ELEMENTAL COMPOSITION OF ATMOSPHERIC PARTICULATE, WATER AND SOIL SAMPLES FROM URBAN AND POLUTED ENVIRONMENTS.

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SUMMARY

Chapter I deals with the reasons for the increased public concern over pollution of the environment, including the deaths of 43 people in Japan in 1953, and the death of over 50,000 sea-birds in the Irish Sea in 1969.

Chapter II discusses methods which have been used in the analysis of metals in environmental samples with comments on their strengths and weaknesses. The two methods which were used in this work, Activation Analysis and Atomic Absorption Spectroscopy are discussed in more detail.

Chapter III deals with atmospheric levels of some 24 elements. Reasons for a study of elemental levels are given.

Sampling problems such as best filter paper, filter blank values, pressure drop across the filter, etc. are considered.

The accuracy of the methods used was checked using standard air pollution filters.

The results of one site sampling over a period of 13 months are given and compared to other world centres. Attempts were made to correlate the levels with weather parameters with only partial success. It was found that although the weather has an effect on levels; fog and calm conditions increasing levels while rain decreased levels, this is not linear. Seasonal variations were also studied with peak values for most elements in winter except for Se and Sb which tend to peak in spring and summer.

Levels at 13 other city sites and 2 rural sites were also measured but no area was found to be consistently high in all elements. The rural sites did in general show lower levels than the city.

Particle size distribution of elements was also studied using a 5 stage cascade impactor the principles of which are discussed. The results are discussed in terms of implications to human health with disturbing results for Cd, Pb and Ni, large proportions of which can penetrate deep into the lung. The results are also compared favourably with those of Liege (Belgium).

A term often used in studying atmospheric levels of elements is the enrichment factor (see Section 3.5.3.3) where atmospheric levels are compared to some standard. When compared to soil the elements show two trends. One class has ratios close to those in soil while the other is enriched by 100 - 10,000 times. It has been suggested that this is consistent with a fuel burning source and is fully discussed.

Good agreement has been found with this theory in all sections of this work. The results of 1 site sampling agree well with those of Liege (Belgium) while the enrichment factors for the other city and rural sites are remarkably constant in the first class (close to soil ratios) with higher and more varied factors for the others. Again the factors of the first class vary little with particle size, the variations being found in the second class.

Chapter IV deals with metal levels in Glasgow's water supply - a constant source of worry due to a combination of soft water and lead pipes. A survey was carried out analysing for 7 elements. The results indicate that Pb levels are higher than W.H.O. limits while Cu could become a problem if W.H.O. desirable limits are applied. Other elements are not a problem at this stage.

Leaching was also studied by a controlled experiment using standard lengths of pipes in common use. Results indicate that altering the material of plumbing will only change the problem of metal levels and not necessarily remove them.

Chapter V deals with some problems associated with the dumping of coal mine waste on land (bings). Bing samples were analysed for 8 metals and the results discussed in terms of plant growth. Only Cu had higher than normal values for normal soil ranges. The effect on surrounding land was also investigated in terms of drainage into streams and seepage and blow-off on to land. The results suggest that these might be occurring but further work is required to confirm the tentative findings of this work.

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CHAPTER I INTRODUCTION

Public concern over levels of metals in the environment has been increasing in recent years, and nowhere more so than in Japan.

The following precis is intended to illustrate some of the events which have led to the increased awareness, and where appropriate, to give examples of biological potency, to human health although the dangers to plants and animals should not be ignored.

Japan in recent years has been showing the effects of industry expanding unchecked into rural peasant areas. The first danger signs came in Minamata, a town that in 1953 was part industrialised, part an overgrown village, where people still caught their own fish in the bay as part of their staple diet. Later it was discovered that a plastics factory had dumped 200 tons of mercury into the bay between 1949 and 1953. The inevitable of course happened - the consumption of contaminated fish caused the deaths of 43 humans and left a further 68, many of them infants and children, permanently and grotesquely disabled. In the following year (1954) 5 out of 12 new cases died and in 1955, 3 out of 15 new cases also died. In 1956, of 50 new cases noted, 10 died and of these 7 were infants born of mothers who did not themselves show any signs of poisoning. A further outbreak occurred in Niigata City in 1970 resulting in 28 severely affected cases, 5 of whom died (1).

Slowly the world came to appreciate the dangers of mercury, but as the element had been widely used for some time in industry and as a seed-dressing in agriculture most of the damage had already been done. The troubles in Japan caused world wide concern, particularly in Sweden which makes considerable commercial use of freshwater fisheries. A national programme was set up to investigate the problem. The findings were disturbing. Eggs and meat produced in Sweden contained more mercury than was found in similar products of neighbouring countries. The findings of the report also included - (1) higher death rates than normal amongst wild seed-eating birds; (2) apparent disappearance of birds of prey; and (3) reduced breeding success was noted with the survivors. Although mercury was found in the various tissues it would be unwise to blame the element by itself.

Mercury becomes bound to the sediments of rivers and lakes, being released only slowly back into the environment, causing long term effects. One lake in Sweden was found to be still highly contaminated in 1970 - 25 years after dumping of mercury ceased. The problem became so serious in Canada that by the end of 1970 fishing was banned from 4 major lakes, 2 major rivers and almost 100 other smaller rivers (1).

