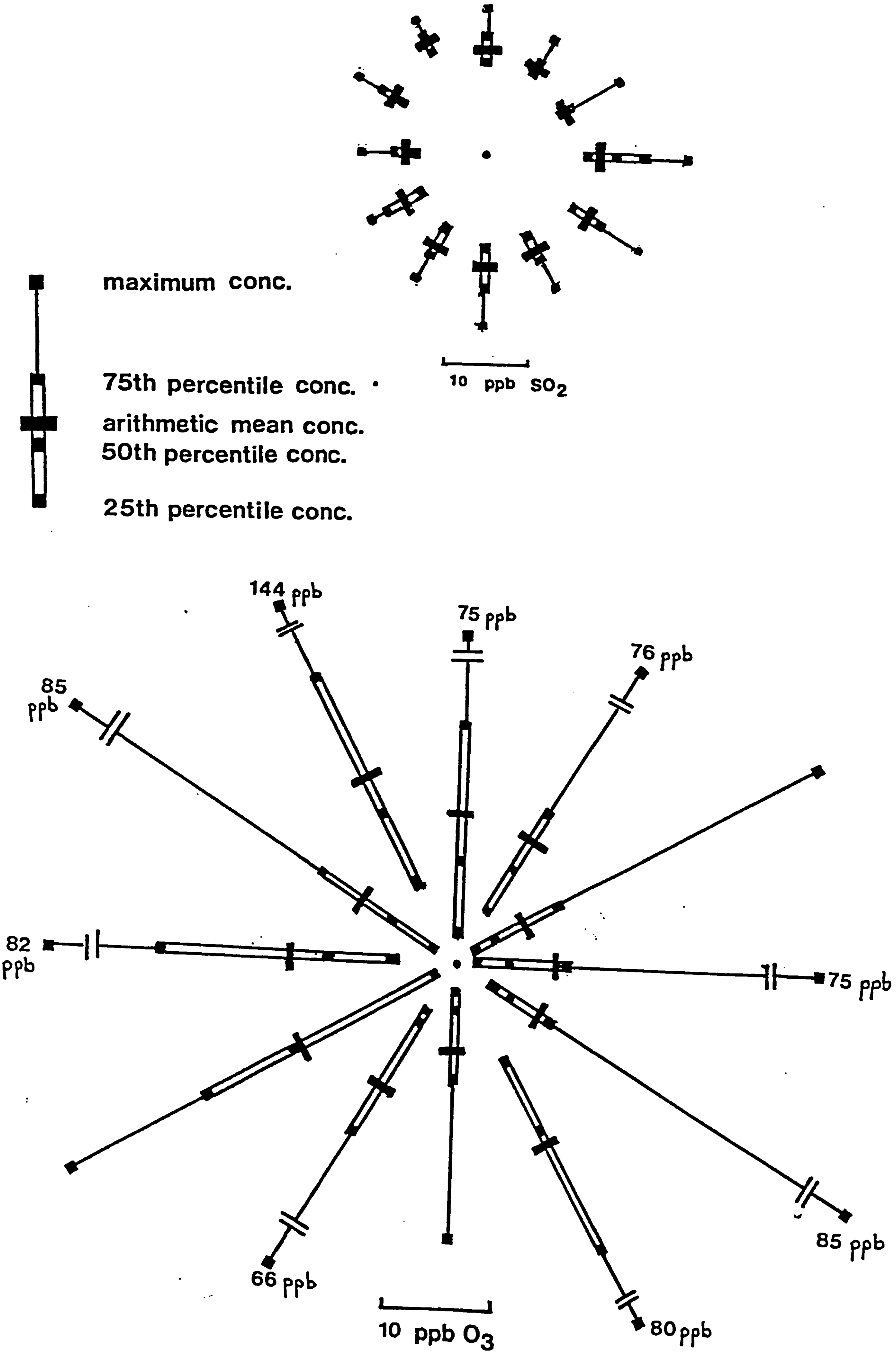


Figure 48 : Pollution roses for NO and NO_2 at the rural site, 1983

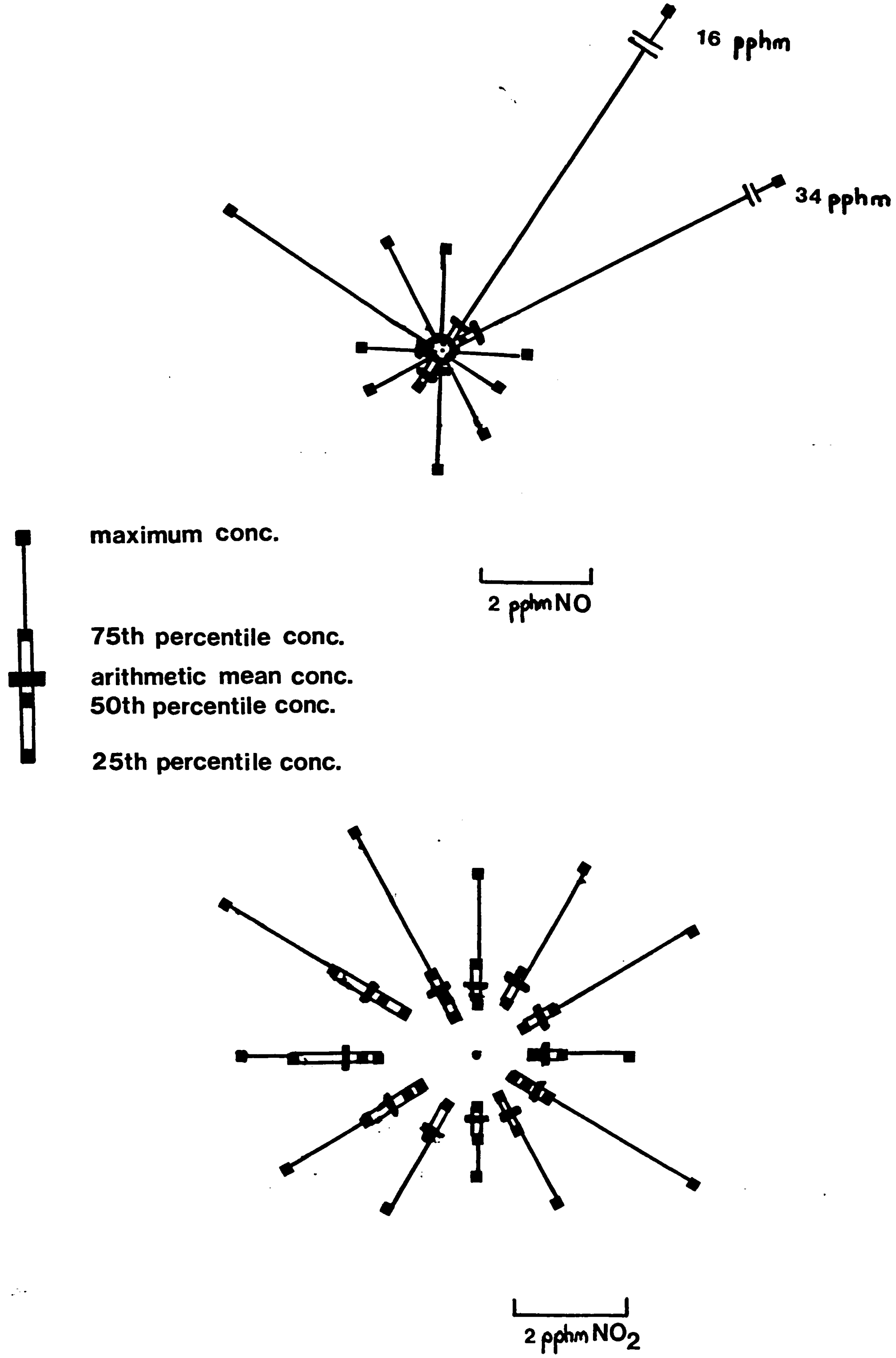
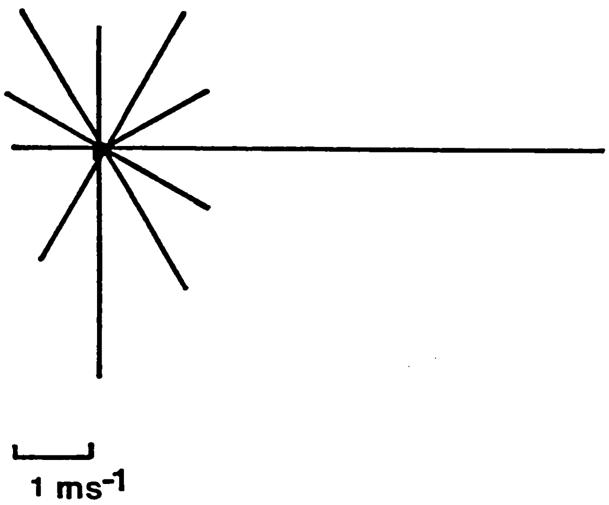
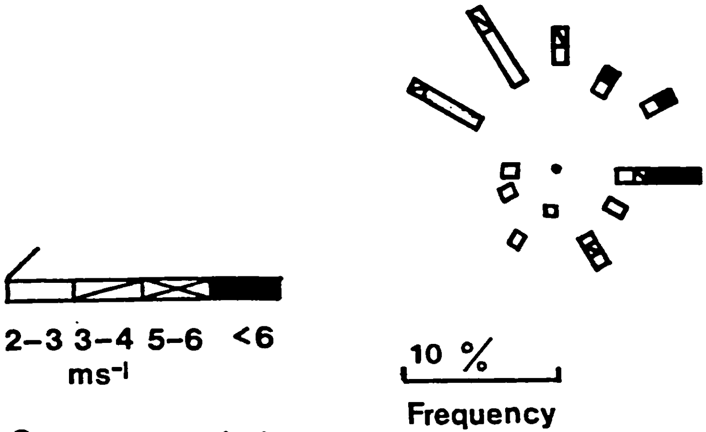


Figure 49 : Composite wind rose and magnitude of mean wind velocity per sector at the rural site, 1983



Mean wind velocity



Composite wind rose

Arithmetic mean concentrations of CH_4, NMHC, CO and SO_2 were similar from all directions but were more pronounced from the southerly directions (180° and 210°). Ozone concentrations were low and only maxima are presented in Figure 49. Maxima arose from the 330°-0° arc and the 90°-120° arc.

Pollution roses for NMHC, CO, SO_2, O_3, NO and NO_2 are presented in Figures 46, 47 and 48. The composite wind rose and the magnitude of mean wind velocity per sector are presented in Figure 49.

Concentrations of NMHC and CO were similar from all directions but exhibited a slight directional bias in the easterly sector. Sulphur dioxide showed no significant directional dependence.

Ozone concentrations were high in all sectors in both arithmetic mean concentrations and maxima (the highest concentration of 144.4 ppb was from the 330° sector). Arithmetic mean NO concentrations were low from all directions although high maxima values (16.10 and 34.5 pphm) were measured when the wind was from the 30° and 60° sectors, i.e. from the London urban area. Nitrogen dioxide concentrations were similar from all directions but showed a slight directional bias in the westerly sectors.

Diurnal variations in wind speed, temperature, CH_4, NMHC, CO, O_3 and SO_2 obtained from the 1982 survey are presented in Figure 50. Ozone concentrations were low but reached a peak at about 1300 hours. Methane, SO_2, NMHC and CO exhibited very similar diurnal variations which indicates that measured concentrations were dependent on the dispersive properties of the atmosphere.

Weekday-weekend differences for O_3, CO and NMHC are presented in Figure 51. No significant variation in O_3 concentrations was noted. Concentrations of NMHC and CO exhibited morning and evening peaks during weekdays. Concentrations rose at night for both pollutants at this site due to the limited dispersive conditions.

The diurnal variations of windspeed, temperature, NMHC, CO, SO_2, O_3, NO and NO_2 are presented in Figure 52. No significant variation in NMHC and CO concentrations was noted. The SO_2 concentrations rose when windspeeds were low.

Figure 50 : Diurnal variations in wind speed, temperature, CH_4, NMHC, CO, O_3 and SO_2 at the rural site, 1982

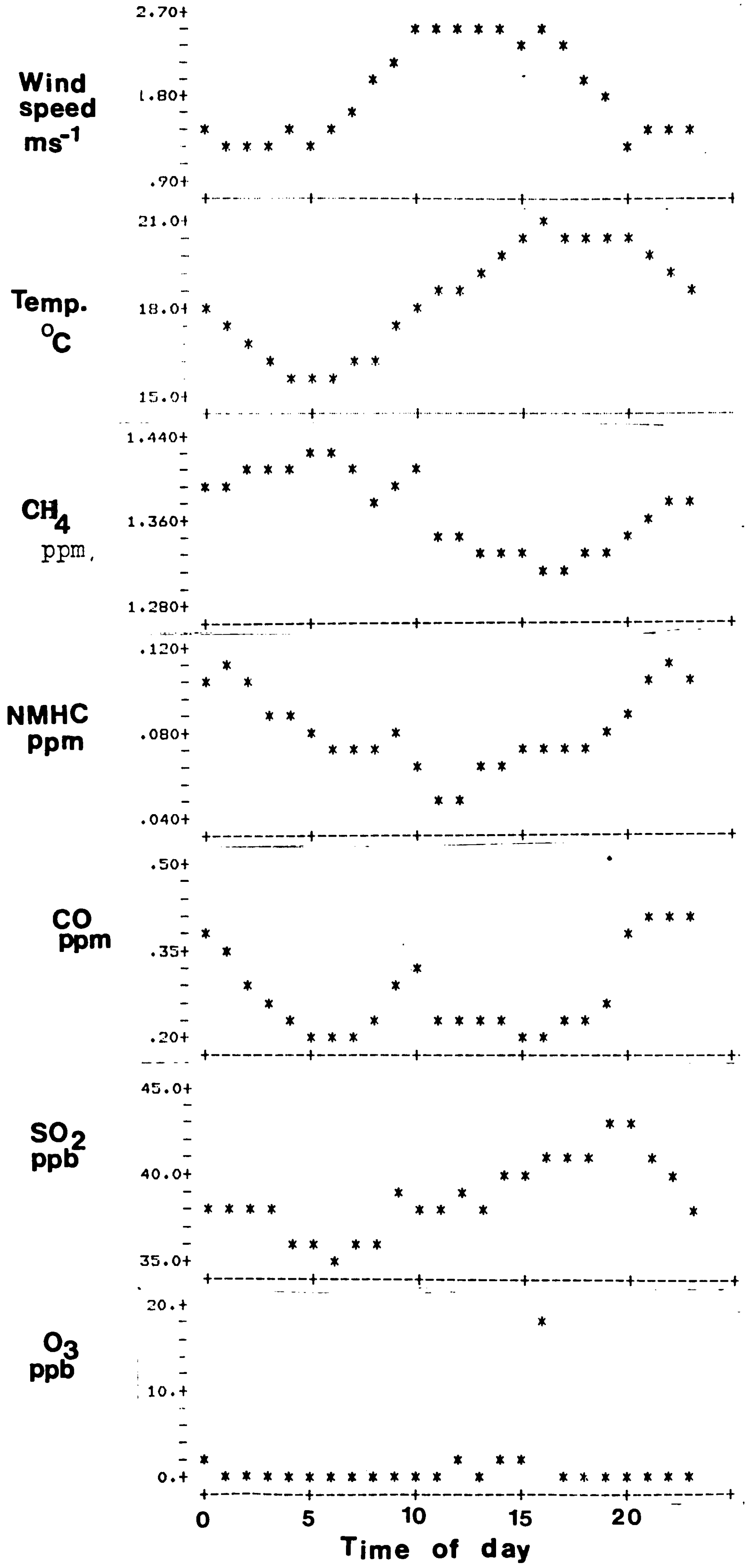


Figure 51 : Weekday-weekend differences in diurnal variation of NMHC, CO and O_3 at the rural site, 1982

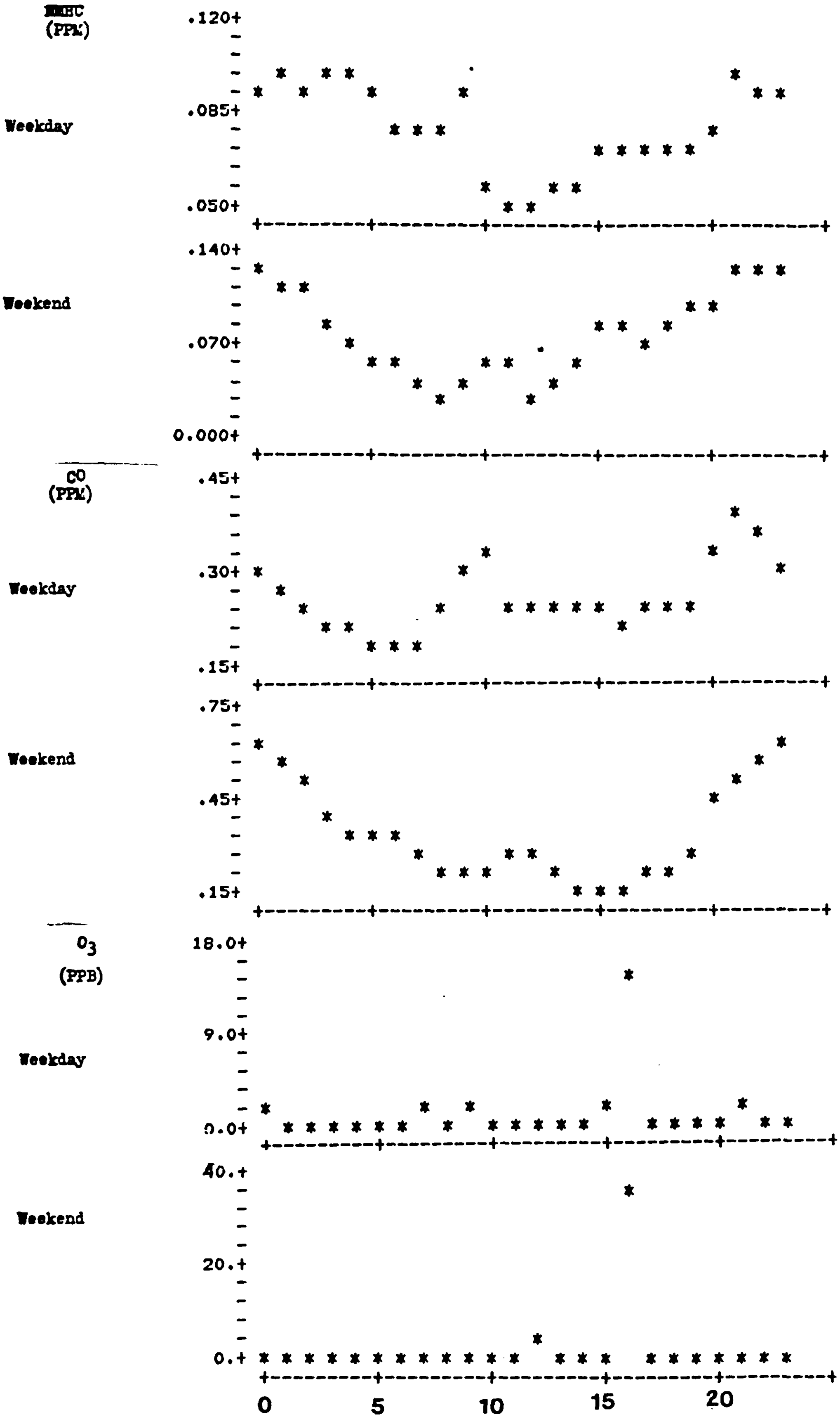


Figure 52 : Diurnal variations in wind speed, temperature, NMHC, CO, SO_2, O_3, NO and NO_2 at the rural site, 1983