Japan was again to be the bearer of further evidence of heavy metal toxicity - this time cadmium and lead. In an isolated village in Northern Japan irrigated by the Jintsu River into which a zinc mine and smelter was pouring its effluent for many years, grain crops and fish became contaminated with cadmium and lead. People living on these foods eventually exhibited severe softening of bones with many fractures and deformities and much pain. Between 1962 and 1968 over 200 cases of this "Itai-Itai-Byo" disease in the above area were reported. The disease itself had been known to the Japanese authorities since 1955 but this was the first major outbreak of the disease (1).

Heavy metals have always of course been in the environment in the minerals of rocks and soil. When they weather, metals are liberated into the atmosphere and surface water. However, in the last 200 years man has significantly affected the natural levels through industrial growth and an ever increasing demand for power. This has increased the levels of metals such as Sn, Se, Sb, Cd, etc. which were of low natural levels and as such, life developed without the need for elaborate mechanisms of detoxification. For example, Pb is stored mainly in bones. In children this can be released during times of high metabolic activity, e.g. during fever, and could lead to lead encephalitis even although blood levels are below that normally regarded as toxic.

The increased levels of elements have been demonstrated by analysing the composition of ice-sheets at the Poles. For 2,000 years prior to 1725 the lead content of the ice at the North Pole was negligible. From 1925 to 1948 with industrial growth a steady rise was recorded, followed by a more rapid increase from 1948 to 1970. The 1970 concentration was 15 times greater than the 1948 levels. No corresponding increase was found at the South Pole since this is in the relatively industrial free Southern Hemisphere (2, 3).

Probably the biggest natural disaster in Britain was the death of 50,000-100,000 seabirds in the Irish Sea in the Autumn of 1969. Subsequent analysis of victims revealed high levels of heavy metals and poly-chloro biphenyls (PCB). Death was attributed to complex inter-acting, but debilitating, contamination effects which left them too weak to survive when they were challenged by moderately harsh conditions. This was said to be caused by the combined inter-action of sub-lethal doses (4).

One of the most dangerous aspects of body absorption of metals is that many nervous pathways are not principally required for one function but duplicate or triplicate other pathways in case of blockage or breakdown. This means that by the time chemical symptoms of nervous disorders appear enormous damage has already been done to the brain and nervous system. In addition of course extensive damage can occur without chemical symptoms being evident.

The metal levels in animals (both wild and domestic) and plants is of course important to humans, particularly if they will eventually be consumed by them. One of the main fears was that of biomagnification which is simply the increase in metal levels by repeated transfer up the food chain. In one study in particular it was found that the top predatory fish had the highest concentration of mercury compounds. However, this is now thought to be less important than originally feared and bioconcentration, i.e. the ability of an organism to concentrate metals from its growth medium is now considered to be the main danger (5). Shell-fish are the best concentrators of all, rapidly concentrating metals to several hundred times the level found in the water in which they live (1).

From the above brief discussion it will be evident that environmental levels of metals are extremely important to the wellbeing of plants and animals alike, since these toxic metals do not degrade and once in the active cycle they remain active until buried deep into sediments. Their period of biological potency has to be measured in thousands of years.

Although for ease of presenting results the environment is divided into atmosphere, land and water, it must be remembered that they are all inter-connected. The air continually maintains contact with land and sea. There are many examples where initially air pollution has caused problems to plants in surrounding areas (6 - 19) and caused deaths of grazing livestock (20 - 24) due to factory emissions. Atmospheric fall-out has also been shown to be responsible for increased levels in Lake Michigan (25). On a more general basis dumping of waste material next to rivers has been known to cause problems in river systems.

AIMS OF PROJECT

The overall aim of the project is, as the title suggests, to study the elemental composition of atmospheric particulate, water and soil samples from urban and polluted environments.

Under this blanket approach the basic aim is to ensure that results quoted are analytically correct within the limits given, and that sufficient samples are taken to include as many contributing conditions as possible.

Chapter II gives a brief account of the main methods used in the analysis of environmental samples, including the advantages and disadvantages of each method. The two methods which were used in this work, Activation Analysis and Atomic Absorption are dealt with in more detail.

Chapter III deals with the elemental composition of atmospheric particulates. Analytical methods used were tested for accuracy by the use of standard filter papers. Some thought was given to sampling problems, collection medium, etc., and to the most economical way of handling the large amount of data acquired. Computer programmes were considered for this latter problem and in most cases found to be useful.

Chapter IV deals with a brief survey of domestic drinking water. This is relevant to the Glasgow area due to the use of lead plumbing in this soft water area. Again consideration is given to the validity of one-off sampling and tests carried out.

Chapter V deals with chemical problems associated with industrial waste and more specifically with metal content of coal mining waste (Coal bings). Problems in terms of reclamation of the actual bing and the effect of seepage, blow-off and run-off on surrounding countryside are investigated. Again thought was given to the choice of site to study and the accuracy of results checked.

CHAPTER II ANALYSIS

2.1 INTRODUCTION

In pollution studies the analytical techniques employed must be accurate, rapid, capable of determining elements in the 10^{-9}g range and if possible allow for the simultaneous determination of a number of elements.

A number of techniques have been employed in the analysis of inorganic pollutants each with their own claimed advantages over other techniques employed, and in some cases the limitations are conveniently over-looked.

It is relevant therefore to discuss briefly the techniques most often employed pointing out their particular advantages and disadvantages.