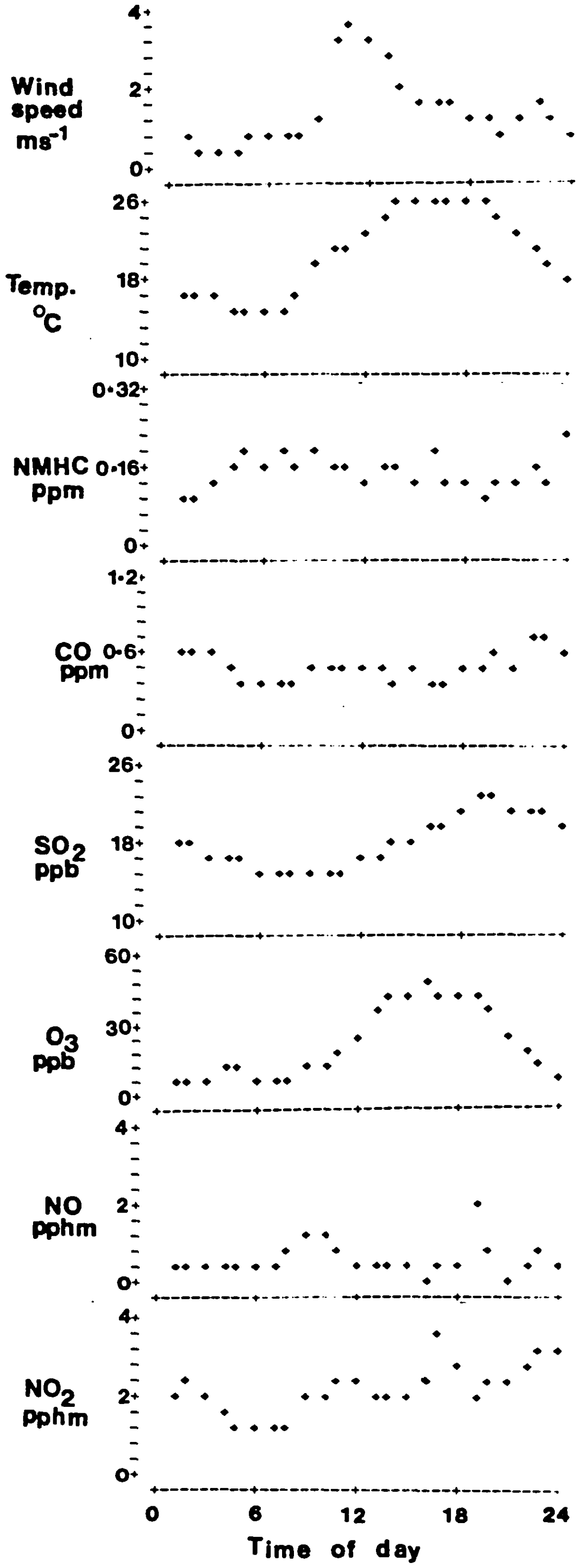


Figure 53 : Weekday-weekend differences in diurnal variation of NMHC, CO and O_3 at the rural site, 1983

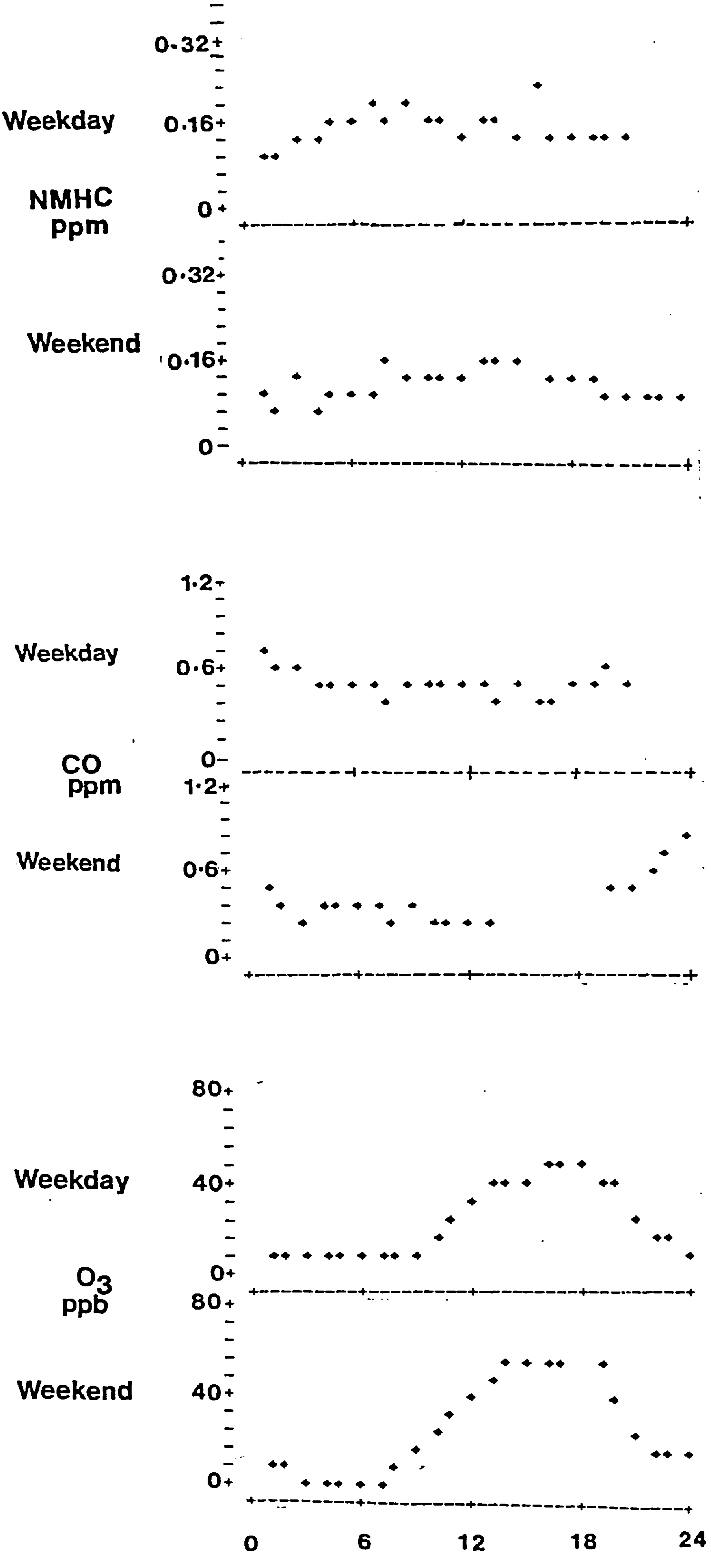
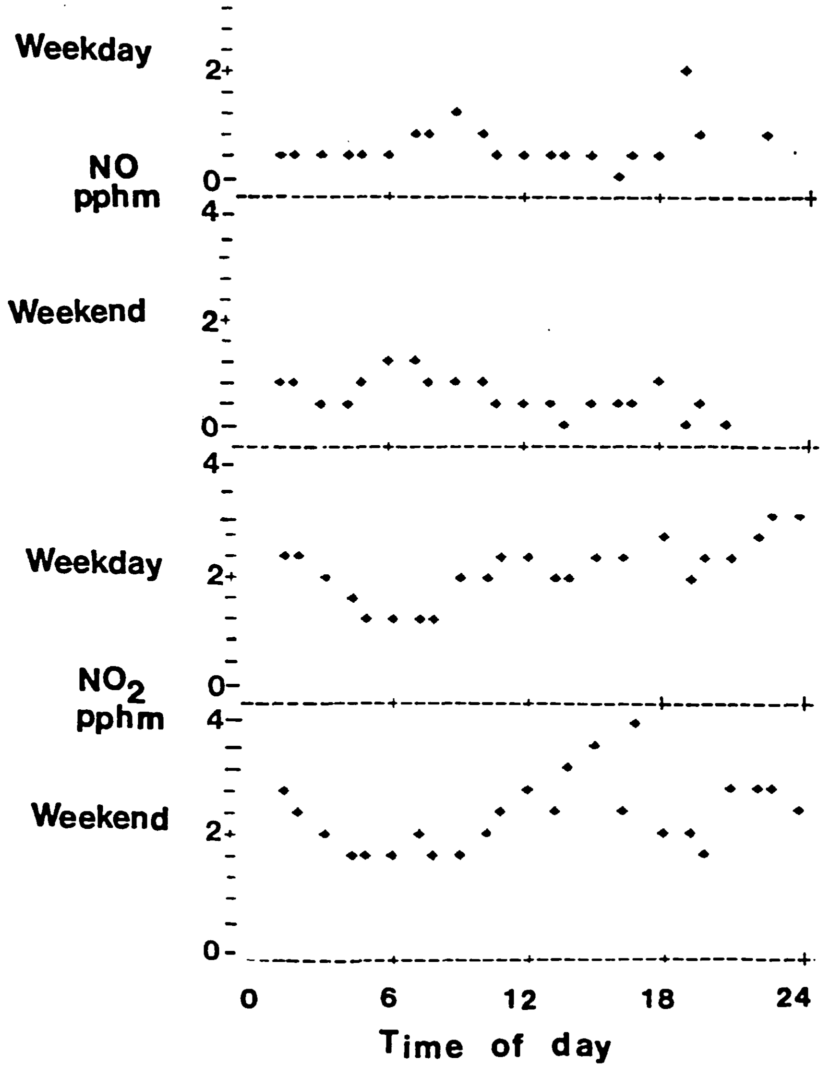


Figure 54 : Weekday-weekend differences in NO and NO_2 at the rural site, 1983



The diurnal variation in O_3 concentrations was the most pronounced, reaching a maxima at approximately 1700 hours and decaying during the night. Nitric oxide concentrations peaked at 0900 and 1900 hours. Nitrogen dioxide concentrations were variable but reached a maximum at the same time as O_3 concentrations (1700 hours) No significant weekday-weekend variations in NMHC, CO, O_3, NO or NO_2 were observed (presented in Figures 53 and 54).

The NO_2/NO ratio throughout the day (presented in Figure 55) did not fall below 1.5 and was usually far in excess of this value, demonstrating that NO_x sources were distant.

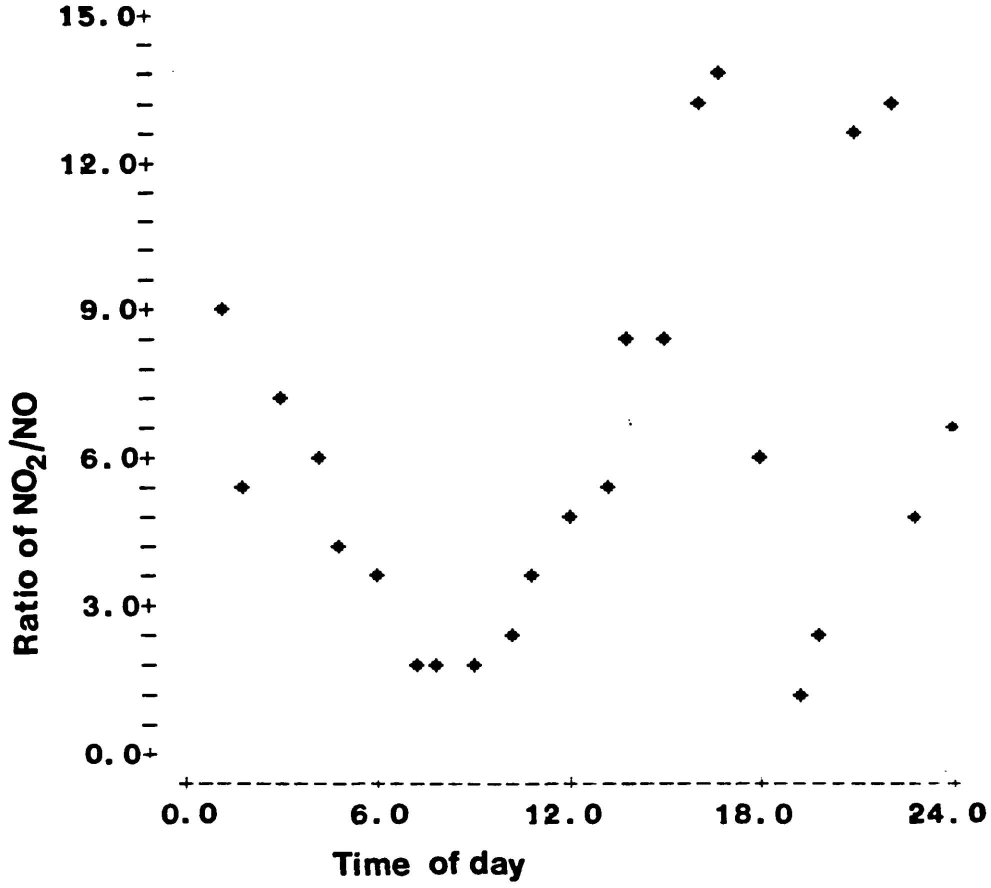


Figure 55 : Diurnal variation of the NO_2/NO ratio at the rural site, 1983

At this site, measured concentrations were low and demonstrated little directional dependence. No major local sources existed and measured concentrations were due to pollutant transport from distant sources (such as the London urban area).

4.1.2.4 Selection of Statistical Analyses Applied at the Urban, Motorway and Rural Sites to Assess Air Quality Impact

In addition to the temporal and spatial characteristics of pollutant distributions in the urban, motorway and rural study areas, a more detailed analysis has been performed.

The application of statistical distributions to air quality data sets can provide a method of interpolation between observed values and extrapolation beyond. Inferences can also be made about the nature of the underlying physical processes.

The techniques of multiple regression analysis can derive a mathematical relationship between meteorological variables persistence (autocorrelation) of observed concentrations and observed concentrations.

The individual and combined effects of the windspeed, temperature and lagged concentration were estimated by applying equations (19) and (20) using partial and multiple regression coefficients of the logarithmically transformed concentration data. The multiple regression statistics obtained from equation (20) are presented, for each of the three motoring sites during the 1982 survey in Table 18. Also included for comparison in the last column is the total explained variance (RMZ^2) obtained by applying equation (19). R_p denotes the partial correlation coefficients, (Rml^2) is the total explained variance (from equation 20) and the constants a, b_1, b_2 and b_3 are the regression coefficients.

Table 18 demonstrated that the single most important parameter in increasing the explained variance of all pollutant concentrations at the three sites was found to be that of lagged concentration. The inclusion of this parameter accounts for the persistence, or autocorrelation, observed in pollutant concentrations, which in turn reflects persistence in both emissions and meteorological conditions.

With regard to wind speed, all the pollutants measured, except CH_4 at Toddington and O_3 at Silwood, exhibited a negative correlation with wind speed. The positive correlation of CH_4 at Toddington indicated the effect on overall CH_4 concentrations of the local sewage works.

Table 18 : Multiple regression statistics at the urban, motorway and rural sites during 1982

Site	Compound	n	a	Wind Speed		Temperature		Lagged Conc.		Rml^2	$Rm2^2$
				b_1	R_p	b_2	R_p	b_3	R_p		
Urban	CH_4	515	0.07*	-0.03	-0.41	0.002*	0.10	0.85	0.88	79.6	18.9
	THC	515	-0.04*	-0.03	-0.14	0.05	0.37	0.84	0.86	76.5	18.9
	NMHC	515	-1.90	0.02*	0.22	0.55	0.35	0.85	0.89	76.7	15.1
	CO	493	-1.24	-0.01*	0.22	0.44	0.52	0.87	0.91	82.5	29.3
	SO_2	547	0.77	-0.05	0.28	-0.03*	0.001	0.81	0.84	72.3	7.0
	O_3	495	-1.22*	0.17*	0.08	0.12*	0.02	0.55	0.56	31.1	0.7
Motorway	CH_4	310	0.01	0.01	0.10	-0.003*	-0.02	-0.02	0.95	91.0	0.5
	THC	415	0.05	-0.01	-0.35	-0.003*	0.42	0.94	0.94	92.7	26.4
	NMHC	310	0.22*	-0.30	-0.55	-0.07	-0.31	0.82	0.82	81.6	35.5
	CO	310	-0.04*	-0.05*	-0.14	0.02*	0.20	0.87	0.87	76.9	5.8
	SO_2	593	0.78	-0.03	-0.34	-0.01	-0.20	0.80	0.85	72.9	14.3
	O_3	593	-2.89	0.15*	0.07	0.26*	0.08	0.42	0.42	17.9	0.6
Rural	CH_4	367	0.08	-0.01	-0.48	-0.01*	-0.09	0.84	0.91	83.8	22.5
	THC	367	0.04	-0.01	-0.63	0.01*	0.01	0.83	0.93	89.1	40.1
	NMHC	367	-1.08	-0.07	-0.34	0.28	0.08	0.92	0.93	88.3	12.7
	CO	352	-0.73	-0.08	-0.58	-0.19	0.15	0.90	0.96	91.8	39.3
	SO_2	436	0.30	0.01*	0.03	0.05	0.42	0.88	0.92	84.4	17.7
	O_3	438	0.27*	0.25	0.215	-0.46*	-0.07	0.62	0.64	42.9	5.6

* The coefficient is not significant at the 5% level

The observed variation in O_3 concentrations is the least explicable, regardless of site. This suggests that consideration of only local meteorological measurements may be insufficient in order to account for the mechanisms that are responsible for O_3 generation and transport.

The NMHC concentrations were more closely correlated with temperature at the urban site than at the motorway site which suggests that fuel evaporation is important in determining NMHC concentrations in the urban environment.

As a result of this analysis, it would appear that equation (20) was more suitable in defining the mathematical relationship between meteorological variables and measured concentrations.

Table 19 : Multiple regression statistics at the urban, motorway and rural sites during 1983

Site	Compound	n	a	Wind Speed b_1	Temperature b_2	Lagged Conc. b_3	RMl^2
Urban	NMHC	572	-1.64	0.04*	0.48	0.75	67.7
	CO	562	-0.21*	0.01*	0.09*	0.87	75.7
	SO_2	562	0.22	-0.001*	0.01*	0.94	91.0
	O_3	562	-0.48*	0.14	0.21*	0.80	66.0
	NO	562	0.47*	0.03*	-0.15*	0.87	73.1
	NO_2	562	0.04*	-0.002*	0.03*	0.92	86.0
Motorway	NMHC	449	-0.44*	0.08	-0.319	0.79	67.3
	CO	356	-0.74	-0.07	0.143*	0.60	45.3
	SO_2	475	0.047*	0.007	0.06	0.94	90.1
	O_3	576	-2.38	0.14	0.99	0.73	78.6
	NO	476	-0.66*	-0.16	-0.08*	0.41	19.2
	NO_2	576	-0.48	0.007*	0.22	0.73	57.9
Rural	NMHC	539	-0.85	0.08	0.242	0.88	84.7
	CO	518	-0.21*	-0.08	0.06*	0.80	72.0
	SO_2	619	0.25	0.004*	0.27	0.92	85.8
	O_3	619	-1.2	0.1267	0.41	0.81	72.6
	NO	619	-0.30	-0.03*	0.136	0.92	87.3
	NO_2	619	-0.30	-0.03*	0.136	0.92	87.3

* The coefficient is not significant at the 5% level

Multiple regression statistics at the urban, motorway and rural sites during the 1983 survey are presented in Table 19. The results demonstrate (as in the 1982 survey) that lagged concentrations are the most significant parameter in increasing the explained variance. RMl^2 values were similar to those presented in Table 18. The regression coefficients for the respective pollutants were similar except in the case of O_3. Ozone correlated positively with wind speed at the urban site and with wind speed and temperature at the motorway and rural sites.

Table 20 : Results of fitting the 1982 air quality data sets to the normal, two-parameter lognormal, and censored three-parameter lognormal distributions

		URBAN			MOTORWAY			RURAL		
		N	LN2	LN3	N	LN2	LN3C	N	LN2	LN3C
CH_4	n	617			323			381		
	R^2	0.937	0.974	0.999	0.961	0.960	0.961	0.840	0.898	0.962
	S	0.049	0.019	0.012	0.034	0.025	0.023	0.045	0.024	0.055
THC	n	617			420			381		
	R^2	0.981	0.995	0.995	0.934	0.959	0.989	0.857	0.911	0.996
	S	0.039	0.011	0.010	0.054	0.026	0.047	0.050	0.027	0.031
NMHC	n	617			323			381		
	R^2	0.058	0.847	0.986	0.886	0.919	0.0986	0.948	0.924	0.986
	S	0.045	0.654	0.039	0.062	0.352	0.072	0.016	0.338	0.045
CO	n	594			316			367		
	R^2	0.906	0.940	0.979	0.897	0.925	0.995	0.846	0.932	0.992
	S	0.396	0.246	0.077	0.156	0.112	0.032	0.098	0.292	0.056
SO_2	n	646			598			446		
	R^2	0.855	0.943	0.984	0.947	0.977	0.997	0.917	0.981	0.995
	S	4.067	0.057	0.060	1.336	0.021	0.019	2.310	0.026	0.022
O_3	n	554			631			450		
	R^2	0.502	0.939	0.990	0.397	0.981	0.987	0.258	0.988	0.922
	S	1.442	0.575	0.140	0.880	0.305	0.206	4.94	0.283	0.194

n = number of hourly data used, R^2 = coefficient of determination, x = standard error or estimate

Table 21 : Results of fitting the 1983 air quality data sets to the normal, two-parameter lognormal, and censored three-parameter lognormal distributions

		URBAN			MOTORWAY			RURAL		
		N	LN2	LN3	N	LN2	LN3C	N	LN2	LN3C
CH_4	n	574			454			542		
	R^2	0.850	0.960	0.990	0.660	0.840	0.951	0.617	0.931	0.990
	S	0.429	0.047	0.305	0.091	0.475	0.121	0.20	0.368	0.086
THC	n	626			365			529		
	R^2	0.900	0.930	0.990	0.860	0.770	0.976	0.615	0.979	0.991
	S	0.423	0.255	0.066	0.1187	0.343	0.057	0.578	0.1177	0.093
NMHC	n	626			484			631		
	R^2	0.850	0.910	0.955	0.840	0.940	0.973	0.942	0.979	0.994
	S	4.83	0.046	0.076	8.748	0.070	0.077	1.946	0.019	0.021
CO	n	626			484			631		
	R^2	0.690	0.930	0.983	0.870	0.850	0.977	0.714	0.947	0.993
	S	3.834	0.264	0.1455	7.783	0.648	0.117	6.507	0.521	0.331
SO_2	n	626			484			631		
	R^2	0.861	0.930	0.950	0.188	0.930	0.988	0.795	0.905	0.905
	S	1.539	0.422	0.208	1.639	0.428	0.119	5.288	0.775	0.767
O_3	n	626			484			631		
	R^2	0.988	0.863	0.960	0.795	0.905	0.905	0.899	0.939	0.977
	S	0.309	0.263	0.074	5.289	0.775	0.772	0.794	0.277	0.549

n = number of hourly data used, R^2 = coefficient of determination, x = standard error or estimate

Nonmethane hydrocarbon concentrations were positively correlated with temperature at the urban site (similar to the 1982 data) but not at the motorway site, reflecting the different importance of exhaust and evaporative emissions. Nitric oxide and NO_2 concentrations at the urban site did not correlate significantly with wind speed which indicates that local sources were so dominant that atmospheric dispersal conditions did not affect measured concentrations.