2.2 X-RAY SPECTROSCOPY

The general principles of this method are well documented in a review by Carr-Brion *et al* (26) and can be briefly summarised as follows -

When electrons are ejected from the inner orbitals of an atom their replacement results in the emission of an X-ray. Each element emits X-rays at certain characteristic energies that are equal to the energies of the corresponding electron transitions. Thus if a substance is suitably excited so that electrons are ejected, the elements composing it can be determined and, as the X-ray intensity at each characteristic energy level depends on the concentration of the element emitting it, quantitive and qualitative analysis become possible.

Existing instruments permit the detection of all elements except hydrogen and helium, although different excitation sources must be used. If sealed X-ray tube excitation is used the range is generally limited to those with atomic numbers higher than oxygen because of the difficulties associated with the excitation of characteristic X-rays from the lighter elements. Radioisotopes can also be used as excitation sources, emitting α, β, γ, and X irradiation as well as protons. X-ray fluorescence (so called when X-rays from a tube or a radio-isotope are used) has been employed in air pollution studies (27-37) and water analysis (38-42). Protons as activating particles have also been used in air pollution studies (43-45) and in water analysis (46).

There are various methods employed in the detection of X-rays, the one most commonly used in pollution studies being energy dispersion using solid state detectors. As the name suggests the X-rays are separated according to their energies, the resolution required being obtained by the semi conductor detector made from Lithium drifted Silicon or Germanium. The spectrum is usually displayed on an oscilloscope screen of a multi-channel analyser and printed out on paper or punched on to computer tape.

2.2.1 Main Advantages

i) It is non-destructive.

ii) No pre-treatment of air pollution filters is necessary with the filter paper being placed directly into the instrument.

iii) It allows for the simultaneous determination of many elements.

iv) It is extremely rapid.

v) Detection limits for most elements are in the 10^{-9}g range.

vi) Since a thin filter paper is used there is no matrix effects due to absorption or scattering of emitted X-rays.

2.2.2 Main Disadvantages

i) It requires sophisticated equipment and skilled operators.

ii) Solutions must be evaporated to obtain a solid sample.

2.3 ANODIC STRIPPING VOLTAMETRY

A comprehensive review of the principles including equations governing the various steps of this method is given by Barendrecht (47).

Basically the process is very simple, based on a reverse polarographic principle. There are three electrodes, a test electrode (hanging mercury drop or wax treated mercury-coated graphite rod), and Ag/AgCl reference electrode and a platinum counter electrode. These are inserted into a cell containing the unknown sample or standard solution. A negative potential (which may be varied) is applied to the test electrode which plates the trace metals out of solution on to the electrode based on their formal potential in the particular matrix. The potential is then reversed and a linear sweep of the required range made, thus stripping the metals off the electrode; the order of stripping being in accordance with the characteristic half-wave potential of the elements. Plating times are usually of the order of 30 minutes and the stripping time about 20 seconds.

Since oxygen interferes in the plating nitrogen is usually bubbled through the solution before plating commenses.

Since the concentration is obtained by comparison with standards and as the amount plated obviously depends on plating time, it must be confirmed that the solution is not completely depleted of ions of interest over the plating time used.

This method is obviously very useful in the analysis of water (48-52) but has also found use in air pollution studies after dissolution of the sample (53-60) and also for biological samples (61-64).

2.3.1 Main Advantages

i) It is very rapid. In the case of water samples results can be obtained within 2 hours of receiving the sample.

ii) Detection limits are in 10^{-9}g range.

iii) It is non-destructive in the case of water.

iv) It allows for the simultaneous determination of a number of elements.

2.3.2 Main Disadvantages

i) The range of elements which can be determined is limited to those which can be reduced by mercury and which have a half-wave potential less than that of hydrogen because of the "over-voltage" phenomena. However, it must be said that this limited range does include some of the important metal pollutants.

The range is: Sb, Bi, Cd, Cu, Au, Pb, Hg, Ag, Tl, Zn.

ii) It is highly dependent on the purity of solvents.

iii) There is the possibility of metal - metal complexes forming, e.g. Sn-Cu, Zn-Pb, etc.

2.4 SPARK-SOURCE MASS SPECTROMETRY

This method is based on the well known principles of mass spectrometry which are well documented elsewhere. (65).

Electrodes formed from the sample are mounted in the ion source and a spark passed between them by applying a pulsed rf voltage. Positive ions representative of the sample are produced in the discharge and are accelerated through an ion gun and passed through resolving slits. An electrostatic analyser provides energy focusing of the ion beam to compensate for the wide spread of initial kinetic energies of the ions in the spark discharge. An electromagnetic analyser then separates the ions according to their masses and focuses them on a single plane. Detection can either take place on a photoplate which effectively integrates the ions detected at each mass thereby reducing the effects of ion beam fluctuations caused by the variations inherent in the spark discharge, or electrically by collection on the first dynods of an electron multiplier and the resulting current amplified. The latter method is much faster and therefore is preferred.

This method has been used in the analysis of air filters (66-69). Spectral interference due to hydrocarbon species is removed by the use of a liquid nitrogen cold trap or a cryogenic pump. It has also been used in water analysis (70-73) and other environmental samples (74-76).

2.4.1. Main Advantages

i) It is fairly rapid.

ii) Detection limits are in 10^{-9}g range.

iii) It allows for simultaneous determination of a number of elements.

2.4.2 Main Disadvantages

i) It is a destructive method since the sample is ground with pure graphite.

ii) Data output is extremely complicated and requires computer processing if backlogs of data are to be avoided.

2.5 EMISSION SPECTROSCOPY

This method depends on excitation of orbital electrons of atoms either by a flame (flame emission spectroscopy) or by a d.c. arc between two electrods (d.c. arc emission spectroscopy). As the electrons return to lower energy states light of energy characteristic to the element of interest is emitted. In flame emission the sample must be presented to the instrument in solution and the emitted light usually detected by a photocell. Flame emission has been used in the analysis of atmospheric particulates (77).

In d.c. arc spectroscopy the sample is ground with pure graphite and forms one of the electrodes across which the d.c. arc is passed. The emitted light is passed through a prism and the resulting line spectrum focused and recorded on a photographic plate; the degree of darkening being proportional to the amount of element present. This is usually done by relating intensity to the known weight of an internal standard. This method has been used in the analysis of atmospheric particulates (78-86). One set of workers (86) actually used the graphite rod as a sampling filter and used this directly as the electrode. It has also been used in water analysis (87).

2.5.1 Main Advantages

(a) Flame
- i) The method is fairly rapid (especially for water samples).
- ii) In the scanning mode it allows for simultaneous analysis.

(b) d.c. arc
- i) The method is fairly rapid.
- ii) It allows for simultaneous analysis.

2.5.2 Main Disadvantages

- i) Both methods are destructive.
- ii) Detection limits tend to be in 10^{-6}g Range.

2.6 GAS CHROMATOGRAPHY

. Until recently gas chromatography was used exclusively in the analysis of organic materials. However, recently more and more attention has been given to the use of this method in metal analysis, and an excellent review has been prepared by Rodriguez-Vazquez (88).

The metals are complexed to either make them volatile or to increase their volatility, using β- diketones (e.g. 2, 4 pentane - dione), acetylacetone or their tri - and hexa - fluoro derivatives. The criteria required are that the complex must be volatile and thermally stable. The sample is then injected on to a suitable column of an inert stationery phase and an active liquid phase. The metals separate according to their retention times on the column, with or without temperature programming. At the end of the column the metals are detected usually by flame ionisation where ions are formed by a flame.

The base of the flame is at a negative potential while the top is neutral. The ions in the flame alter the electric current, the amount of alteration being proportional to the number of ions. Many alternative detectors exist. One often employed is electron capture where the metals are excited by a radioactive source and the radiation emitted by the unstable isotope formed, measured.

This method is usually used with an internal standard for quantitive analysis.

There are several papers on the general principle of metals by gas chromatography (88-90); gas chromatography in the analysis of aerosols (91-93); in the analysis of water (94-97); and in the analysis of other environmental samples (98-106).

It is too early to discuss the advantages and disadvantages of this method in any detail. Advantages include - (i) It is fairly rapid. (ii) Detection limits are in the 10^{-9}g range at least. (iii) The method enables one instrument to be used in the analysis of both organic and inorganic pollutants thus reducing costs.

Disadvantages include - (i) The method is destructive. (ii) At the moment only a few elements have been determined simultaneously.

The two methods which are probably most widely used in environmental analysis are activation analysis and atomic absorption spectroscopy.

As these are the methods which were used in this work a deeper understanding of the theories was required in order to appreciate limitations, overcome problems which may arise during analysis, and to realise where errors will occur.

For these reasons in the following two sections a more detailed discussion is given of these two methods.

Additional reasons for using atomic absorption and neutron activation analysis are :-

i) Atomic Absorption is comporitively cheap and has wide element coverage.

ii) Neutron activation analysis is more sensitive than atomic absorption and better element coverage, and

iii) Both are available.

2.7 ACTIVATION ANALYSIS

The principles of this method are well documented (106). When a suitable element is bombarded with sub-atomic particles it is converted to another isotope. If this isotope is unstable it reverts to a lower energy state emitting the excess energy in the form of irradiation (α, β, γ rays) - the energy being characteristic of the element.

There are three main nuclear reactions:-

i) Energy is given to the nucleus by high energy photons or electrons, the excess energy being released by emission of nuclear particles (γ, n) (γ, p). This method has been used to analyse atmospheric particulates (107-110).

ii) Charged atomic particles (protons, deutrons) suitably accelerated can be used as bombarding particles giving rise to emission of other nuclear particles as in (i) e.g., (p, x n) (d, x n) (d, p) or incorporated into the nucleus producing a nucleus of different mass, charge and radioactive status. This has also been used for atmospheric particulate and also water samples (113-115).

iii) Neutrons can be incorporated into the nucleus. Neutrons are uncharged and are therefore incorporated more readily than charged particles which must overcome coulombic repulsion between the nucleus and bombarding particles.

Neutrons are the most widely used bombarding particles because they are more readily available mostly from nuclear reactions.

Although fast neutrons have been used to determine silicon in aerosols (115), thermal neutrons are more widely used because of their higher capture cross sectional area: they have been used for atmospheric particulates (55, 116-131), and water (132-138).

2.7.1 Interaction of Neutrons and Nuclei

Neutrons of thermal energy are obtained by moderators which slow down fission neutrons from reactor fuel. These thermal neutrons are easily captured by nuclei of most elements to give an (n,γ) type of nuclear reaction. If the isotope produced by the absorption of neutrons into the nucleus is unstable the resulting radioactivity can be measured.