Atmospheric dispersal conditions were important at the motorway and urban sites in determining measured concentrations of NO. However, temperature (an indication of daytime insolation) correlated significantly with O_3 and consequently NO_2.

The least squares criterion was used to compare the goodness-of-fit of the 1982 and 1983 data sets to the normal (N), two-parameter lognormal (LN2), and censored three-parameter lognormal (LN3C) distributions. The results are presented in Tables 20 and 21.

The LN3C distributions gave a significantly better - or at least equivalent - fit, compared to the other two distributions on all occasions. The parameters calculated by least squares minimisation, as a result of fitting the air quality sets from 1982 and 1983 to the LN3C distribution are presented in Tables 22, 23 and 24, where they are compared to the observed parameters assuming a 'perfect fit' (calculated from equations (15) and (16). Also included is P(0), the probability of occurrence of zero concentration values, for those data sets for which the third parameter (K) is negative corresponding to the point of censorship.

Generally, positive values of K were associated with those pollutants which occurred at appreciable concentration levels throughout the day, and indicate the lowest concentration levels that these would be expected to attain. However, a positive K value of 1.01 in 1982 and 0.088 in 1983 was determined for CO at Silwood although measured concentrations were low. Negative values of K were associated with those pollutants which often occurred at low concentrations (O_3, CO, NMHC and NO_2), although this distinction is not absolute.

Table 22 : Parameters calculated by least squares minimisation as a result of fitting the urban air quality data sets to the LN3C distribution

	mg(e)	mg(o)	Sg(e)	Sg(o)	K	P(o)
(a) 1982						
CH_4	0.546	0.547	1.386	1.385	+1.01	-
THC	2.060	2.060	1.146	1.146	-0.25	0.0
NMHC	0.605	0.609	1.407	1.386	-0.40	11.30
CO	2.061	2.061	1.699	1.705	-0.71	2.30
SO_2	7.27	7.27	1.675	1.700	+7.69	-
O_3	0.372	0.388	4.399	4.008	-0.071	13.10
(b) 1983						
NMHC	0.746	0.746	1.350	1.348	-0.425	3.07
CO	1.941	1.940	1.760	1.763	-0.51	0.91
SO_2	8.22	8.258	1.432	1.432	+12.57	-
O_3	3.036	3.069	3.074	3.009	-0.56	6.50
NO	3.065	3.073	2.580	2.629	-0.58	3.84
NO_2	7.925	7.931	1.434	1.454	-2.962	0.004

mg(e) = estimated geometric mean
mg(o) = observed geometric mean (obtained from actual data)
Sg(e) = estimated standard geometric deviation, by least squares minimisation
Sg(o) = observed standard geometric deviation (obtained from actual data)
K = 3rd parameter
P(o) = probability of occurrence of zero concentration values (expressed as a percentage)

In order to assess further the adequacy of the LN3C distribution to describe the data, a comparison between calculated 50th and 99th percentiles (derived from equation (17) with values of z equal to 0 and 2.33 respectively) was made with the corresponding observed values. This is presented for the 1982 and 1983 surveys for each site in Tables 25 and 26.

The prediction of 50th percentile values (geometric means) at the urban site gave good agreement with observed values. Observed over expected values of 95.0% to 108.2% were found at this site in 1982 and 95.4% to 119.3% in 1983.

Table 23 : Parameters calculated by least squares minimisation as a result of fitting the motorway air quality data sets to the LN3C distribution

	mg(e)	mg(o)	Sg(e)	Sg(o)	K	P(o)
(a) 1982						
CH_4	1.495	1.495	1.119	1.121	-0.11	0.0
THC	0.436	0.436	1.546	1.546	+1.07	-
NMHC	0.243	0.244	1.836	1.826	-0.085	4.3
CO	0.947	0.947	1.442	1.443	-0.29	0.2
SO_2	5.844	5.844	0.577	0.576	+9.528	-
O_3	0.047	0.054	8.690	6.098	-0.013	27.8
(b) 1983						
NMHC	0.180	0.183	1.724	1.719	-0.069	3.84
CO	0.714	0.714	1.436	1.439	-0.24	0.13
SO_2	10.562	10.548	1.589	1.589	+6.42	-
O_3	21.328	21.349	1.596	2.153	-5.77	4.36
NO	0.289	9.292	2.944	2.892	-0.045	4.27
NO_2	1.543	1.550	10.91	12.102	-0.001	0.0

mg(e) = estimated geometric mean
mg(o) = observed geometric mean (obtained from actual data)
Sg(e) = estimated standard geometric deviation, by least squares minimisation
Sg(o) = observed standard geometric deviation (obtained from actual data)
K = 3rd parameter
P(o) = probability of occurrence of zero concentration values (expressed as a percentage)

However, a less successful agreement between observed and expected 50th percentiles was found at the motorway and rural sites in 1982 and 1983, particularly for those pollutants involved with photochemical reactions (O_3, NO and NO_2).

The prediction of 99th percentiles was also most successful at the urban site with observed over expected values varying between 64.6% for O_3 and 103.8% for SO_2 in 1982 and 62.0% for NO and 104.7% for SO_2 in 1983. Poor agreement was found at the other sites between observed and predicted 99th percentile concentrations for both years.

The minimum number of samples (n_{min}) that was required to obtain the sample geometric mean to within ±10%, with a 95% confidence level,

Table 24 : Parameters calculated by least squares minimisation as a result of fitting the rural air quality data sets to the LN3C distribution

	mg(e)	mg(o)	Sg(e)	Sg(o)	K	P(o)
(a) 1982						
CH_4	0.344	0.344	1.317	1.322	+1.01	-
THC	0.227	0.227	1.669	1.664	+1.19	-
NMHC	0.166	0.167	1.474	1.454	-0.10	9.5
CO	0.298	0.299	1.317	1.322	+1.01	-
SO_2	9.252	9.252	0.546	0.545	+5.81	-
O_3	0.096	0.108	11.715	8.913	-0.012	46.8
(b) 1983						
NMHC	0.206	0.207	2.361	2.321	-0.049	4.74
CO	0.462	0.462	2.713	2.708	+0.088	-
SO_2	8.062	8.086	1.305	1.305	+8.606	-
O_3	2.423	2.489	5.755	5.524	-0.22	8.53
NO	1.573	1.580	10.697	11.828	-0.0057	0.89
NO_2	3.857	3.866	1.716	1.733	-1.50	4.01

mg(e) = estimated geometric mean
mg(o) = observed geometric mean (obtained from actual data)
Sg(e) = estimated standard geometric deviation, by least squares minimisation
Sg(o) = observed standard geometric deviation (obtained from actual data)
K = 3rd parameter
P(o) = probability of occurrence of zero concentration values (expressed as a percentage)

has been presented in Table 27 for both 1982 and 1983 data sets (calculated from equation (18)).

The number of hourly samples taken was adequate in obtaining the sample geometric mean (to within ±10%) for all pollutants at the three sites except for O_3 at the rural site in 1982 and NO_2 at the motorway site in 1983. Both are pollutants involved in photochemical reactions and demonstrated high measured concentration variability.

These selected statistical techniques demonstrated that equation (20) best explained the variation of pollutant concentrations and meteorological variables. The LN3C distribution fit provided an ade-

Table 25 : Comparison of LN3C estimated 50th and 99th percentiles with observed values for the 1982 data sets

Urban	50th(o)	50th(e)	$\frac{o}{e} \times 100$	99th(o)	99th(e)	$\frac{o}{e} \times 100$
CH_4 (ppm)	1.55	1.57	98.7	2.18	2.18	100
THC (ppm)	1.82	1.81	100.7	2.59	2.58	100.4
NMHC (ppm)	0.19	0.20	95.0	0.85	0.94	90.4
CO (ppm)	1.44	1.35	106.7	5.82	6.38	91.2
SO_2 (ppb)	16.19	14.96	108.2	33.13	31.9	103.8
O_3 (ppb)	0.29	0.30	96.7	7.54	11.67	64.6
Motorway	**50th(o)**	**50th(e)**	$\frac{o}{e} \times 100$	**99th(o)**	**99th(e)**	$\frac{o}{e} \times 100$
CH_4 (ppm)	1.42	1.35	105.2	1.66	1.66	100
THC (ppm)	1.49	1.42	104.9	2.15	1.97	109.1
NMHC (ppm)	0.17	0.066	257.6	0.73	0.31	23.5
CO (ppm)	0.67	1.31	51.1	2.57	1.58	162.6
SO_2 (ppb)	17.09	15.1	113.2	25.49	8.07	315.9
O_3 (ppb)	0	0	-	4.69	29.7	15.8
Rural	**50th(o)**	**50th(e)**	$\frac{o}{e} \times 100$	**99th(o)**	**99th(e)**	$\frac{o}{e} \times 100$
CH_4 (ppm)	1.34	1.38	97.1	1.74	1.83	95.1
THC (ppm)	1.41	1.51	93.4	1.87	2.27	82.4
NMHC (ppm)	0.06	0.16	37.5	0.30	0.92	32.6
CO (ppm)	0.21	0.66	31.8	1.27	1.93	65.8
SO_2 (ppb)	16.69	15.37	108.6	28.21	11.15	25.3
O_3 (ppb)	0.07	0.03	43.0	37.82	7.23	523.1

quate method of predicting the 50th percentile concentration. Prediction of the 99th percentile was less successful with only the urban data set achieving reasonable agreement between observed and predicted values.

These techniques provided little information on the relationship between vehicle-operating mode and air quality at sites of high traffic density.

Table 26 : Comparison of LN3C estimated 50th and 99th percentiles with observed values for the 1983 data sets

Urban	50th(o)	50th(e)	$\frac{o}{e} \times 100$	99th(o)	99th(e)	$\frac{o}{e} \times 100$
NMHC (ppm)	0.34	0.33	106.2	1.09	1.08	100.9
CO (ppm)	1.51	1.43	105.6	6.15	6.73	91.4
SO_2 (ppm)	19.8	20.75	95.4	33.04	31.54	104.7
O_3 (ppm)	2.59	2.48	104.4	28.47	40.99	69.4
NO (ppb)	2.96	2.48	119.3	16.95	27.3	62.0
NO_2 (ppb)	5.72	4.96	115.3	11.56	15.4	75.1
Motorway	**50th(o)**	**50th(e)**	$\frac{o}{e} \times 100$	**99th(o)**	**99th(e)**	$\frac{o}{e} \times 100$
NMHC (ppm)	0.14	0.11	127.3	1.41	0.57	247.4
CO (ppm)	0.57	0.47	121.3	5.95	1.42	419.0
SO_2 (ppm)	16.67	16.98	98.0	23.67	37.49	63.2
O_3 (ppm)	2.58	15.56	16.6	50.92	57.62	88.4
NO (ppb)	3.06	0.24	1254.1	52.21	3.53	1481.9
NO_2 (ppb)	2.50	1.54	162.2	11.57	400.7	2.89
Rural	**50th(o)**	**50th(e)**	$\frac{o}{e} \times 100$	**99th(o)**	**99th(e)**	$\frac{o}{e} \times 100$
NMHC (ppm)	0.10	0.16	63.7	0.90	1.48	60.8
CO (ppm)	0.40	0.55	72.7	1.60	4.82	33.0
SO_2 (ppm)	15.88	16.67	95.3	39.23	23.61	166.2
O_3 (ppm)	15.70	2.20	713.0	80.40	142.7	56.3
NO (ppb)	0.20	1.56	12.8	3.00	393.46	0.7
NO_2 (ppb)	1.90	2.12	89.0	6.20	12.07	51.4

Table 27 : Minimum number of hourly samples needed to obtain the sample geometric mean to within ±10%

	Urban		Motorway		Rural	
(1982)	n	n_{min}	n	n_{min}	n	n_{min}
CH_4	617	43	323	6	381	31
THC	617	8	420	73	381	95
NMHC	617	52	323	127	381	55
CO	594	104	316	53	367	32
SO_2	646	102	598	110	446	128
O_3	554	383	631	478	450	532
(1983)						
NMHC	574	36	454	99	542	212
CO	626	114	365	49	529	266
SO_2	626	51	484	76	631	29
O_3	626	300	484	172	631	134
NO	626	255	484	266	631	563
NO_2	626	55	484	514	631	109

n = actual number of hourly samples

n_{min} = minimum number of samples that would be required for a precision of ±10% of the sample geometric mean with a confidence level of 95%

4.1.2.5 Ambient Air Concentrations of Particulate Lead at the Urban, Motorway and Rural Sites

Airborne particulate lead at the three contrasting sites was sampled weekly (see Section 2.1) to investigate the influence of vehicle emissions on air quality. The data from the 1982 and 1983 surveys are presented in Table 28. These data for airborne particulate lead concentrations have been treated separately because of the smaller number of samples compared to the gaseous pollutants.

Table 28 : Ambient air particulate lead concentrations at the three sites surveyed in 1982 and 1983

Site	Date of Sample		Concentration	
Urban	6-13 June	1982	255	$\bar{x}$ = 443 ngm^{-3}
	12-20 June	1982	120	
	20-27 June	1982	783	
	27 June - 4 July	1982	677	
	4 July - 11 July	1982	381	
	15 - 22 May	1983	216	$\bar{x}$ = 192 ngm^{-3}
	22 - 29 May	1983	192	
	29 May - 5 June	1983	167	
	5 - 11 June	1983	192	
Motorway	8 - 15 August	1982	1277	$\bar{x}$ = 1141 ngm^{-3}
	15 - 22 August	1982	707	
	22 - 29 August	1982	1100	
	29 Aug - 4 Sept	1982	1480	
	12 - 19 June	1983	168	$\bar{x}$ = 171 ngm^{-3}
	19 - 26 June	1983	89	
	26 June - 3 July	1983	256	
	3 - 10 July	1983	172	
Rural	12 - 18 July	1982	30	$\bar{x}$ = 28 ngm^{-3}
	18 - 25 July	1982	15	
	25 July - 1 August	1982	20	
	1 - 8 August	1982	47	
	11 - 18 July	1983	100	$\bar{x}$ = 82 ngm^{-3}
	18 - 25 July	1983	89	
	25 July - 1 August	1983	94	
	1 - 8 August	1983	44	

The weekly concentrations at the urban site during the 1982 survey varied between 120 and 783 ng m^{-3} and between 167 and 216 ngm^{-3} during the 1983 survey. The monthly mean values during the two sampling periods were 443 ngm^{-3} and 192 ngm^{-3} in 1982 and 1983, respectively. The difference between the two periods is not considered significant because of the high variability in weekly concentrations.

Concentrations at the motorway site differed significantly with the maximum value (1480 ngm^{-3}) and highest monthly mean (1155 ngm^{-3}) occurring during the 1982 survey. During the 1983 survey the monthly mean concentration was considerably lower (171 ngm^{-3}) and was comparable to the monthly mean concentrations at the urban site. The composite wind roses during the monitoring periods (Figures 29 and 33) were also considerably different and the elevated concentrations during the 1982 survey occurred when the wind was predominantly blowing across the motorway towards the mobile laboratory. Wind speeds were also high during this period which may have resulted in a greater degree of re-entrainment of particulate lead from the road surface.

The monthly mean particulate lead concentrations at the rural site (selected as a control) were lower during the 1982 and 1983 surveys (28 and 82 ngm^{-3} respectively) than at the urban and motorway sites.

These data compare favourably with the gaseous air pollutant data considered previously, as they demonstrate the role of transport-related emissions on air quality. They also indicate that meteorological factors (such as wind speed and wind direction) can significantly influence measured particulate lead concentrations particularly at the motorway site. The data from the rural site can be considered as representative of background concentrations.

4.2 Evaluation of Techniques for the Measurement of Aromatic and Halogenated Hydrocarbons in Ambient Air and Vehicle Exhaust

It has been estimated that NMHC in ambient air contain approximately 30% aromatic hydrocarbons (Nelson and Quigley, 1982). An evaluation of various techniques and the effects of various sampling parameters were performed to allow an assessment to be made of concentrations of motor vehicle-related aromatic and halogenated hydrocarbons in vehicle exhaust and ambient air.

4.2.1 Tenax GC Sampling Tube Method

A comparison between direct injection of liquid standards and thermal desorption of spiked sampling tubes, using five replicates for each analysis, is presented in Table 29 for benzene, toluene and 1,2-dichloroethane. The flasher, operated at 250°C, demonstrated high desorption efficiencies for benzene (97.4%), toluene (103.6%) and 1,2-dichloroethane (101.1%).

Table 29 : Comparison between direct injection of standard solution and thermal desorption of spiked sampling tubes for benzene, toluene and 1,2-dichloroethane

Compound	Direct Injection Relative Response		Thermal Desorption Relative Response		$\frac{\text{Thermal Desorption}}{\text{Direct Injection}}$ %
	$\bar{x}$	RSD(%)	$\bar{x}$	RSD(%)	
Benzene	132.2	2.1	128.8	1.33	97.4
Toluene	89.7	2.37	93	1.26	103.6
1,2-Dichloroethane	64.7	2.5	65.4	1.4	101.1

The permeation tube oven-exponential dilution flask method of calibration proved to be accurate in loading a precise mass of organic vapour onto a sampling tube. Calibration data for benzene are presented in Table 30, which demonstrate a loading efficiency of 101% with a relative standard deviation (RSD) of 4.8%. Storage of tubes, calibrated for benzene and toluene for up to 21 days, had no significant effect on the repeatability of analysis.

Table 30 : Comparison of expected and actual benzene vapour loadings on Tenax GC sampling tubes

Tube Number	Expected Vapour Loading (μg)	Actual Vapour Loading (μg)	$\frac{\text{Actual}}{\text{Expected}}$ %
1	3.11	3.31	106
2	2.95	2.80	95
3	2.28	2.21	97
4	1.85	1.82	98.4
5	1.10	1.15	105
6	0.53	0.57	107.5
			Mean = 101.5%
			RSD = 4.8%

The sampling tubes can be regarded as short chromatographic columns operating at ambient temperatures. Therefore chromatographic theory can be applied to evaluate whether a particular organic vapour may be sampled efficiently using Tenax GC sampling tubes under varying conditions.

The results of a frontal analysis for benzene are presented in Figure 56. With a carrier gas flow-rate of 50 ml min^{-1}, the retention volume (V_g) for benzene was 6.6 l (after dead volume correction). Elution analysis retention volumes calculated from equation (22) are presented in Table 1 together with the regression constants.

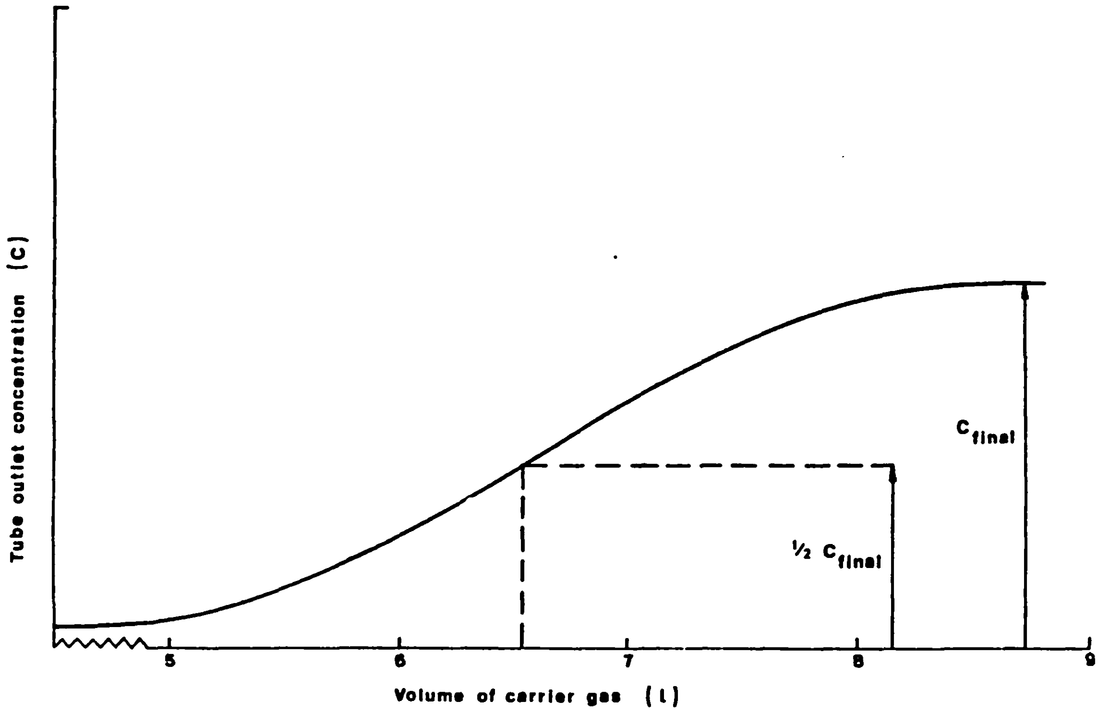


Figure 56 : Frontal analysis for benzene

Table 31 : Extrapolated retention volumes of selected aromatic and halogentated hydrocarbons at 20°C determined by elution analysis

Compounds	Constants*		Regression Coefficient	Retention Volume (l)
	A $\times 10^3$	B		
Benzene	3.0076	6.4648	0.99	6.31
Toluene	3.759	7.0136	0.99	65.4
o-Xylene	3.7507	7.5234	0.97	189.2
Ethyl benzene	5.2846	2.8111	0.99	20.4
p-Ethyl toluene	4.375	8.7882	0.97	1291.6
o-Diethyl benzene	5.0	10.24	0.99	6680
1,3,5-Trimethyl benzene	4.1909	8.347	0.99	905
1,2-Dichloroethane	2.8676	6.1933	0.99	3.92
1,2-Dibromoethane	3.8991	7.6572	0.99	446.9

* A and B are constants in the equation log V_g = A.T-B

The retention volume for benzene (6.3 l at 20°C) is in excellent agreement with the 6.6 l determined by frontal analysis. Similar agreement was found for toluene.

The number of theoretical plates (N) of the sampling tube for benzene, as determined by frontal analysis using equation (23) was 34 which compares favourably with a value of 35 determined by elution analysis using equation (24).

The accurate measurement of aromatic and halogenated hydrocarbons using a trapping technique is limited by the lowest retention volume of an individual compound of interest where a mixture is present. The two lowest retention volume values presented in Table 31 are for EDC and benzene (3.92 l and 6.31 l respectively) which are well below those of other compounds, e.g. toluene (65 l). Consequently, experiments to determine the effect of various sampling parameters have been performed using compounds with low retention volumes, as any demonstrable effect of sampling parameters will have the largest influence on the sampling volumes of these compounds.

It is known that peak asymmetry, retention time and the number of theoretical plates of Tenax GC chromatographic columns are affected by the column load (Daemen et al., 1975). The effect of adsorbate concentrations of benzene, toluene and EDC was determined by elution analysis. The results, presented in Figure 57, indicate that no significant change in retention volumes occurred until the injected concentrations approached 3000 ppm.

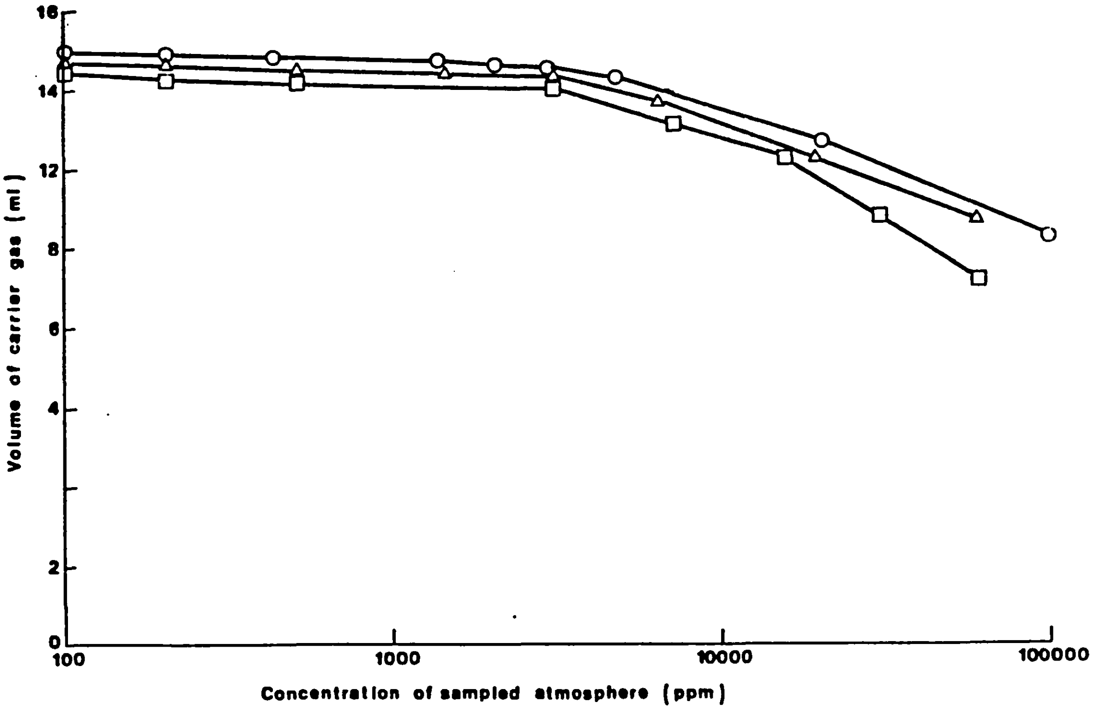


Figure 57 : The effect of concentration on retention volumes determined by elution analysis

However, when high concentrations of aromatic hydrocarbons (benzene, toluene and o-xylene) were prepared in an exponential dilution flask and 10 minute samples were drawn through Tenax GC sampling tubes (50 ml min^{-1} flow-rate), a different effect was observed. The results of this frontal technique, presented in Figure 58, demonstrated that the arbitrary limit of linearity of adsorption of these compounds was approximately 1 ppm.

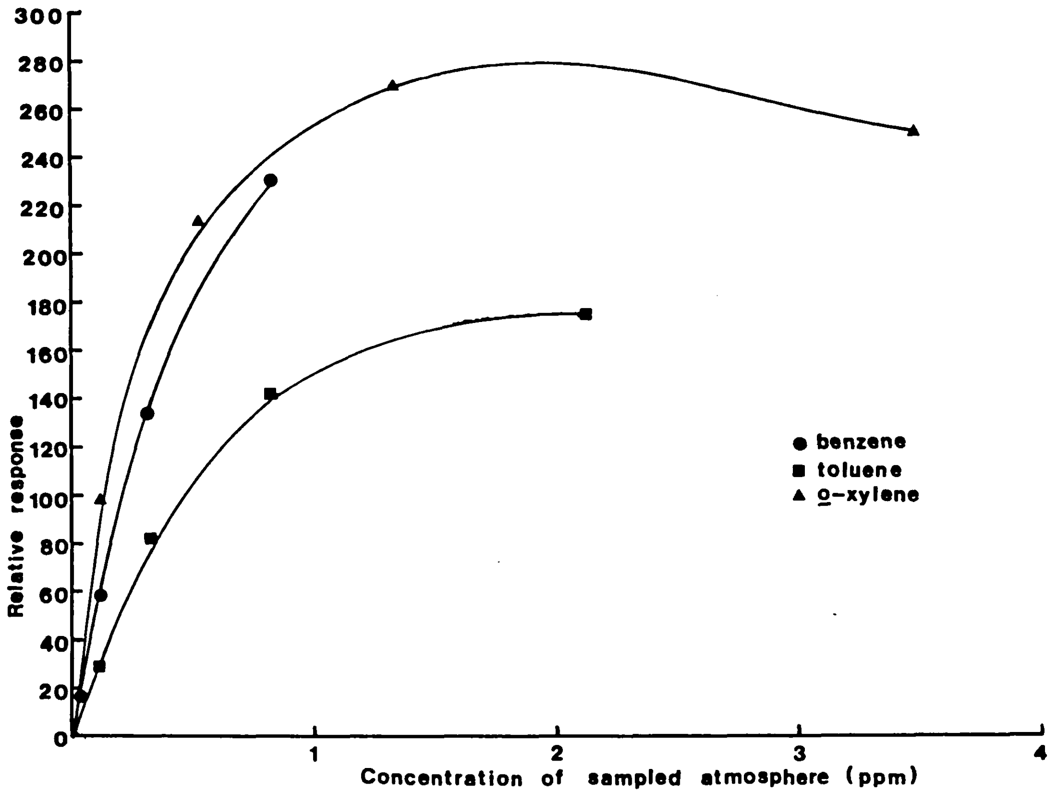


Figure 58 : The effect of concentration on retention volumes determined by frontal analysis

The effects of humidity on the Tenax GC sampling tubes used in this study are presented in Table 59 for the adsorbates benzene, toluene and EDC.

Table 32 : Effect of humidity on retention volumes at 20°C of benzene, 1,2-dichloroethane and toluene

Compound	Retention Volume (1)		$\frac{V_g \text{ Humid}}{V_g \text{ Dry}}$
	High Humidity	Dry	
Benzene	4.98	6.31	0.79
1,2-Dichloroethane	3.48	3.92	0.89
Toluene	53.42	65.0	0.82

The effect of flow-rate on the theoretical plate values is presented in Figure 64. The number of plates decreased with increasing flow-rates between 10 and 200 ml min^{-1}, from 51 to 22. No appreciable

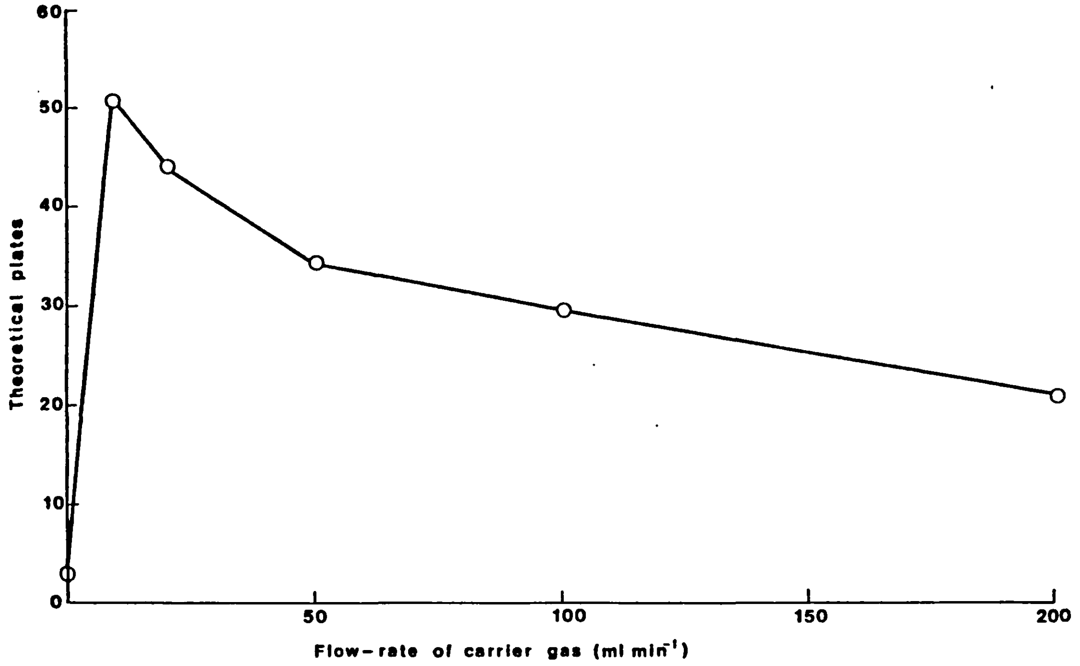


Figure 59 : The effect of flow-rate on the number of theoretical plates

change in retention volumes was detected in the range of flow-rates between 10 and 200 ml min^{-1}.

Table 33 : Safe sampling volumes for benzene and EDC at various flow-rates and sampling efficiencies

Compound	V_g (l)	Flow-Rate (ml min^{-1})	Safe Sampling Volumes (l)		
			99.9%	99%	95%*
Benzene	6.3	10	4.35	5.17	6.10
		20	3.91	4.91	5.98
		50	3.72	4.72	5.86
		100	3.28	4.6	5.73
		200	3.02	4.28	5.48
1,2-Dichloroethane	3.92	10	2.70	3.21	3.80
		20	2.43	3.06	3.72
		50	2.31	2.94	3.64
		100	2.04	2.86	3.58
		200	1.88	2.66	3.41

* sampling efficiency

The safe sampling volume is dependent not only on the retention volume but also on the number of theoretical plates. Safe sampling volumes for benzene and EDC are presented in Table 33, for flow-rates between 10 and 200 ml min^{-1}, at 99.9%, 99% and 95% sampling efficiencies.

These results demonstrate the versatility of approach that can be achieved by adopting different flow-rates according to the sampling time and efficiency that is required. The effect of various sampling parameters has been evaluated and it is evident that this method is suitable for monitoring ambient air concentrations of aromatic and halogenated hydrocarbons.

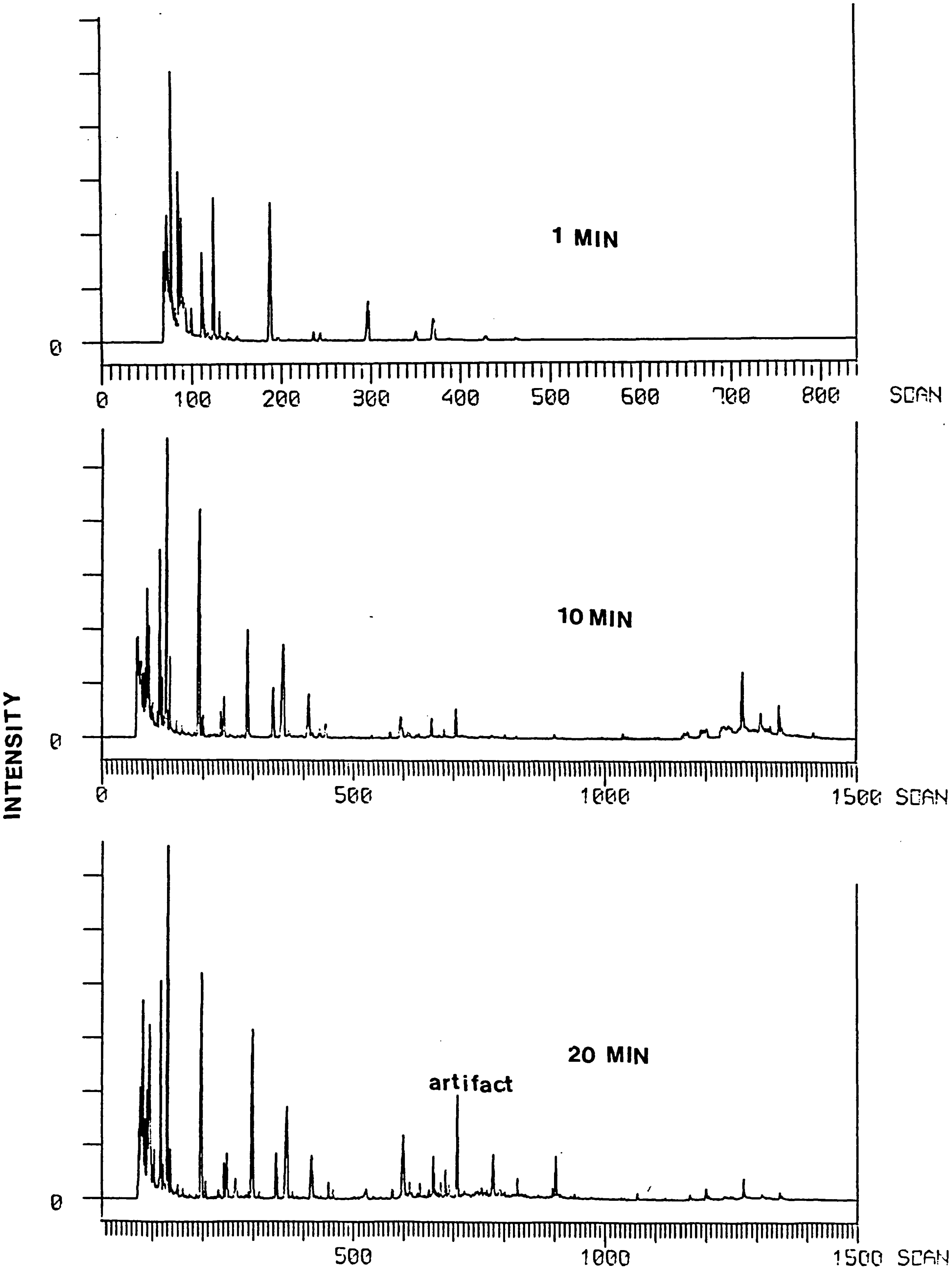
4.2.2 Analysis of Aromatic Hydrocarbons by GC/MS

Desorption tests of identical samples (presented in Figure 60) demonstrated that the Bendix flasher unit was efficient in removing adsorbed material from Tenax GC sampling tubes at reduced carrier gas flow-rates. However, 20 min desorption times significantly affected the production of artifacts (e.g. fluorotrimethylsilane) from the Tenax GC tubes and a desorption time of 10 min was adopted as a compromise between desorption efficiency and artifact production. Sampling tubes, spiked with a direct injection of a 10 ng mixed aromatic standard, demonstrated complete desorption after 10 min.

An example of the computer mass spectral library search facility is presented in Appendix B along with an example of a 0.5 h (3.75 l) Tenax GC sample taken at the urban site. Concentrations of selected aromatic hydrocarbons were benzene (9.0 ppb), toluene (9.3 ppb), ethylbenzene (1.3 ppb), m and p-xylene (2.4 ppb), o-xylene (1.2 ppb), isopropylbenzene (0.4 ppb), 1,3,5 trimethylbenzene (1.5 ppb), o-ethyltoluene (0.9 ppb), diethyltoluene (1.1 ppb) and tetramethyltoluene (0.2 ppb).

It must be noted that at this flow-rate a 0.5 h sample would trap 99% of benzene. A 1.0 h sample (7.5 l) would have a benzene collection efficiency of <95%. This method was suitable for collection of data on a wide range of compounds but was far more time consuming than the GC method evaluated in Section 4.2.1.

Figure 60 : Desorption tests with GC/MS



4.2.3 Photoionisation Detector Gas Chromatograph

Photoionisation detectors have the potential of measuring low concentrations of aromatic hydrocarbons in air without preconcentration when interfaced to a gas chromatograph. A PID/GC has been evaluated to determine its suitability for measuring these compounds over a wide range of concentrations.

An example of a concentration/response graph is presented in Figure 61 for benzene. Similar graphs were used in determining detection limits of aromatic hydrocarbons using a PID/GC. Detection limits for benzene and toluene were 0.3 ppb and 1 ppb for o-, m- and p-xylene and ethylbenzene.