Factors which determine the amount of radioactivity under the influence of neutron bombardment are:-

i) the weight of element present, (W)
ii) the fractional abundance of the isotope undergoing the (n,γ) reaction, (θ)
iii) the activational cross-section for the nuclide concerned, (σ)
iv) the neutron flux, (ϕ)
v) the half-life with which the radioactive species decays, $(t_{\frac{1}{2}})$
vi) the length of time of irradiation (t_i)

Radioactive atoms follow the normal law of radioactive decay

$$A_t = A_o e^{-\lambda t}$$

A_t = activity in disintegrations per unit time at time = t
A_o = activity in disintegrations per unit time at time = 0

λ = radioactive decay constant which is related to half-life

$$t_{\frac{1}{2}} = \frac{0.693}{\lambda}$$

If N^* is the number of radioactive atoms formed after a time t_i seconds the rate $\frac{dN^*}{dt}$ at which the number of radioactive atoms increase is given by $\frac{dN^*}{dt} = \phi\sigma N - \lambda N^*$ ________________(1)

where N = number of atoms of isotope being activated present in the sample and is given by:-

$$N = (6.025 \times 10^{23})\,\theta \cdot \frac{W}{M}$$

M = mass number of the isotope being activated.

N represents the rate of formation of radioactive atoms and λN^* their rate of decay.

Integration of (1) gives the number, N^*, of radioactive atoms present after time t_i.

Since N^* is very small compared with N, N can be assumed to remain constant.

Integration gives: $\phi\sigma N e^{-\lambda t} = \phi\sigma N - \lambda N^*$

Activity A_t in dps due to atom N^* produced after t_i is given by

$$A_t = \lambda N^* = \phi\sigma N\,(1 - e^{-0.693 t_i/t_{\frac{1}{2}}})$$

$$= 6.025 \times 10^{23}\phi\sigma\theta\left(\frac{W}{M}\right)(1 - e^{-0.693 t_i/t_{\frac{1}{2}}})$$

When t_i becomes long compared to $t_{\frac{1}{2}}$ then $(1 - e^{-0.693 t_i/t_{\frac{1}{2}}})$

approaches unity and the saturation activity A_∞ is obtained, i.e., for $t_i \gg t_{\frac{1}{2}}$

$$A_\infty = 6.025 \times 10^{23} \phi\sigma\theta(\tfrac{W}{M})$$

This is shown in Figure 2.1 and its consequences will be discussed later.

At the end of the irradiation the activity of the radioactive isotope will decay with its characteristic half-life so that at time t_d after the end of the irradiation the activity A_d will be given by:-

$$A_d = 6.025 \times 10^{23} \phi\sigma\theta(\tfrac{W}{M})\ (1 - e^{-\,0.693t_i/t_{\frac{1}{2}}})\ (1 - e^{-0.693t_d/t_{\frac{1}{2}}})$$

Thus the highest activity and therefore the highest sensitivity for a given weight of element is obtained if the neutron flux, isotopic abundance and capture cross section are high.

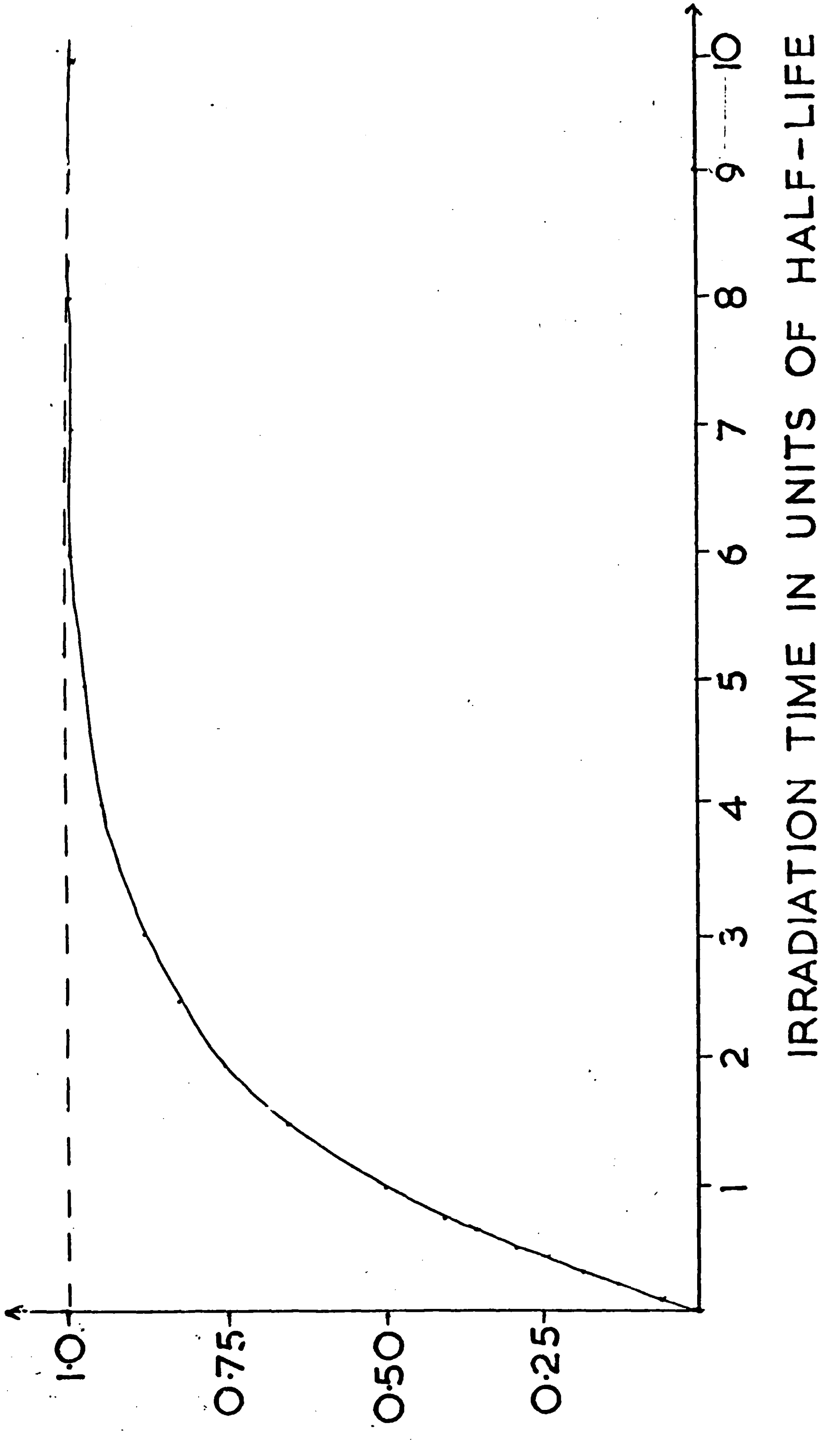
This method is rarely if ever used because of difficulties associated with accurate determination of neutron flux and total disintegration rate. It is more common to use a comparative method by running samples and standard amounts of element together.