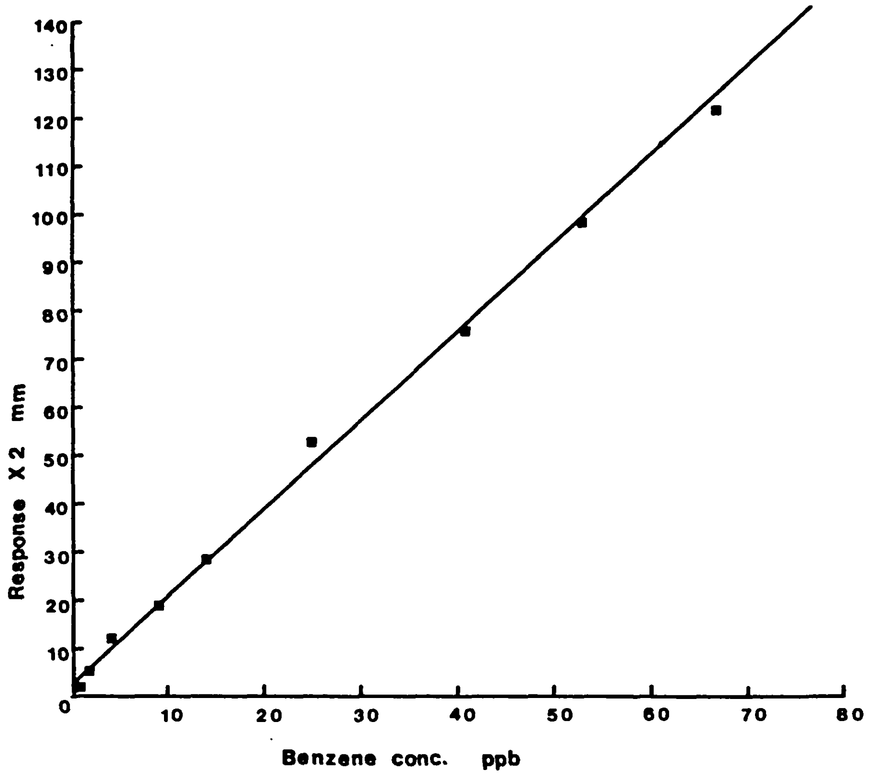


Figure 61 : Benzene concentration/response graph measured by PID/GC

However, by using 1 ml injection aliquots calibrations above 1 ppm benzene and 3 ppm toluene become non-linear. Because of the high sensitivity of the instrument, it was possible to reduce injection volumes down to 0.05 ml and maintain linearity. At higher concentrations up to 100 ppm, the instrument no longer maintained linearity with this injection volume (0.05 ml). Smaller injection volumes would aid linearity even at the 100 ppm level.

Compounds with an ionization potential below 11 eV (such as H_2O) are not "seen" by this PID. As a consequence it is possible to analyse vehicle exhausts by direct injection without interference by water vapour. However, because the column operates at ambient temperature, only limited separation of exhaust aromatic hydrocarbons was possible using a 1.5 m × 3.1 mm od containing 1.5% OV17 + 1.95% QFI on Supelcoport 100/120.

Although detection limits for ethyl benzene and o, m and p-xylene are considerably lower than with FID/GC, the instrument may not be suitable for measuring low ambient air concentrations.

4.3 An Assessment of the Impact of Motor Vehicle-Related Emissions of Aromatic and Halogenated Hydrocarbons and Organic and Particulate Lead on Air Quality

In order to maintain the octane quality of petrol in the UK and other European countries while decreasing the lead content to 0.15 gl^{-1}, the approach that most oil refining companies have adopted is to increase the aromatic content in petrol. The ambient air concentrations of aromatic and halogenated (EDC and EDB) hydrocarbons are therefore predicted to change.

In order to assess possible changes in air quality and the role of vehicle-operating mode on emissions of these pollutants, monitoring surveys have been carried out at the urban, motorway and rural locations. These surveys were performed in conjunction with the general air quality monitoring surveys in 1982 and 1983 presented previously (see Section 3.4).

At each site, in both the 1982 and 1983 surveys, one week of intensive sampling was performed. Ambient air was sampled for 20 min and trapped on Tenax GC sampling tubes (see Section 3.4). The tubes were thermally desorbed and analysed by FID or EC equipped gas chromatographs.

Summaries of the hourly concentrations of aromatic and halogenated hydrocarbon in the ambient air at the three sites are presented in Tables 34 and 35.

Concentration differences between the 1982 and 1983 surveys were minimal. At the urban site the highest hourly mean aromatic hydrocarbon concentrations were those of benzene (8.81 and 9.69 ppb) and toluene (13.48 and 15.54 ppb) in both 1982 and 1983. Maxima concentrations of 26.42 and 42.37 ppb were found for benzene and toluene respectively, in 1983. Maxima concentrations of these compounds in 1982 were similar. Hourly mean concentrations of EDC were 0.26 and 0.3 ppb in 1982 and 1983 respectively while hourly mean EDB concentrations were 0.03 ppb in both surveys.

The motorway site at Toddington demonstrated lower mean concentrations than the urban site except in the case of EDB. Mean hourly concentrations for benzene, toluene, EDC and EDB were 2.82, 2.09, 0.02 and 0.05 ppb and in the following year, 2.6, 2.69, 0.02 and 0.04 ppb.

The rural site (at Silwood Park) demonstrated concentrations approximately one order of magnitude lower than the urban site. Mean hourly concentrations during the 1982 survey for benzene, toluene, EDC and EDB were 1.55, 1.33, 0.02 and 0.15 ppb respectively. Similar concentrations were found during the 1983 survey. Maxima did not exceed those at the urban site.

Diurnal averages for aromatic and halogenated hydrocarbons are presented in Figures 62 (a-f) and 63 (a-f) for the three sites during the 1982 and 1983 surveys. The diurnal variation in traffic numbers is presented in Figure 20 for the urban site in 1982 and Figures 35 and 38 for the motorway site in 1982 and 1983. This emphasizes the relationship between traffic density and emissions of aromatic hydrocarbons.

Correlation analysis was performed on the concentration data from the three sites. In general, only benzene and toluene were consistently well correlated at each site for both the 1982 and 1983 surveys. The coefficient of variation (r) varied between 0.84 (rural site in 1982) and 0.96 (urban site in 1983). However, reasonable correlations between EDC and EDB were found at the urban (0.65 and 0.76 respec-

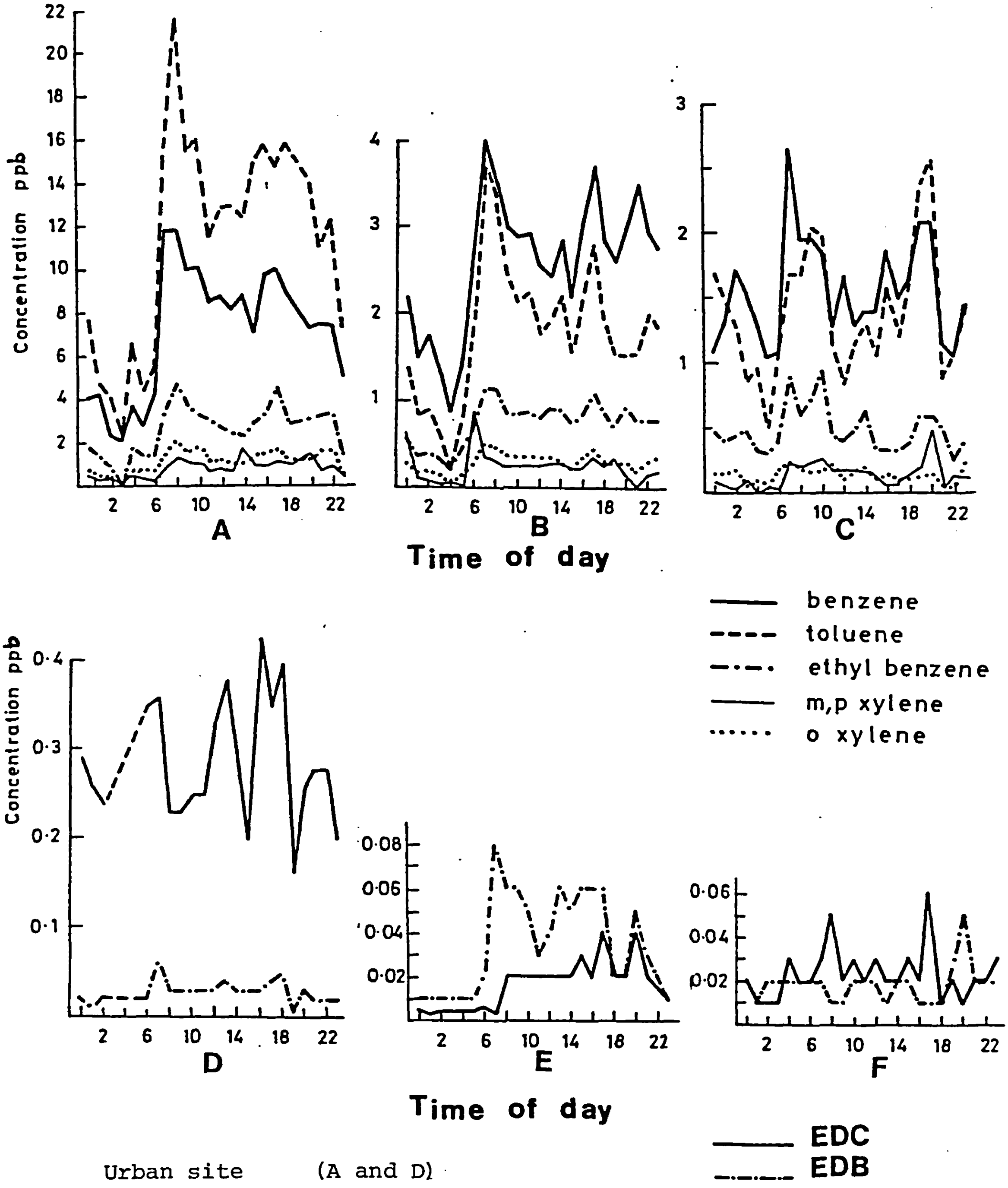
Table 34 : Summary of hourly concentrations of aromatic and halogenated hydrocarbons measured at the urban, motorway and rural sites in 1982

		Concentrations in ppb							
Site		benzene	toluene	ethyl benzene	m & p xylene	o-xylene	total xylenes	EDC	EDB
Urban	mean ($\bar{x}$)	8.81	13.48	0.88	2.76	1.23	4.31	0.26	0.03
	standard deviation (σ)	3.61	7.65	0.61	1.12	0.52	2.59	0.15	0.02
	minimum	1.00	1.00	0.00	0.00	0.00	0.00	0.05	0.01
	maximum	21.40	38.00	3.30	8.80	4.00	12.60	0.78	0.13
	n = 256								
Motorway	mean ($\bar{x}$)	2.82	2.09	0.25	0.85	0.36	1.19	0.02	0.05
	standard deviation (σ)	0.99	1.05	0.15	0.24	0.14	0.46	0.02	0.06
	minimum	0.60	0.10	0.00	0.00	0.00	0.00	0.00	0.00
	maximum	5.70	7.00	0.70	2.10	0.80	2.60	0.13	0.26
	n = 198								
Rural	mean ($\bar{x}$)	1.55	1.33	0.12	0.49	0.17	0.63	0.02	0.015
	standard deviation (σ)	0.73	0.90	0.12	0.25	0.08	0.46	0.02	0.01
	minimum	0.50	0.20	0.00	0.00	0.00	0.00	0.00	0.00
	maximum	6.00	6.20	0.60	3.40	3.40	4.10	0.12	0.10
	n = 175								

Table 35 : Summary of hourly concentrations of aromatic and halogenated hydrocarbons measured at the urban, motorway and rural sites in 1983

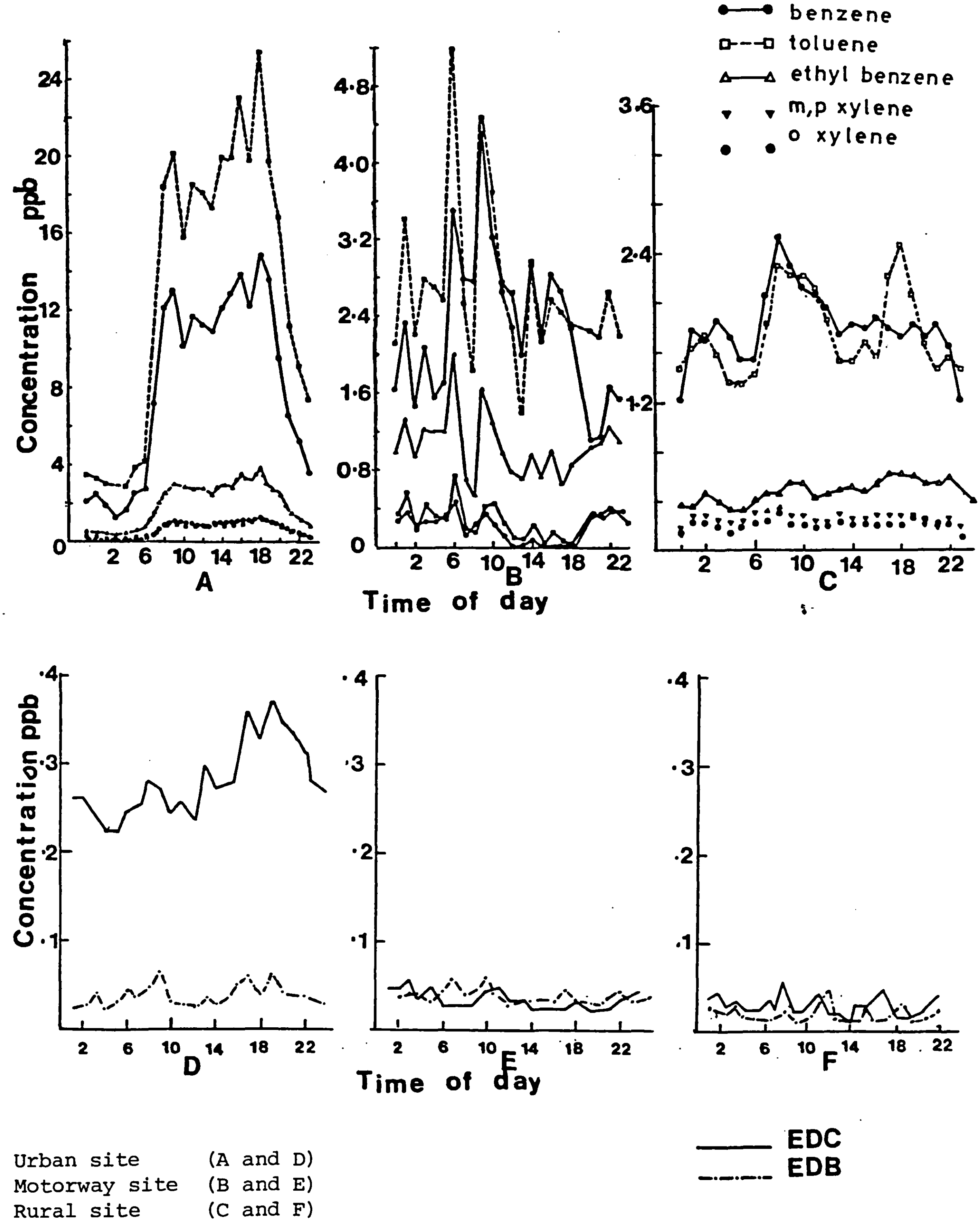
Site		Concentrations in ppb							
		benzene	toluene	ethyl benzene	*m* & *p* xylene	*o*-xylene	total xylenes	EDC	EDB
Urban	mean ($\bar{x}$)	9.69	15.54	0.78	2.30	0.77	3.07	0.30	0.03
	standard deviation (σ)	5.41	8.83	0.49	1.32	0.45	1.84	0.12	0.02
	minimum	0.64	0.84	0.05	0.11	0.02	0.06	0.03	0.01
	maximum	26.42	42.37	2.17	6.30	2.27	8.50	0.87	0.08
	n = 267								
Motorway	mean ($\bar{x}$)	2.6	2.69	0.17	1.02	0.27	1.29	0.02	0.04
	standard deviation (σ)	2.02	2.66	0.26	0.98	0.35	1.07	0.18	0.30
	minimum	0.06	0.07	0.00	0.00	0.00	0.00	0.00	0.00
	maximum	12.72	15.67	1.14	6.41	2.06	8.20	0.10	0.15
	n = 184								
Rural	mean ($\bar{x}$)	1.64	1.27	0.14	0.50	0.21	0.71	0.02	0.019
	standard deviation (σ)	0.80	0.90	0.11	0.31	0.08	0.63	0.02	0.01
	minimum	0.40	0.20	0.00	0.00	0.00	0.00	0.00	0.00
	maximum	5.00	6.40	0.70	4.10	3.70	4.24	0.10	0.04
	n = 204								

Figure 62 : Diurnal averages for aromatic and halogenated hydrocarbons during the 1982 survey



Urban site (A and D)
Motorway site (B and E)
Rural site (C and F)

Figure 63 : Diurnal averages for aromatic and halogenated hydrocarbons during the 1983 survey



Urban site (A and D)
Motorway site (B and E)
Rural site (C and F)

tively) and motorway sites during the 1982 and 1983 surveys (0.79 and 0.60, respectively).

A comparison of coefficients of variation between diurnal aromatic concentrations and traffic flow is presented in Table 36. Good agreement was found between coefficients during the 1982 survey at the urban and motorway sites (except in the case of ethylbenzene). However, toluene, o-, m- and p-xylene did not correlate significantly at the motorway site in 1983. A different wind pattern was observed over the two surveys as illustrated by the composite wind roses (see Figures 29 and 33). It is possible that an additional source of these compounds contributed to ambient concentrations as a small mobile fuel tank was situated nearby during the 1983 monitoring period. However, the degree of contribution was small as measured mean concentrations were similar in both the 1982 and 1983 surveys.

Table 36 : Correlations of diurnal hourly average aromatic hydrocarbon concentrations and traffic flow at the urban and motorway sites

Compound	Urban 1982	Motorway 1982	Motorway 1983
benzene	0.66	0.69	0.69
toluene	0.71	0.74	NC*
ethylbenzene	0.62	NC*	NC
m- and p-xylene	0.65	0.70	NC
o-xylene	0.63	0.65	NC

* NC indicates no significant correlation

The ratio between toluene and benzene on a weight-to-weight (w/w) basis has been calculated for each site during the 1982 and 1983 surveys. The ratio at the urban site was similar over both periods (1.80 and 1.89 respectively). The ratio at the motorway site was lower than at the urban site in both the 1982 and 1983 surveys (0.87 and 1.22 respectively). Typical vehicle-operating modes were different at these sites. At the urban site, traffic was moving slowly with frequent deceleration and acceleration due to the busy road conditions. At the motorway, vehicles were operating at a high and constant speed. The lower ratios at the motorway site indicate that increased dealkylation of higher aromatic hydrocarbons took place during this operating mode.

A higher ratio was obtained for the motorway site during the 1983 survey than during the 1982 survey and this provides further evidence for an additional toluene source (mobile fuel tank).

The rural site was chosen as a control i.e. a low incidence of vehicular pollutant sources in the immediate area (see Tables 16 and 17). The ratios between toluene and benzene (w/w) during both monitoring periods were lower (1.01 and 0.91 respectively) than those obtained from the urban site and were comparable to the ratios derived from the motorway site. The rural site is still within the influence of the urban fringe of London and is near several small towns. These areas are the probable sources, along with nearby roads, of aromatic and halogenated hydrocarbons. The low ratios at this site indicate that toluene is probably more subject to photochemical decay reactions than benzene.

4.3.1 Ambient Air Organic and Particulate Lead Concentrations

Organic and particulate lead concentrations were measured during the intensive sampling periods in order to ascertain ambient air concentrations at these sites of different vehicle influence. In order to obtain this data, ambient air was sampled for 24 h at the urban and motorway sites and 48 h at the rural site. The method involved passing sample air through a filter and a solution of iodine monochloride to trap particulate and organic lead (see section 2.4 and Appendix B).

Organic and particulate lead ambient air concentrations at the three sites during the 1982 and 1983 sampling periods are presented in Table 37. Particulate lead concentrations at the motorway site

Table 37 : Concentrations of particulate and organic lead measured at the urban, motorway and rural sites

Site		Particulate Lead ngm^{-3}	Organic Lead ngm^{-3}	Total Lead ngm^{-3}
Urban	(1982)	443	31	474
	(1983)	204	18	222
Motorway	(1982)	1155	19	1174
	(1983)	196	15	211
Rural	(1982)	56	1.7	57.7
	(1983)	92	3.7	95.7

(1155 ng m^{-3}) were consistently higher during the 1982 survey than those found at the urban (443 ng m^{-3}) or rural (56 ngm^{-3}) sites. The concentration at the motorway site in 1982 was also more elevated than that determined at this site in 1983 (196 ngm^{-3}). Organic lead concentrations, during the 1982 survey were highest at the urban site (31 ngm^{-3}) in 1982 compared to the rural (1.7 ngm^{-3}) and motorway (19 ngm^{-3}) sites. Concentrations during the 1983 survey were similar at the urban and motorway sites (18 and 15 ngm^{-3} respectively). Lower concentrations were found at the rural site (3.7 ngm^{-3}).

The ratios between organic and total lead at each site for both monitoring periods, expressed as a percentage, have been calculated. Similar ratios at the urban site were found during the 1982 and 1983 surveys (6.5% and 8.1%) respectively. At the motorway site a ratio of 1.6% was determined in 1982 compared to 7% in 1983. The difference in total lead concentrations during the two monitoring periods was considerable; however organic lead concentrations were similar which provides additional evidence of re-entrainment of particulate lead from the road surface (see Section 4.1.2.5). Similar ratios were determined at the rural site (1.7% and 3.7% in 1982 and 1983).