2.7.2 Methods of Neutron Activation Analysis

There are three main approaches:-

i) Destructive method in which the radioactive isotope of interest is separated completely from interfering active isotopes by chemical methods. It has been used in the analysis of environmental samples usually where the matrix itself is a strong γ- ray emitter (139-143). Separation is achieved

FIGURE 2.1 ACTIVITY V TIME FOR RADIOACTIVE DECAY



either by passing through an ion exchange column or by adding a fixed amount of inactive carrier after irradiation. In the latter case the chemical yield is determined and hence quantitative recovery is not required.

ii) Group separation of isotopes into sample fractions such that interfering isotopes are separated from each other. This allows for a larger number of elements to be determined than (i) and has also been used in environmental analysis (114-146).

iii) Instrumental γ-ray spectroscopy where the elements are separated according to energies of γ-rays. This allows for the simultaneous determination of many elements but they must have reasonable natural abundance and active isotopes which decay with γ-ray emission of suitable energy free from interference from other isotopes. A reasonable half-life is also required.
The development of solid state Ge (Li) detectors has made this possible for as many as 33 elements in the one sample. The theory behind this is well documented elsewhere. (147). Instrumental γ-ray spectrometry is the most widely used in environmental analysis. (55, 116-131).

2.7.3 Main Advantages

i) Detection limits are in 10^{-9}g range.

ii) Simultaneous determination of a number of elements (by instrumental method) is possible.

iii) Non-destructive methods are unaffected by reagent impurities.

2.7.4 Main Disadvantages

i) There must be a readily available reactor or other neutron source for isotopes with short half-lifes.

ii) The instrumental method requires a long cooling period for some isotopes to allow interfering isotopes to decay. This will be discussed in more detail in the appropriate chapter (See Section 3.5.2.2).

2.8 ATOMIC ADSORPTION SPECTROSCOPY

This is probably the most widely used method of metal analysis because of the ease of handling of the equipment, the sensitivity and the range of elementswhich can be detected. The principles have been well discussed (148, 149).

In brief the method can be simply defined as the absorption of radiant energy by atoms. This absorption and its quantitative correlation with the concentration of metal ions originally present in a sample solution serves as the basis of analytical atomic absorption. The atoms are produced from their compounds either by a flame or a furnace and by absorbing radiation of a particular wavelength will reach a higher allowed state. The allowed transitions are such that spectral rules are not broken, i.e., in terms of Russell-Saunders coupling, L should change by ±1 and J by ±1 or 0. Also the multiplicity of the two spectral terms should remain the same. (Occasionally these rules are broken by heavy metals such as Hg).

This absorption of energy in practical terms means that the intensity of the light passing through the sample is reduced and this reduction is proportional to the concentration of the metal in the sample solution.

The Beer-Lambert Law:

$$I_\lambda = I_o e^{-K_\lambda l}$$

where I_o = the intensity of source at wavelength λ

I_λ = the intensity of transmitted radiation

k_λ = the absorption coefficient

l = the length of light path through sample

is difficult to apply directly to atomic absorption since there is seldom a system of atoms in a steady state of homogeneous distribution. However, the principles of the Law must apply in that the intensity of unabsorbed light is a function of the negative log of the absorption coefficient.

The value of K_λ will vary with wavelength since the absorption line has a finite width and according to the classical theory of dispersion, the integrated absorption coefficient $\int K_\lambda d\lambda^\lambda$ (within the limits $\lambda \rightarrow \lambda + d\lambda$) is given by

$$\int K_\lambda d\lambda = \frac{\pi e^2}{mC} N_\lambda f$$

where e = electron charge

m = electron mass

C = velocity of light

N_λ = number of atoms per cm^3 capable of absorbing radiation of wavelength λ.

f = oscillator strength = average number of electrons per atom which can be excited.