4.3.2 Comparison of the Tenax GC Sampling Tube Method with the PID/GC for the Measurement of Aromatic Hydrocarbons in Ambient Air

Laboratory evaluation of the PID/GC established detection limits for a range of aromatic hydrocarbons (see Section 4.2.3) in ambient air without preconcentration. In order to futher evaluate this method a field trial was carried out at the urban site in conjunction with the 1982 survey of aromatic hydrocarbons. The Tenax GC preconcentration method provides an average concentration over the 20 min sampling time. The PID/GC provides instantaneous concentration measurements.

Throughout the monitoring period, good agreement was obtained between concentrations of benzene and toluene by the two methods. The mean concentration of benzene was 10.6 ppb (20% difference with the Tenax GC method). The mean concentration of toluene was 12.1 ppb (10.2% difference).

Concentrations of ethylbenzene, m-, p- and o-xylene were too low to be determined consistently by the PID/GC method.

A typical time history over 10 h of toluene concentrations is presented in Figure 64. This demonstrates the different information that can be obtained from the two methods.

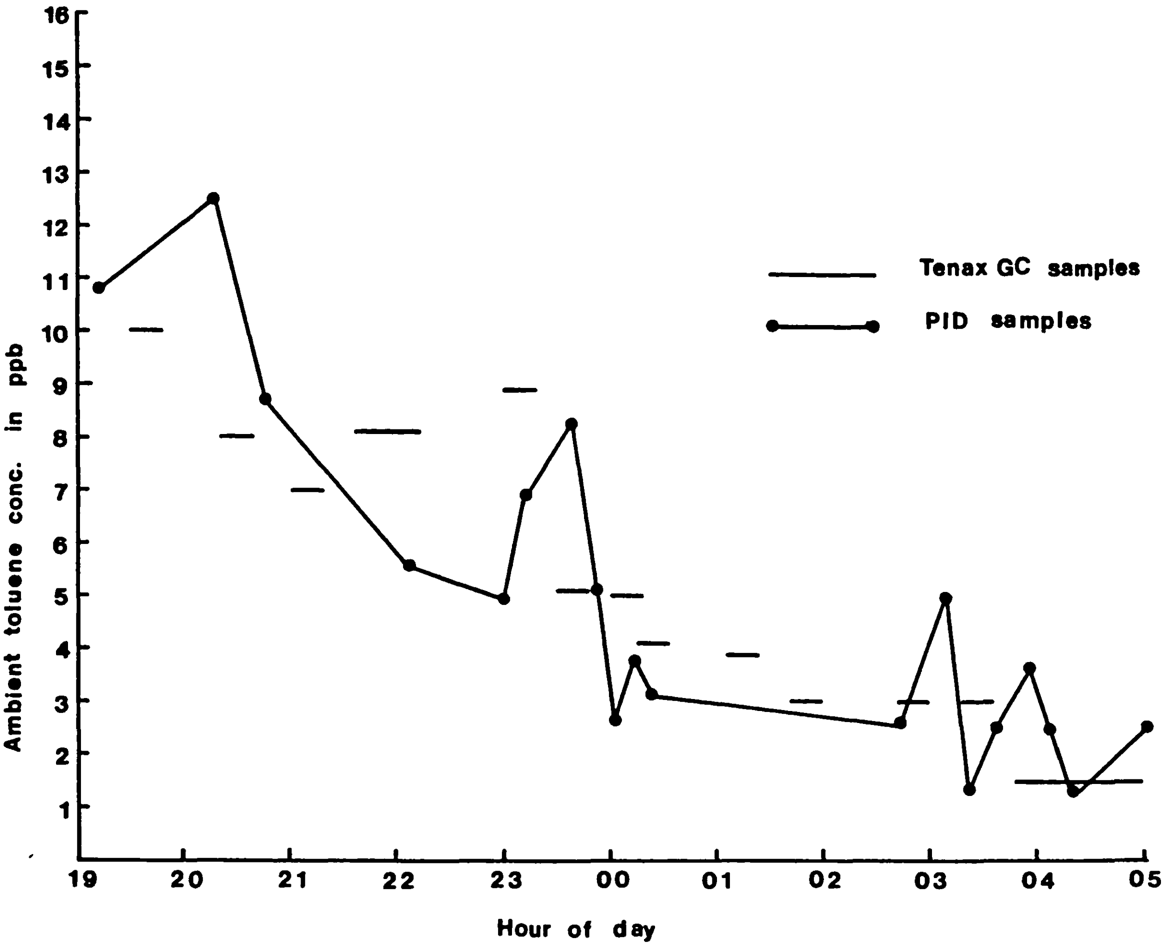


Figure 64 : Comparison of the time history of ambient concentrations of toluene by PID/GC and Tenax GC sampling tube method

This experiment demonstrated that the PID/GC method is suitable for measurements of benzene and toluene in field conditions. It also provided an independent check on the Tenax GC sampling tube method. However, ambient concentrations of other aromatics were difficult to measure consistently.

Table 38 : Dynamometer studies of the effects of vehicle operating mode and fuel composition on aromatic hydrocarbon exhaust emissions

Fuel	Compound	Exhaust Concentration			
		ECE-15		90 kmh^{-1}	
0.64 gl^{-1} lead content	Benzene	30.7	$\bar{x}$ = 30.1	30.2	$\bar{x}$ = 31.7
		29.6	SD = 0.55	33.5	SD = 1.37
		30.1	RSD = 1.8%	31.3	RSD = 4.3%
	Toluene	43.5	$\bar{x}$ = 42.5	38.0	$\bar{x}$ = 39.3
		41.7	SD = 0.92	41.7	SD = 1.72
		42.3	RSD = 2.2%	38.1	RSD = 4.4%
	Xylenes	62.4	$\bar{x}$ = 58.9	56.6	$\bar{x}$ = 54.6
		54.6	SD = 3.97	54.6	SD = 0
		59.8	RSD = 6.7%	54.6	RSD = 0%
	Ethylbenzene	26	$\bar{x}$ = 23.4	20.8	$\bar{x}$ = 20.8
		20.8	SD = 2.6	20.8	SD = 20.0
		23.4	RSD = 11.1%	20.8	RSD = 0%
0.40 gl^{-1} lead content	Benzene	30.6	$\bar{x}$ = 28.3	47.7	$\bar{x}$ = 42.8
		26.6	SD = 2.1	42.2	SD = 3.7
		27.7	RSD = 7.3%	38.6	RSD = 8.79
	Toluene	42.25	$\bar{x}$ = 40.1	62.0	$\bar{x}$ = 56.1
		36.9	SD = 4.5	55.0	SD = 4.47
		38.1	RSD = 11.3%	51.2	RSD = 8.0%
	Xylenes	62.4	$\bar{x}$ = 46.8	83.0	$\bar{x}$ = 73.6
		31.2	SD = 15.6	72.8	SD = 9.0
		46.8	RSD = 33.3%	65.0	RSD = 12.3%
	Ethylbenzene	23.4	$\bar{x}$ = 19.1	33.8	$\bar{x}$ = 28.6
		15.6	SD = 4.0	28.6	SD = 5.2
		18.2	RSD = 20.1%	23.4	RSD = 18.2%
0.15 gl^{-1} lead content	Benzene	29.5	$\bar{x}$ = 27.6	40.4	$\bar{x}$ = 42.1
		25.9	SD = 1.8	39.3	SD = 3.9
		27.3	RSD = 6.6%	46.6	RSD = 9.3%
	Toluene	48.8	$\bar{x}$ = 44.4	54	$\bar{x}$ = 57.93
		40.4	SD = 4.21	54.8	SD = 6.1
		44.0	RSD = 9.5%	65	RSD = 10.6%
	Xylenes	70.2	$\bar{x}$ = 64.1	72.8	$\bar{x}$ = 79.7
		54.6	SD = 8.3	78	SD = 7.94
		64.6	RSD = 13.0%	88.4	RSD = 9.96%
	Ethylbenzene	28.6	$\bar{x}$ = 24.3	31.2	$\bar{x}$ = 32.9
		20.8	SD = 4.0	31.2	SD = 3.00
		23.4	RSD = 16.4%	36.4	RSD = 9.1%

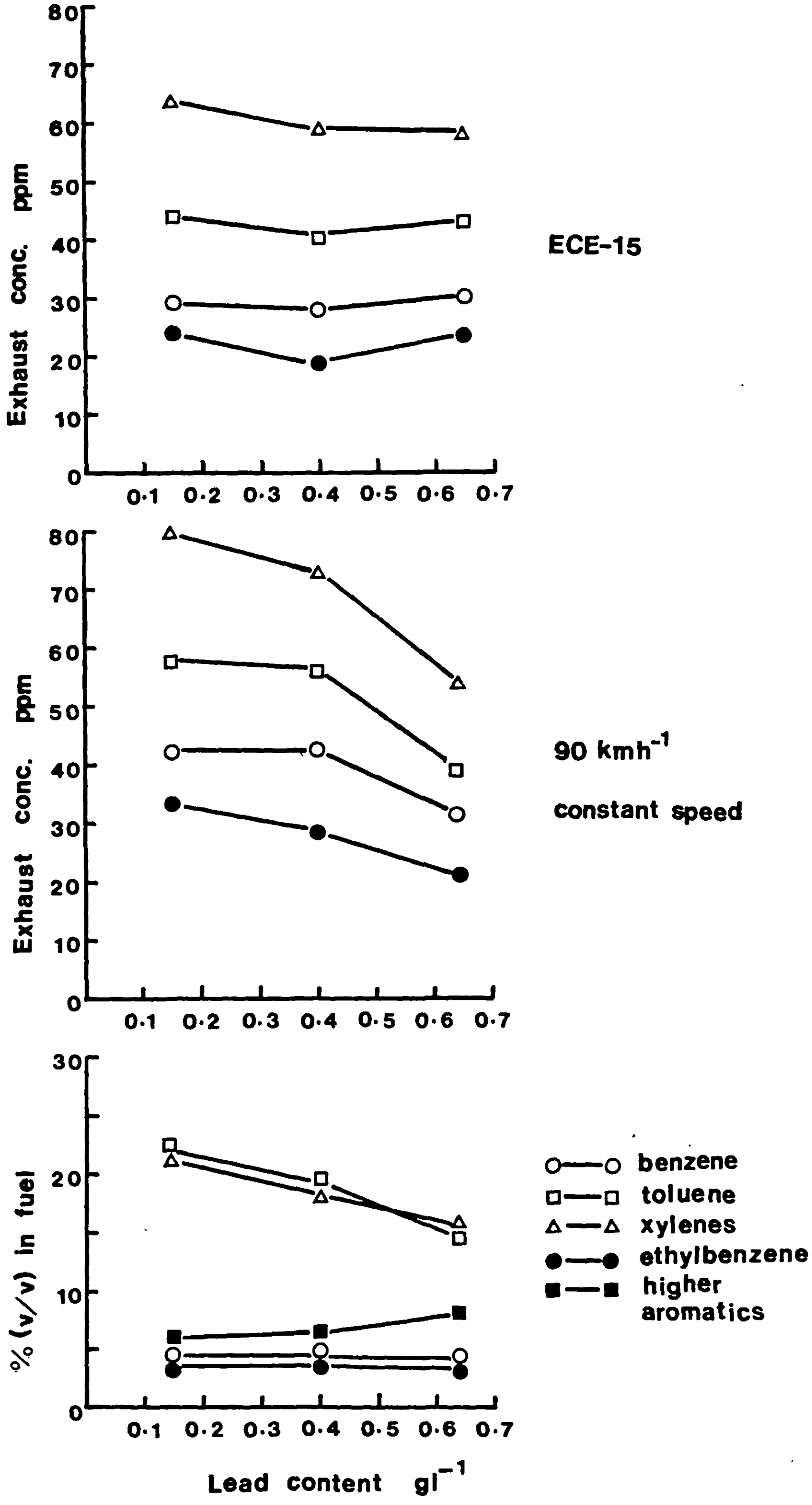


Figure 65 : Aromatic hydrocarbon exhaust concentrations during ECE-15 test cycles and 90 kmh^{-1} constant speed tests compared to varying aromatic hydrocarbon fuel composition

4.4 Investigation of the Effects of Changing Fuel Composition on Vehicle Emissions of Aromatic Hydrocarbons

The effect of changing fuel composition on emissions of aromatic hydrocarbons has been evaluated by means of a dynamometer study (see Section 3.5). Three different test fuels of similar RON and benzene content and varying lead and aromatic content were utilised during an ECE-15 test cycle (representative of urban driving patterns) and a 90 kmh^{-1} constant speed test (representative of motorway driving patterns).

The results of the study are presented in Table 38 and Figure 65. Also presented in Figure 65 are the test fuel compositions.

No significant change in aromatic hydrocarbon emissions was observed during the ECE-15 test cycle with the three different test fuels. The content of ethyl benzene and benzene were similar in each fuel but higher emissions of benzene were observed. The content of toluene and xylenes varied in a similar fashion in each fuel. Exhaust emissions of xylenes were higher than toluene, suggesting that toluene undergoes more complete combustion in the engine. The higher emissions of benzene compared to ethylbenzene indicates that benzene may also be formed by dealkylation of the other aromatics. This effect is more pronounced in the 90 kmh^{-1} constant speed test where the engine was operating at a higher load and temperature. Emissions of benzene, toluene, ethylbenzene and xylenes were all significantly increased compared to the ECE-15 test cycle. The fuel content of ethylbenzene and benzene was constant in each fuel yet both exhaust emissions of these compounds increased. The data indicates that benzene emissions are more dependent on engine operating conditions and total aromatic fuel content than benzene fuel content.

The ratios between toluene and benzene on a w/w basis are presented in Table 39.

A consistent difference between the ratios derived from the ECE-15 cycle and the 90 kmh^{-1} constant speed tests was observed which further demonstrates the role of different operating conditions on the emissions of aromatic hydrocarbons.

Table 39 : Ratios between toluene and benzene exhaust concentrations at different operating conditions and fuel composition

Lead Content	ECE-15 T/B (w/w)	90 kmh^{-1} T/B (w/w)
0.64	1.67	1.46
0.4	1.67	1.55
0.15	1.90	1.62

5. DISCUSSION

In a regulatory context, environmental impact assessment (EIA) procedures, under which AQIA can be regarded as a specific application with regard to the atmospheric environment, are not mandatory in the UK. However, they have been conducted on a number of occasions, on an *ad hoc* basis (Keddie *et al.*, 1979; Williams *et al.*, 1980; Clark, 1981). They are likely to be increasingly employed, especially where major developments are being considered due to the promulgation of the CEC Draft Directive concerning the assessment of the environmental effects of certain public and private projects (Commission of the European Community, 1980).

Measurements of data play an important role in AQIA in that they characterise present air quality. They can also provide

(i) a comparison with air quality standards or criteria;

(ii) background data for air quality simulation models;

(iii) a validation of air quality simulation models,

and (iv) the basis of statistical models for short-term forecasts of air quality.

Ambient air quality monitoring can therefore be defined as a 'systematic, planned means of determining the quality of air using whatever methods are consistent with the obtaining of data over a reporting interval and at a frequency of collection required by the monitoring objectives involved' (Bryan, 1977).

Transport-related sources have a large influence on atmospheric concentrations of CO, HC, NO_x, particulates, photochemical oxidants and lead (Brice and Derwent, 1978, Apling *et al.*, 1979; Cohn and McVoy, 1982). Of these sources, aircraft (and related activity) and motor vehicles are the most important (Cohn and McVoy, 1982) and have attracted the most attention in the scientific community and from the general public (Williams *et al.*, 1980; Yamartino *et al.*, 1981; Pearce, 1983; Rondia *et al.*, 1983).

During the evaluation of air quality at Stansted Airport measured CO concentrations (0.21-0.49 arithmetic means) were comparable to concentrations measured at Gatwick Airport (0.4-1 ppm arithmetic mean) by Williams et al. (1980). However, CO concentrations were considerably lower than those found at a central London site (2.9 ppm arithmetic mean) presented in Table 4. During the period of monitoring, the values of CO measured at all sites were below the one-hour and 8-hour US air quality standards of 35 and 9 ppm CO respectively (Table 7). There have been documented violations of the one-hour and eight-hour CO air quality standards at airports in the US (Los Angles Air Pollution Control District, 1971; Thayer et al., 1974). However, aircraft-related emissions have not been identified as the major influence. Violations have occurred near the inside terminal buildings, in areas heavily influenced by motor traffic and beside runways. Studies evaluating CO emissions from aircraft queues at the end of runways do not indicate a significant problem; concentrations measured did not exceed air quality standards with the exception of a single episode when snowploughs were operating nearby (Segal, 1980; Smith and Heinhold, 1980; Yamartino et al., 1980). Other studies, in which CO concentrations emitted during taxiing of aircraft (commercial and general) were measured, indicated that the impact on air quality was low (Segal, 1979; Yamartino et al., 1980).

Source analysis, by means of pollution roses, at Stansted Airport (Site A) demonstrated that nearby roads are the major influences on measured CO concentrations. A similar finding was determined at Gatwick Airport (Williams et al., 1980). Data from Williams AFB, a busy airforce base located 64 km from the nearest large urban area, demonstrated that maximum CO concentrations occurred at sites most heavily influenced by vehicular traffic (Daley and Naugle, 1979).

NO_x (82-96% in the form of NO) is emitted during aircraft takeoff. Assessments of potential violations of NO_2 air quality standards or guidelines are complicated by the conversion of NO to NO_2 in the atmosphere. The US standard for NO_2 is 5 pphm annual average, and although measurements were not made for a year at Stansted, it seems unlikely that this standard would have been exceeded at any of the sites where arithmetic means of approximately 1-2 pphm with 99th percentiles of 6 pphm and below were recorded.

However, at Sites B and F the WHO criterion value of 10-17 pphm (Table 7), not to be exceeded more than once a month, was exceeded during six non-consecutive hours. It was also exceeded at the central London site (Table 4) but not at any of the sites monitored at Gatwick (Williams et al., 1980). A study documenting violations of the NO_2 annual air quality standard at US airports did not determine what fraction of the concentrations were attributable to aircraft (Platt et al., 1971).

The importance of non-airport NO_x sources is demonstrated by the pollution rose data presented in Figure 13, which clearly demonstrate that nearby roads were the dominant source. A similar conclusion was formed during the Gatwick study (Williams et al., 1980). Background concentrations at Washington DCA accounted for 70% of the mean total NO_x, further demonstrating the influence of non-airport sources over takeoff emissions of NO_x which have been shown not to exceed a maximum of 5 pphm at the end of a runway (Yamartino et al., 1980). The range of NO_2 hourly measurements at US airports (2.5-5.0 pphm) indicated that a stringently applied short-term air quality standard could be violated in many cases.

The US standard for NMHC is a maximum 3 h concentration (6 am to 9 am) of 0.24 ppm not to be exceeded more than once per year. As was the case at Gatwick (Williams et al., 1980), this standard was exceeded at all sites on occasions, but the exact implications for air quality in the Stansted region are unclear as the meteorological conditions necessary for the production of a photochemical smog are rare in the UK. The standard was also exceeded in reported US and UK measurement studies (Yamartino et al., 1980). In view of the complex photochemistry involved, the problem of airport-related NMHC cannot be considered in isolation from other sources.

Particulate lead measurements over calendar quarters only took place at Site A and from the results obtained (Table 11), it would seem unlikely that the US standard and DHSS guidelines (Table 7) would have been exceeded at any of the sites. Measured concentrations were similar to those at Gatwick Airport (Williams et al., 1980) and were comparable with measured concentrations in the UK urban areas (McInnes, 1976). The particulate lead measurements at Stansted indicate the relative importance of traffic sources in comparison with aircraft as jet fuel contains only negligible amounts of lead.

An earlier study at Stansted Airport (Keddie et al., 1973) concluded that background air pollutant concentrations were as significant as those derived from local sources including the airport, nearby roads and local urban areas in determining overall air quality.

It is clear from the analysis of measurement data that concentrations were, in general, relatively low, verifying the conclusion regarding the significance of background concentrations.

The use of sites of contrasting degrees of vehicle influence, two sites influenced greatly by traffic and one rural site used as a control, permits the relationship between traffic and air quality to be further assessed. This dual-monitoring approach was suggested by Ott (1971) as the most suitable in assessing primary traffic-related pollutants (CO, NMHC and NO_x).

Measured arithmetic mean concentrations of CO at the three sites during the 1982 and 1983 surveys were 1.66 and 1.76 ppm (urban), 0.75 and 0.84 ppm (motorway) and, 0.28 and 0.48 ppm (rural). Concentrations of CO did not exceed either the one-hour or eight-hour US air quality standards (35 and 9 ppm CO respectively) at any of the sites. The highest arithmetic mean and maximum CO concentrations were found at the urban site. These concentrations are directly comparable to kerbside concentrations measured in London (Schwar and Ball, 1983).