Thus for a transition initiated from the ground state for which N_λ for practical purposes is equal to N (the total number of atoms per cm^3) the integrated absorption coefficient is proportional to the concentration of free atoms in the absorbing medium.

For most elements the characteristic wavelength that is used is the spectral resonance line, that is the transition from the ground or unexcited state to the lowest excited state. Since this transition involves the lowest energy it is usually the strongest line in the metal spectrum. However, the neutral atom can absorb radiation in discrete steps at different wavelengths which can be used in concentrated samples or in the case of spectral interferences from other elements.

2.8.1 Light Source

At temperatures between 2000 and 3000°K the width of an absorption line is about 0.02 Å The factors which establish the line width are:

i) The natural width of the line due to the finite life-time of any atom in an excited state. (of the order of 10^{-4} Å).

ii) Doppler broadening caused by the thermal motion of the emitting or absorbing atoms relative to the observer.

iii) Pressure broadening due to collisions with neighbouring atoms, (resonance broadening if due to same kind of atoms).

iv) Stark broadening due to external electric fields or charged particles (i.e., splitting of electronic levels of atoms).

All these effects manifest themselves depending on the source used. (ii) is the main factor if atomic vapour is produced in a low pressure furnace, (ii) and (iii) occur in flame sources and (ii), (iii) and (iv) are all associated with arc and spark excitation sources.

These factors could make it difficult to measure the integrated absorption accurately. However, by measuring the absorption coefficient at the centre of the line using a sharp line source which emits lines with a much smaller half-width than the width of the absorption line, accurate measurements can be made provided high resolution equipment is available. This is usually obtained with a hollow cathode lamp in which the cathode is made from, or contains, material of the element to be determined; each element of interest requiring a separate lamp. Because of the sharpness of the source, minor fluctuations in output become more critical but can be controlled using double beam instruments in which the beam is chopped in two, one passing through the sample and the other not. The beams are focussed after the sample, and the ratio taken. If the shape of the absorption line is determined completely by Doppler broadening then

$$K\ max = \frac{2\lambda^2}{D_\lambda}\left(\frac{\log_e 2}{\pi}\right)^{\frac{1}{2}}\frac{\pi e^2}{m\,C^2}\,.\,N.f$$

where $K\ max$ = absorption coefficient at the centre of the line

D_λ = Doppler line width

and D_λ is given by:-

$$D_\lambda = \frac{1.67\lambda_o}{C}\left[\frac{2RT}{Ma}\right]^{\frac{1}{2}}$$

where R = gas constant

C = speed of light

T = temperature

λ_o = wavelength at centre of line

Ma = atomic weight of absorbing species.

Hence since D_λ is proportional to $\sqrt{\text{temperature}}$, K max does not vary significantly with small changes in temperature and the relation between absorption and concentration of the free atoms in the absorbing medium is maintained.

It practice it is extremely difficult to measure the absorption coefficient and the absorbance of the sample solution is compared to the absorbance obtained from standard solutions of known concentration of the element of interest.

2.8.2 Production of Free Atoms

There are two main methods of producing free atoms.

2.8.2.1 Flame

Here a combination of gases is burned in the light path. The sample solution is aapirated into the flame where the solvent is dried off to form a clotlet. The clotlet is thermally dissociated into free atoms and finally the free atoms absorb radiant energy. The whole process takes a matter of seconds.

The main types of flames used are:-

(a) Air/Acetylene with a temperature of approximately 2300°C and is the preferred flame for about thirty-five elements.

(b) Nitrous oxide/Acetylene with a maximum temperature of 2900°C and is used for determination of elements which form refractory oxides, e.g. aluminium.

(c) Argon/Hydrogen with an extremely low temperature of 300-800°C using diffused air as an oxidant shows considerably less absorption in the far U V (190-220 nm) than other flames and therefore is useful for the determination of As (194 nm) and Se (196 nm). Because of the low temperature, chemical and matrix interferences may be encountered and the use of exactly matched standards or the method of Standard Additions is strongly recommended.

(d) Air/Hydrogen with a temperature of about 2000°C is useful for the determination of alkali metals (Cs, Rb, K, Na) as the lower temperature considerably reduces ionization.

2.8.2.2 Flameless Atomisation

As the title suggests the flame is replaced either by a carbon furnace or a tantalum filament with maximum temperatures of about 2600°C and 3200°C respectively.

The improvement in sensitivity in many cases allows for direct analysis of a solution where previously pre-concentration was necessary. With suitable matrices solid samples can also be measured directly. Detection limits are also increased to 10^{-13}g range.

In the flameless system the stages which the sample goes through (drying, etc.) can be controlled electrically. The solution is first dried at a temperature just below the boiling point to prevent spluttering and then the temperature is increased (stepwise or programmed) to a value at which the accompanying material will be thermally destroyed without causing a loss of the element of interest. Finally the temperature is very rapidly increased so that the element will be thermally dissociated into its atoms. If residues remain after the atomisation they may be removed by heating at maximum temperature.