Measured arithmetic mean concentrations of NMHC during the 1982 and 1983 surveys were also highest at the urban site (0.24 and 0.36 ppm respectively). These compare to arithmetic mean concentrations of 0.21 and 0.25 ppm at the motorway site and 0.08 and 0.11 ppm at the rural site. The US air quality standard for control of photochemical oxidants was frequently exceeded at the urban and motorway sites as was the case at Stansted. Recent work by Derwent and Hov (1980) demonstrated that in the UK and Europe, control of photochemical oxidants would best be achieved by control of NMHC emissions.

Measured NO_x concentrations were highest at the motorway site (12.1 pphm arithmetic mean) compared to 9.8 pphm at the urban and 2.7 pphm at the rural sites. This reflects the effect of high engine speed and load on NO_x emissions. NO_x concentrations at the urban site are also comparable to those measured in London (Schwar and Ball, 1983). Concentrations of NO_x at the motorway site were also comparable with those measured at similar sites (Hickman and Lunn, 1981).

Although measurements of NO_2 did not take place over a year, it is unlikely that concentrations at any of the sites would exceed the US annual air quality standard of 5 pphm. However, the 95th percentile (corresponding to ca. 7 h over the survey) did exceed the WHO short-term NO_2 standard (10-17 pphm hourly mean).

Measurements of O_3 were subject to a number of difficulties as the siting criteria for primary traffic pollutants is not suitable for the measurement of O_3. Ozone has important sinks at ground level such as surfaces and atmospheric NO. Due to the time delay in formation in the atmosphere, maximum O_3 concentrations would generally occur at some distance downwind of the urban and motorway study areas. The most elevated O_3 concentrations were measured at the rural site (144 ppb maximum hourly concentration which did exceed the US air quality standard of 120 ppb). Low concentrations of O_3 were measured at the urban and motorway sites due to the ground and atmospheric sinks present. In order to assess better photochemical pollutants, monitors should be placed along the direction of the prevailing summertime winds away from significant NO sources.

Transport-related sources of SO_2 only contribute approximately 2.5% of national SO_2 emissions (Table 2). Measurements of SO_2 at the three sites were comparable with nearby National Survey sites and did not exceed air quality standards or guidelines.

Interpretation of the pollution roses for the urban site (for all the pollutants considered) is generally difficult for the following reasons. Wind speeds recorded at this site were low (particularly during the 1982 survey), frequently registering below 1 ms^{-1}. Under such 'calm' conditions, it is difficult to specify wind direction. The direction of the wind across the street near ground level is difficult to specify from measurements available at 10 m, in streets surrounded by buildings. A typical example is the 'helical' or 'leeward-windward' circulation which has been observed in urban streets, whereby the direction of the wind across the street at ground level, is opposite to the roof-level wind direction (Sobottka, 1980; Chock, 1982).

However, some general conclusions can be drawn from the pollution rose data at this site. The primary arithmetic mean of the traffic pollutants, CO, NMHC and NO, were generally highest for wind sectors other than those parallel, or nearly parallel, to Exhibition Road. This is in keeping with observations that the dispersion of pollutants in streets is facilitated when the wind direction is parallel to the road (National Society for Clean Air, 1980).

The NO_2 pollution rose did not reflect the primary traffic pollution roses discussed previously, in that it showed no strong directional dependence. An interesting feature of the O_3 pollution rose is that maximum arithmetic mean concentrations occurred in directions away from the strong NO source (i.e. the road) demonstrating the reaction between O_3 and NO to form NO_2. Pollution roses of SO_2 and CH_4 concentrations reflected their ubiquitous nature in the atmosphere.

The relationship between primary traffic-related pollutants was also demonstrated by pollution rose data at the motorway site, particularly by CO and NO concentrations.

However, the NMHC pollution rose derived from 1983 data was atypical in that it demonstrated a strong directional dependence away from the motorway suggesting the presence of a secondary source of NMHC. During the monitoring period a small mobile fuel tank was present near to the mobile laboratory and it is conceivable that this was responsible for the directional bias in NMHC concentrations.

In general, the highest arithmetic means occurred in sectors parallel and perpendicular to the motorway. This is in slight contrast with observations that on highways, vehicle-related pollutant concentrations decrease more rapidly with distance in parallel, than in perpendicular wind directions (Sistla et al., 1979). However it is possible that vehicular-induced atmospheric turbulence could account for elevated concentrations.

It is evident from Figure 36 that minimum O_3 concentrations occur in directions in which NO is the most elevated. It is suggested that although the measurement of O_3 is subject to difficulties, it does provide information on the oxidation of NO to NO_2.

Pollution rose data at the rural site demonstrated no strong directional bias which indicates that it was suitable as a control site for the measurement of traffic-related pollutants. Temporal analysis of pollutant concentrations by means of diurnal averages demonstrated the importance of two controlling influences: source strength and meteorological factors. As the source strength of traffic-related pollutants is dependent on vehicle numbers (and operating mode), it is not surprising that NMHC, CO and NO_x concentrations reflected diurnal variations in traffic numbers. Meteorological variables measured (wind speed and temperature) provided a general indication of atmospheric turbulence. The effect of turbulence on measured concentrations was best demonstrated by pollutants of approximately constant source strength such as CH_4 and SO_2 (Figures 23 and 26).

The analysis of O_3 data was far more complex than for the other pollutants, particularly from the 1982 data sets. Ozone concentrations in urban areas would generally be expected to demonstrate an increase throughout the day, reaching a maximum around midday or early afternoon, when temperature and sunlight are at their highest, and to decrease thereafter, remaining at a minimum overnight (Steinberger and Ganor, 1980). The overnight minimum in urban areas occurs as a result of the effect of continuing emissions of NO and through interaction, particularly under nocturnal temperature inversions (Anderson, 1979).

However, the results from the 1982 and 1983 monitoring surveys at the urban site showed some characteristic deviations from the expected patterns. A consistent peak at 0500 hours was observed. An explanation of this occurrence is the persistence of high O_3 concentrations above the nocturnal inversion and, upon break-up of the inversion in the morning, rapid mixing of the air mass downwards (Coffey et al., 1978; Harrison and Holman, 1979). Peak O_3 concentrations during the 1983 survey occurred between 0300 and 0400 hours. This can be explained by the absence of NO sources at this time. The maximum O_3 concentrations during the 1982 survey at the motorway site are also consistent with this explanation.

A somewhat different pattern would be expected in rural areas, downwind of urban areas. Formation of O_3 occurs during daylight and if the plume passes through rural areas, there will be no fresh NO emissions to act as an O_3 sink. Ozone concentrations peak during the afternoon in the urban plume, arising from morning rush hour precursor emissions. The diurnal variation in O_3 concentrations at the rural site (1982 and 1983) and the motorway site in 1983 are consistent with this behaviour described above.

The weekday-weekend differences in diurnal variation were generally not significant although weekday maxima concentrations tended to be more defined and occurred at different times.

The diurnal variation in the NO_2/NO ratio provided information on the location of NO_x sources. The minimum ratio at the urban site and motorway sites occurred at peak traffic times in the morning which also coincided with low ozone concentrations. The maximum value for the ratio at the urban site occurred between 0000 and 0600 hours indicating that the air mass was aged. Similar high ratios were found at the rural site throughout the day which indicates that no strong local emissions of NO_x were present. The ratio at the motorway site was at a maximum at the time of maximum O_3 concentrations. This further demonstrates the importance of O_3 in determining ambient NO_2 concentrations in the presence of strong NO sources.

Concentrations of airborne particulate lead did not exceed either the US air quality standard (1500 ng m^{-3} 3 month mean) or the DHSS Working Party guideline (2000 ng m^{-3} annual mean). Concentrations at the urban site (443 and 192 ng m^{-3}) were comparable with other roadside lead concentrations in London (Schwar and Ball, 1983).

High concentrations (monthly mean of 1141 ng m^{-3}) were found at the motorway site during the 1982 monitoring period compared to the later survey (monthly mean of 171 ng m^{-3}). Meteorological conditions were different over the two periods with strong winds blowing consistently perpendicular from the motorway towards the mobile laboratory during the 1982 survey. However, both sets of data are consistent with previously published work on motorway airborne lead concentrations (Little and Wiffen, 1978).

Concentrations at the rural site were low in comparison to the other two sites - illustrating the lack of vehicle-related emissions at this site.

The general usefulness of applying a statistical distribution to air quality data has been summarised by Ott and Mage (1976).

(i) they provide a convenient means for interpolation between observed values, and extrapolation beyond these;

(ii) they give a simple and compact representation of the entire distribution;

(iii) they allow inferences to be made about the nature of the underlying physical processes,

and (iv) they form a basis for performing further statistical analyses.

Using the least squares criterion, the results of fitting the N, LN2 and LN3C distribution to the air quality data sets indicated that the latter distribution provided the best or at least equivalent fit of the data. Although applications of the LN3C distributions have been relatively few, this finding is generally in accord with other work (Holland and Fitz-Simons, 1982). Ott and Mage (1976) concluded, by treating the diffusion equation as a stochastic differential equation, that a physical rationale exists which provides support for the LN3C distribution.

Common to most distributions applied to air quality data is the implicit assumption that air pollutant concentrations are independently and identically distributed (Gumbel, 1958; Curran and Hunt, 1975; Mage and Ott, 1978).

However, air quality data is both highly serially correlated, and subject to systematic seasonal, weekly and diurnal periodicities (and are therefore said to be generated by a non-stationary stochastic process). Neustadter and Sidik (1974) and Darby and Gregory (1976) have found that for long averaging times (e.g. 24 h) or for data from intermittent sampling schemes, the effect of autocorrelation was not substantial. The effect of autocorrelation on short averaging times was found to be an underestimation of maximum hourly annual concentrations of air pollutants for any averaging time (Hirtzel and Quon, 1979). However, this is in contrast with the work of Horowitz and Barakat (1979) which demonstrated that if autocorrelation is not taken into account, the expected maximum hourly mean can be substantially overestimated.

Both these effects were found by comparing the observed and predicted (LN3C) 99th percentile values (Table 25 and 26). The prediction of 50th percentiles was far more successful at the urban site. However, agreements between observed and expected values were not as successful at the other sites, particularly with those pollutants involved in photochemical reactions. However, Table 27 demonstrates that the number of samples required to obtain the sample geometric mean (with the assumption of lognormality), to within ±10% with a 95% confidence level, was sufficient except for O_3 at the rural site in 1982 and NO_2 at the motorway site in 1983.

Deviations from the assumed lognormality have also been observed (albeit from the LN2 distribution) for a number of cases; inhomogeneity of source distribution around the monitoring site (Benarie, 1980), proximity of the site to strong isolated sources, especially in rural surroundings (Larsen, 1977). These situations are comparable to those at the motorway and rural locations.

In deriving the mathematical relationship between concentrations and meterological variables, the techniques of multiple regression analysis were applied to logarithmically transformed concentration data. This demonstrates that the single most important parameter evaluated was that of lagged concentrations (Tables 18 and 19). This parameter accounts for the persistence (or autocorrelation) in observed pollutant concentrations. If not included, significant reductions in the total explained variance were found (Table 18). Similar effects have been observed by Keddie et al. (1979). As discussed previously, the autocorrelation of pollutant concentrations affects the prediction of high percentile concentrations by the LN3C distribution.

The multiple regression analysis provided information on the effects of wind speed and temperature on measured concentrations. Temperature had a number of effects on the various pollutants. A positive correlation between NMHC and temperature was found at the urban site, illustrating the importance of evaporative emissions. Estimates of the percentage of total NMHC arising from vehicle evaporative emissions vary between 20 and 30% (Black et al., 1980; Nelson et al., 1981). A significant negative correlation was found at the motorway site between these parameters, which reflects the effect of increased atmospheric turbulence related to the rise in ambient temperatures. However, increasing temperature also reflects increasing daytime insolation. This resulted in a positive correlation between temperature and O_3 (except at the urban site). Ozone in the presence of the strong NO source at the motorway site increased the production of NO_2, hence the positive correlation between NO_2 and temperature at this site.

Wind speed exhibited a negative correlation with most of the pollutants measured because of increased atmospheric dispersion. Ozone generally correlated positively with wind speed which suggests that consideration of only local meteorological measurements may be insufficient in order to account for the mechanisms that are responsible for O_3 generation and transport. This is in agreement with the work of Evans et al. (1983).

Multiple regression equations of this type are sometimes considered as statistical models (as are frequency distributions) and are applied in short-term forecasting schemes. However, as with all statistical models, these need to be continuously updated, and cannot be extrapolated to other locations (Keddie et al., 1976; Benarie, 1980).

As discussed previously, the computer modelling work of Derwent and Hov (1980) indicated that control of photochemical oxidants would be best achieved by control of NMHC emissions. However, the reactivity of different species of NMHC compounds varies significantly. Aromatic hydrocarbons can undergo photochemical decomposition (Hov et al., 1978), reactivity, increasing in the order benzene < toluene < xylene < trimethylbenzene (Altshuller and Bufalini, 1971).

As a result of reducing the lead content in petrol to 0.15 gl^{-1} and increased use of catalytic reformating refinery processes, increasing aromatic hydrocarbon content in fuel is predicted to occur in order to maintain octane numbers (Hall et al., 1983). Subsequent increases in ambient concentrations of aromatic hydrocarbons (Oelert et al. 1974) and PAH (Pederson et al., 1980) may also occur.

The use of porous polymer adsorbants such as Chromosorb 102 has been previously reported for the measurement of EDB (Leinster et al., 1978). The use of Tenax GC sampling tubes has also been reported (Tsani-Bazaca et al., 1981) for the measurement of aromatic and halogenated hydrocarbons in ambient air. However the method was not fully evaluated, particularly with respect to sampling efficiency. Tenax GC is preferred for the packing of sampling tubes because of its high thermal stability (van Wijk, 1970). A number of studies have been reported demonstrating its use (Brown and Purnell, 1979; Pellizzari, 1982; Hampton et al., 1983).

Chromatographic theory was applied in assessing various sampling parameters. A comparison between frontal and elution analysis (Figure 61) demonstrated that elution analysis techniques are suitable for the determination of retention volumes of the compounds of interest. This is in accord with the findings of Gallent et al. (1978).

The regression constants presented in Table 31 can be used to assess the effect of ambient temperature on retention volumes (during sampling) using equation 22. For instance, the retention volume for benzene at 25°C is reduced to 4.2 l from 6.3 l at 20°C.

The influence of concentration on retention volumes of the Tenax GC sampling tubes was assessed by elution and frontal analysis techniques. It is clear from the elution analysis results (Figure 62) that concentration had a limited effect on retention volumes. Similar findings for acetone on Tenax GC sampling tubes have been presented by

Brown and Purnell (1979) using elution analysis techniques. However, the authors also demonstrated that the continuous introduction of 100 ppm of acetone vapour did have a significant effect on retention volume because of a more rapid overload of the Tenax GC column with a continuous atmosphere. Direct measurements of sorption equilibria at varying gas-phase concentrations to determine distribution constants of acetone on Tenax GC (Vejrosta et al., 1981a) are also in accord with the findings of Brown and Purnell (1979).

The frontal analysis data (presented in Figure 63) for benzene, toluene and o-xylene, was in contrast with that determined by elution analysis (Figure 62), demonstrating that the arbitrary limit of linearity of adsorption of these compounds was approximately 1 ppm. This difference between frontal and elution analysis is in direct agreement with further work by Vejrosta et al. (1981b) which concluded that the retention volume was independent of benzene concentrations only up to a concentration of ca. 1 ppm. The determination of retention volumes of high concentration adsorbates by frontal analysis represents the more realistic sampling condition and therefore concentrations above 1 ppm should be avoided when using Tenax GC sampling tubes. However, ambient concentrations of this magnitude are extremely unlikely to occur and, in this range, a concentration step would not be required. At expected ambient concentrations, no discernable effect on retention volumes was observed.

Previous studies (Janák et al., 1974; Piecewicz et al., 1979) have investigated the influence of water vapour on retention volumes of various compounds using Tenax GC sampling tubes and have concluded that the effect on retention volumes under conditions of high ambient humidity is dependent upon the polarity of the adsorbate. The work of Piecewicz et al. (1979) indicates that ethyl bromide and 2-butanone, both Kiselev Group B compounds - slightly polar (Kiselev and Yashin, 1969) which have a similar polarity to aromatic and halogenated hydrocarbons, exhibit decreases in retention volumes of 22% and 31% respectively, at high ambient humidity. This compares well with previous work (Janák et al., 1974) which found a 21% decrease in retention volume for benzene (Group B polarity). The decrease in retention volume of benzene (presented in Table 32) is identical with the findings of Janák et al. (1974). The smaller decreases in retention volumes for EDC and toluene (11 and 18% respectively) are comparable to the values reported by Piecewicz et al. (1979). This study also reported an additional 25% decrease in retention volumes in the presence of 10% (v/v) carbon dioxide and high humidity, conditions typical of gaseous effluent from combustion processes. It can therefore be seen that Tenax GC sampling tubes are not suitable for the analysis of vehicle exhaust aromatic emissions due to the effects of concentration and high humidity on retention volumes.

For the collection method to be quantitative, the volume of air sampled containing a particular compound must not exceed a predetermined safe sampling volume. The safe sampling volume is dependent not only on the retention volume, but also on the number of theoretical plates. An explicit expression for the adsorbate concentration at the outlet of the sampling tube as a function of the sampled volume, the adsorbate retention volume and the number of theoretical plates has been derived by Senum (1981). Although the efficiency of an adsorbate sampler increases with increasing adsorbent theoretical plates, a compromise exists between theoretical plate numbers and the time taken to sample sufficient air for analysis. This expression has been used to calculate the safe sampling volumes (Table 33) over a range of flow-rates for benzene and EDC (the limiting compounds of interest). This method is exact for all plate numbers, as it contains no approximations, unlike expressions derived in previous studies (Raymond and Guichon, 1975; Butler and Burke, 1976; Brown and Purnell, 1979), which can be inaccurate when the number of theoretical plates is decreased below 30 (Senum, 1981). The results presented in Table 33 demonstrate the versatility of approach that can be achieved by adopting different flow-rates according to the sampling time and efficiency that is required.

Moreover, the method was applicable for analysis by GC/MS. High desorption efficiencies of sampling tubes at the flow-rates required by capillary columns were achieved by an increase in desorption time with subsequent cryogenic trapping of desorbed material onto a loop of the column. However, significant production of artifacts from the Tenax GC was observed (e.g. fluorotrimethylsilane) at longer desorption times which interfered with the MS analysis. This effect has been observed by other workers (Hampton et al., 1983). The US EPA is at present engaged in research on new adsorbents (e.g. Thermid 600) which overcome the problem of artifact production but maintain high retention volumes and temperature stability (Jungers et al., 1983). The GC/MS sampling tube method for the analysis of aromatic hydrocarbons has the facility of providing information on a large range of compounds. However the method is time-consuming and requires expensive analytical instrumentation in comparison to the packed column GC/FID and GC/EC methods.

Recent developments of the PID have led to the capability of directly measuring ambient concentrations of aromatic hydrocarbons without preconcentration of sample air. Previous work by Driscoll (1977) demonstrated that PID sensitivity was 30-fold greater than FID for aromatic hydrocarbons. In addition a number of authors have demonstrated that PID/GC is a viable technique in the measurement of a wide range of organic compounds such as formaldehyde, EDB and vinyl chloride in air (Driscoll et al., 1978; Dumas, 1982; Dumas and Bond, 1982).

The results of an evaluation of a portable PID/GC (see Section 3.2.3) demonstrate that sub-ppb detection limits for benzene and toluene and 1 ppb for ethylbenzene, o-, m- and p-xylene, by direct injection, were attainable in ambient air. However, a subsequent field trial demonstrated that ambient air concentrations of aromatic hydrocarbons (other than benzene and toluene) were generally too low to measure consistently. Similar results have been presented by Hester and Meyer (1979) for a differently designed detector.

In comparison with measurements obtained by the sampling tube method, direct measurement by PID/GC agreed to within 20% for benzene and toluene. However the two methods provide two distinct types of information on concentrations and are not amenable to direct comparison. Instantaneous concentrations are measured by the PID/GC using, essentially, a 'grab' sampling method whereas the adsorbent tube method provides information on the average concentration over the sampling period (Figure 70).

The PID/GC instrument was capable of measuring from sub-ppb to 100 ppm concentrations of aromatic hydrocarbons. Due to the specificity of the detector, the instrument is suitable for the measurement of vehicle exhaust emissions of aromatic hydrocarbons by direct injection without interference from water vapour.

Relatively few baseline measurements of aromatic and halogenated hydrocarbons have been performed in the UK. The application of the Tenax GC sampling tube method makes evaluation of these concentrations feasible. At the three contrasting sites (urban, motorway and rural) highest mean and maxima concentrations of aromatic and halogenated hydrocarbons were exhibited at the urban site. The close correlation between diurnal traffic flow at the urban and motorway sites in 1982 clearly demonstrates the influence of vehicle activity on ambient concentrations. However, less successful correlations were achieved at the motorway site in 1983, possibly due to the different meteorological conditions experienced and the presence of an additional source of hydrocarbons.

Hydrocarbon emissions from motor vehicles have been shown to be dependent on driving mode and are most elevated during deceleration and acceleration, a driving mode typical of urban roads. In addition evaporative losses from vehicles can also contribute between 20 and 30% of the total hydrocarbon vehicle emissions (Black et al., 1980; Nelson et al., 1981). As discussed previously, temperature correlates positively with NMHC concentrations at this site. High concentrations also occur because of the limited atmospheric dispersal conditions. The diurnal pattern of aromatic hydrocarbons is similar to that observed in Los Angeles (Altshuller et al., 1971).

The aromatic hydrocarbon data compare well with data collated in Table 40. Particularly interesting is the wide range of sampling and gas chromatographic analytical techniques employed in these studies over different averaging times. Common features are the use of glass bottles and Mylar or Tedlar bags to obtain 'grab' samples of ambient air with subsequent preconcentration utilising cryogenic/adsorbent techniques (Pilar and Graydon, 1973; Louw et al., 1977; Nelson and Quigley, 1982) and also the use of preconcentration on charcoal with carbon disulphide extraction (Grob and Grob, 1971; Burghardt and Jeltes, 1975; Louw et al., 1977).

EDC concentrations were highest at the urban site ($\bar{x}$ = 0.26 ppb and $\bar{x}$ = 0.3 ppb) in the 1982 and 1983 surveys which is similar to the mean concentration determined (0.22 ppb) at the same site in 1979 (Tsani-Bazaca et al., 1981) and to concentrations determined in the vicinity of an industrial complex ($\bar{x}$ = 0.34 ppb) in Iberville, LA (Pellizari, 1982) and also at Los Angles (0.52 ppb) in the US (Singh et al., 1981). EDB concentrations ($\bar{x}$ = 0.03 ppb) measured at the urban site in both 1982 and 1983 are in the same range (0.01-0.04 ppb) determined by other workers (Johns, 1976; Leinster et al., 1978; Singh et al., 1981; Tsani-Bazaca et al., 1981) at similar locations.

At the motorway, vehicle numbers passing the site were high (<3500 vehicles h^{-1}). However, the low emission rates of hydrocarbons from vehicles travelling at constant high speeds and suitable conditions for adequate dispersal of pollutants resulted in low concentrations of measured aromatic hydrocarbons and EDC. The concentrations of EDB at the motorway ($\bar{x}$ = 0.05 ppb and $\bar{x}$ = 0.05 ppb) in 1982 and 1983 respectively, are higher than those at urban and rural sites. The explanation of these elevated concentrations is unclear at present.

The particulate and organic lead concentrations measured at the three locations (Table 37) compare well with data from other workers at similar locations (Birch et al., 1980; De Jonghe et al., 1981; Gibson and Farmer, 1981). An interesting feature of the results is that the ratio of organic lead/total lead, expressed as a percentage varied between 1.6% and 7% at the motorway site and 1.7% and 3% at the rural site whereas the ratio at the urban site was more consistent, varying between 6.5% and 8%. This supports evidence on the importance of evaporative emissions of organic lead at the urban site (Harrison and Perry, 1977).

The toluene/benzene ratio has been suggested as an indication of the extent to which motor traffic contributes to air pollution (Lonneman et al., 1968). The average ratio derived from other workers, excluding this work, is 2.55 ± 0.83 on a w/w basis. This ratio derived from the urban site was 1.81 during the 1982 survey and 1.59 during the latter survey. These compare favourably to the ratio of 1.8 derived in the US in vehicle exhausts (Lonneman et al., 1968) and also with the ratio of 1.67 derived from the 0.4 gl^{-1} test fuel/ECE-15 dynamometer work (Table 39). The lower ratio in 1983 reflects the higher ambient temperatures experienced during this survey (benzene has a lower vapour pressure than toluene).

Criticism of the applicability of the toluene/benzene ratio has been expressed because of the variation in the concentrations of these compounds in petrol (Ioffe et al., 1979). It is therefore suggested that the toluene/benzene ratio should be used in conjunction with the ratio present in petrol. Samples of premium and regular petrol recently surveyed in the southeast of the UK gave an average ratio of 2.79 ± 0.4 in 1982 and 2.99 ± 0.7 in 1983 (Associated Octel, personal communication, 1983).

Low toluene/benzene ratios of 0.87 and 1.00 were determined at the motorway site which suggests that where vehicles are operating at high speeds and load, dealkylation of higher aromatics occurred, resulting in higher benzene exhaust emissions. Significantly lower ratios were also found in the 90 kmh^{-1} constant speed test compared to the ECE-15 test cycle in the dynamometer studies.

The ratio of 1.01 at the rural site and the low-level of aromatic hydrocarbon concentrations indicates that the air mass sampled was aged, as toluene is subject to more rapid photochemical decay than benzene (Hov et al., 1978).

The dynamometer studies utilising fuels with lead contents varying between 0.15 gl^{-1} and 0.64 gl^{-1} and a four-cylinder 1.6 l engine vehicle, demonstrate that dealkylation of toluene, xylenes and higher aromatics can occur in conditions of high speed and load (90 kmh^{-1} constant speed test). These results are similar to the findings of Oelert et al. (1974). Black et al. (1980) and Morris and Dishart (1971) have suggested that this process is the critical factor in defining vehicular benzene emissions.

Considerable debate over the relationship between lead in petrol and health effects remain (Parkinson, 1983; Pearce, 1983). However the government has regulated to decrease the lead content in petrol from 0.4 gl^{-1} to 0.15 gl^{-1} by the end of 1985 (Government of Great Britain, 1980) and is committed to move towards lead-free petrol by 1990 (Government of Great Britain, 1983). This move can only be completed in conjunction with other European countries in abolishing the lower limit in petrol lead content embodied in EC Directive 78/611/EEC (Council of the European Communities, 1978). The UK initiatve within

Table 40 : Comparison of aromatic hydrocarbon concentrations measured at different locations

Location	Year	Concentrations in pptm						References
		Benzene	Toluene	Ethylbenzene	*m*-xylene	*p*-xylene	*o*-xylene	
Los Angeles	1968	15.0	27.0	6.0	23		8	Lonnemann *et al.* (1968)
Zurich	1971	54.0	39.0	8.7	9.0	21	9.3	Grob & Grob (1971)
Toronto	1971	13.0	30.0	-	-	-	-	Pilar & Graydon (1977)
The Hague	1975	8.9	17.9	3.1	12.4		3.1	Burghardt & Jeltes (1975)
Berlin	1975 (Nov)	15.1	26.1	-	18.1		-	Seifert & Ullrich (1978)
	1976 (Jul)	15.1	27.4	-	13.6		-	Seifert & Ullrich (1978)
	1976 (Nov)	18.1	38.4	-	22.6		-	Seifert & Ullrich (1978)
Johannesburg	1977	3.4	10.3	1.9	4.5		1.6	Louw *et al.* (1977)
Los Angeles	1979	6.0	11.7	2.25	4.61		1.93	Singh *et al.* (1982)
Sydney	1980	2.6	8.9	1.3	1.3		1.5	Nelson & Quigley (1982)
London	1982	8.8	13.5	0.88	2.8		1.2	(this work)
	1983	9.7	15.5	0.8	2.3		0.8	(this work)

the EEC already has the strong support of the Federal Republic of Germany, the Netherlands and Denmark, and the Commission has been requested by the Council of EC Environment Ministers to examine ways of reducing lead in petrol, including eliminating it altogether (National Society for Clean Air, 1983).

Due to changing refinery pratice (increased use of catalytic reformate) and the need to maintain octane numbers, it has been predicted that the content of aromatic hydrocarbons in petrol will increase by approximately 20% (Hall et al., 1983) in countries reducing the lead content to 0.15 gl^{-1} in petrol. This has several important implications on the emission of aromatics such as benzene (a known carcinogen) and PAH. The relationship between aromatics in petrol and exhaust emissions of PAH is generally accepted (Candeli et al., 1983; Jacob, 1983; Pederson et al., 1981) although this has been a point of some contention (Nunnerman et al., 1983). Many PAH compounds have proven carcinogenic or mutagenic properties (Haroz, 1983). It is probable that increasing aromaticity in fuel will lead to increases in PAH concentration in ambient air.

Since it is economically infeasible to maintain octane numbers in lead-free petrol by the addition of aromatics alone the use of volume oxygenate additives is expected to increase (Tims, 1983). These oxygenates include methanol, TBE (teriary butyl ether) and MTBE (methyl tertiary butyl ether).

Improvements in engine design (such as the lean/burn engine, Nissan S-Z high swirl/dual spark plugs combustion chamber, clutched-in Roots turbocharger system and the 4 valve inlet/exhaust combustion chamber) will lead to a higher fuel economy in new engines without the need to maintain high octane numbers in petrol (French, 1983). These engine changes will also lead to a reduction in emissions of PAH by reducing cylinder wall 'quench' volumes and operating predominantly with lean air/fuel ratios (Lepperhof, 1983). The lean air/fuel ratios will also decrease hydrocarbon emissions due to increased combustion efficiency. However these improvements would only apply to new cars and it is therefore predicted that increased oxygenate and aromatic content will be needed to fuel existing models with a consequent increase in emissions of aromatic and PAH compounds.

6. CONCLUSIONS

6.1 The use of air quality impact assessment, as a decision-making tool, is likely to increase. Data obtained by measurement studies modelling are complementary and can be combined in a rational approach to perform impact assessments.

6.2 Measured concentrations of transport-related air pollutants (CO, NMHC, NO_x and particulate lead) at Stansted Airport were generally low in comparison to reported concentrations at urban sites and were comparable with other air quality measurements at UK airports.

6.3 Concentrations of CO, NMHC, NO_x and O_3 at three sites, representative of heavily trafficked urban, motorway locations and a rural site chosen as a control, were comparable with previously reported data from similar sites.

6.4 The influence of motor vehicles on air quality (particularly NMHC and NO_2 concentrations) was most severe at the urban site due to limited dispersion of pollutants, the high traffic density and the mode of vehicle operation. High concentrations of other transport-related pollutants can also occur at the motorway site (NO and particulate lead) and the rural site (O_3).

6.5 The location of monitoring sites was suitable for the assessment of primary transport-related air pollutants. The urban and motorway sites were not suitable for the measurement of O_3 concentrations because of the presence of strong NO sources.

6.6 Measured data generally did not exceed relevant air quality standards or guidelines except in the case of NMHC and NO_2 concentrations at the Stansted (Sites A and G), and the urban and motorway monitoring locations.

6.7 Violations of the US air quality standard for NMHC, promulgated for the control of photochemical oxidants are frequent at these sites. However, meteorological conditions in the UK are rarely conducive for the production of photochemical smogs. Therefore these concentrations are not seen as particularly significant in this context.

6.8 The WHO short-term guideline for NO_2 was also exceeded at Sites B and F at Stansted and the urban and motorway sites. Comparable data suggest that this guideline is exceeded at many sites influenced by vehicular sources.

6.9 Spatial and temporal distributions of measured air pollutants and meteorological variables provide useful information on location and importance of sources and controlling mechanisms such as dispersion and changing source strengths.

6.10 Spatial analysis of the air quality data at Stansted Airport indicates that vehicle traffic has a large influence on the measured concentrations at this site.

6.11 Mathematical relationships between meteorological variables and measured concentrations, derived from multiple regression analysis, demonstrated the role of high ambient temperature in increasing NMHC evaporative emissions, particularly at the urban site, and defining atmospheric turbulence, particularly at the motorway site. The influence of high wind speed on aiding atmospheric turbulence with regard to med concentrations was also evaluated.

6.12 Persistence (or autocorrelation) in meteorological conditions was found to be the dominant parameter in defining measured air pollutant concentrations.

6.13 Using the least squares criterion, the LN3C distribution provided the best, or at least equivalent, fit of the air quality data sets; obtained from the three contrasting sites, compared to the N and LN2 distributions.

6.14 Comparisons of observed and predicted 50th and 99th percentile concentrations were most successful at the urban site.

6.15 The LN3C distribution model is suitable for the prediction of high percentile values of NMHC, CO and SO_2 at the urban site but, like all statistical models, it needs to be continuously updated.

6.16 Considerable errors in the prediction of 99th percentile values by the LN3C distributions were found for the motorway and rural air quality data sets particularly for those pollutants involved in photochemical reactions. Improvements in prediction have been reported when the autocorrelation of air quality data is taken into account.

6.17 A Tenax GC sampling tube method has been found to be suitable for the measurement of aromatic and halogenated hydrocarbons in ambient air. However the method is not suitable for the measurement of aromatic hydrocarbons in vehicle exhaust because of the effect of high concentrations and humidity on retention volumes (and therefore on safe sampling volumes). The method can be adapted for analysis by GC/MS which can provide information on a wide range of aromatic compounds.

6.18 A portable PID/GC was found to be suitable for the measurement of benzene and toluene in ambient air by direct injection of sample air (but not ethylbenzene or xylenes) and also for the analysis of benzene, toluene, ethylbenzene and xylenes in vehicle exhaust.

6.19 Baseline data on aromatic and halogenated hydrocarbons demonstrated that highest ambient air concentrations are generally found in the urban environment where the degree of vehicle influence is the greatest.

6.20 At the urban site, the importance of vehicle evaporative emissions of aromatic hydrocarbons and organic lead was demonstrated.

6.21 The toluene/benzene (w/w) ratio is suitable for the assessment of vehicle influence on air quality when the range of variation of these compounds in petrol is low.

6.22 Baseline data on the toluene/benzene ratio at the motorway site and the dynamometer work demonstrated the effect of high engine speed on increasing aromatic hydrocarbons emissions by a dealkylation process of the higher aromatic hydrocarbons present in petrol.

6.23 Possible increases in the aromatic content in petrol (as a result of decreasing lead content in fuel) will result in increased emissions of these compounds into ambient air. Increases in vehicle exhaust emissions of PAH may also occur.

6.24 In the long term, improvements in high efficiency engine design with lower octane number requirements and subsequent lower aromatic content may result in decreased emissions of aromatic hydrocarbons and PAH compounds.

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APPENDIX A

Worked Example of the Static Dilution Procedure

Atmospheric pressure = 755.2 mm Hg
Atmospheric temperature = 21.5°C ≡ 294.5 K
$1/K \times 10^{-3}$ = 3.395

From a graph of vapour pressure vs reciprocal of absolute temperature prepared from data presented in the CRC Handbook of Chemistry and Physics, the vapour pressure of benzene at 21.5°C = 77 mm Hg.

From General Gas Law $v_1 = \frac{p_2 v_2}{p_1}$

For 1 ml headspace above benzene liquid

$$v_1 = \frac{77}{755.2} = 0.102 \text{ mls benzene}$$

0.102 mls is injected into static dilution flask of 11,767 mls volume.

∴ benzene concentration in flask is 8.67 ppm.

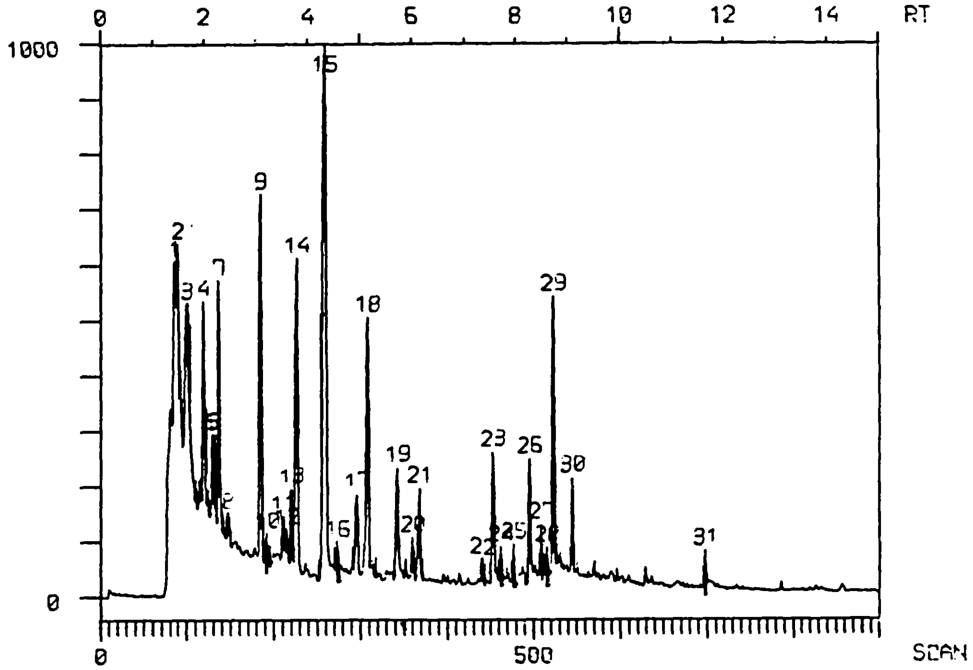
Subsequent dilution can be achieved by taking samples from this flask and injecting into additional static dilution flasks.

Reference

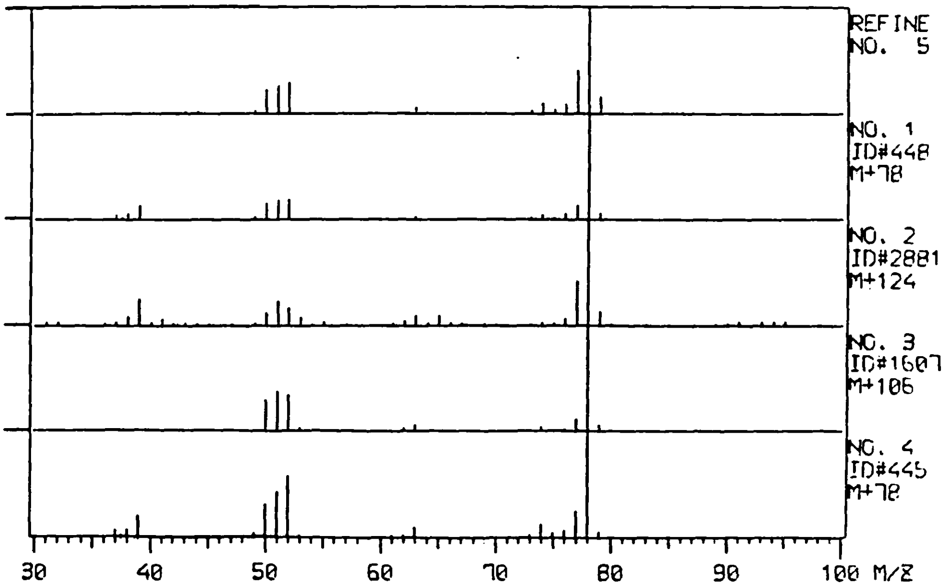
Weast and Astle (eds.). Handbook of Chemistry and Physics, 59th edition, CRC Press, West Palm Beach, Florida, U.S.A.

APPENDIX B Example of the computer mass spectral library search facility and a 0.5 h Tenax GC sample

```
SPECTRUM REDUCTION TABLE
SAMPLE : SAMPLE-2, 10MIN DESORB TIME 28/4/83
SRC. FILE: FIXED -FIXED (6)RDC. FILE: FIXED -FIXED (9).....TABLE=31
```



REFINED/REFERENCE SPECTRA COMPARISON



```
NO. 1  S.I.=0.742  BENZENE:462,AA-102-1
NO. 2  S.I.=0.724  O-HYDROXYBENZYL ALCOHOL:3067,AA-520-1
NO. 3  S.I.=0.711  TROPONE:1699,DC-18-1
NO. 4  S.I.=0.708  1,5 HEXADIENE-3-YNE (DIVINYL ACETYLENE):459,AA-100-5
```

ERRATA

Page	Line	Correction
2	12	carbon monoxide,
9	27	1983
13	2	1 pphm = 1 part per hundred million (10^8)
13	7	1 ppb O_3 = 2.0 μgm^{-3}
13	8	1 pphm NO
33	Table 6	Protection
34	17	Protection
35	16 up	(Dermerjian *et al.*, 1976)
36	13 up	controversial
37	12	dehydratase (ALAD)
40	4 up	photochemical
48	9	sites
50	14	36 m^2s^{-1}
55	1 up	0.1 M EDTA
72	Figure 6	mph, kph
107	13	Figure 26
121	11	Summaries
128	Figure 46	NMHC
139	9	variables
156	5 up	Table 32
168	21	delete '(see Section 2.4 and Appendix B)'
176	2	0.21-0.49 ppm
189	16	4.2.3
190	18	1979
196	13 up	measured concentrations.
201	20	Clark
206	4 up	Jungers
209	11 up	Sidik

Addenda to References

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