In flames interferences can be minimised by preparing the solutions in a chloride medium thus helping to overcome the most prevalent type of chemical interferences, i.e., formation of stable oxides or mixed oxides. In a furnace (or tantalum ribbon) however, it appears that there are fewer oxide type interferences and that the hot carbon surface provides an efficient reducing surface. Interferences are clearly reduced in fact when solutions of salts such as nitrates or sulphates which break down thermally via the oxide, are used (150) (in complete contrast to the flame). Chloride solutions appear to result in the volatilisation of molecular chlorides of many elements and these are not subsequently atomised in the vapour phase. With many metals the use of nitrate solutions produces metal oxides which remain on the surface of the atomiser until they are reduced to the metal and released as metal atoms. It has been suggested (151) that this reaction is

$$MO(s) + C(s) \longrightarrow M(g) + CO(g)$$

When thermodynamic data is used to calculate the lowest temperature at which this reaction is favourable for suitable elements the results correlate well with the temperature at which the same elements appear in atomic form in the graphite furnace (152). This correlation can only be considered valid if it is assumed that when the appropriate temperature is reached, the rate of reaction of metal oxide with carbon is fast so that there is no delay in the appearance of metal atoms.

In a study on the kinetics of copper in the carbon furnace (153) the following was suggested:-

$$\mathrm{Cu_2O} + \mathrm{C} \xrightarrow{\text{slow}} 2\,\mathrm{Cu}\,(S/l) + \mathrm{CO}(g)$$
$$\mathrm{Cu}\,(S/l) \xrightarrow{\text{fast}} \mathrm{Cu}\,(g)$$

where S,l and g represent the solid, liquid and gas phases respectively.

This theory tends to break down with elements which form stable carbides, e.g. Al, Cu, Cr, Mo, Ti, V.

2.8.3 Interferences

There are five main types:-

2.8.3.1 Chemical Interferences

These occur when the element of interest combines with some other cation or anion in solution to form a compound which influences the degree of reduction to free atoms, i.e., reducing the number of atoms capable of absorbing radiation at the resonant energy.

Examples are - the reduction of the calcium signal in the presence of phosphate and the reduction of the magnesium signal in the presence of aluminium.

Chemical interferences can be overcome or controlled in two ways -

i) Use of a higher temperature flame which produces additional energy to break down the compound formed.

ii) By addition of a releasing agent, that is, a chemical species which when added to the sample solution will preferentially react with the element of interest or the interferent.

2.8.3.2 Matrix Interferences

These occur when the physical characteristics of the sample and the standards differ considerably, e.g., when the sample solution contains high concentrations of dissolved salts or acids (i.e., a different viscosity which alters the aspiration rate) or when the sample and the standards are at a different temperature.

Matrix effects can be controlled by

i) Dilution of the sample until the effect of dissolved salts or acids become negligible.

ii) Matching sample and standard solutions for major constituents.

iii) Use of the method of Standard Additions. Three aliquots of the sample are taken. One is diluted to a known volume with solvent. The second and third aliquots are diluted to the same volume with suitable quantities of known standards added so that the final solutions contain different additions of the metal to be determined. The absorbance is measured for each solution and plotted against the added concentration. The resulting straight line is extrapolated through zero absorbance and the intercept on the concentration axis gives the concentration of the metal in the diluted sample solution. For an accurate determination, the working curve must be linear over the concentration range covered by the sample plus additions and additions should be of approximately the same concentration as that anticipated for the diluted sample solution.

2.8.3.3 Ionisation Interferences

These occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom giving a positively charged ion and reducing the number of metal atoms in the flame.

The effect can be controlled by -

i) Using a cooler flame which will have less energy available to produce ionisation.

ii) The addition to both sample and standard of a large excess of an easily ionised element (e.g., alkali metals) which works due to a form of mass action effect, i.e., as the amount of an easily ionised element in a flame is increased the proportion of ionised to unionised atoms of the element of interest is decreased with a corresponding rise in the number of atoms in the atomic ground state.

For example in the analysis of Na, 1000-2000 ppm K is added to sample and standards

$$\begin{tikzcd}
\mathrm{Na\,X} \arrow[r, "\Delta"] & \mathrm{Na}^{o} \arrow[d, shift left] & + \; X^{o} \\
 & \mathrm{Na}^{+} \arrow[u, shift left] & + \; e^{-}_{1}
\end{tikzcd}$$

$$\begin{tikzcd}
\mathrm{KX} \arrow[r, "\Delta"] & \mathrm{K}^{o} \arrow[d, shift left] & + \; X^{o} \\
 & \mathrm{K}^{+} \arrow[u, shift left] & + \; e^{-}_{2}
\end{tikzcd}$$

$$e^{-}_{1,2} + \mathrm{Na}^{+} \rightleftharpoons \mathrm{Na}^{o}$$

2.8.3.4 Spectral Interferences

Spectral interferences can occur when an absorbing wavelength of an element present in the sample but not being detected falls within the width of the absorption line of the element of interest giving an erroneously high result.

This can be overcome by

i) Use of a smaller spectral slit width.

ii) Using an alternative wavelength of the element of interest.

2.8.3.5 Background Absorption

Background absorption is the collective term used to describe the combined effects of flame absorption, molecular absorption and light scattering.

i) Flame absorption which becomes increasingly significant below 250 nm may be controlled by properly set fuel and oxidant flow rates or by using a flame with less absorption at the wavelength of interest.

ii) Molecular absorption can often be controlled by using a higher temperature flame with sufficient energy to break down the absorbing molecular species.

iii) Light scatter is a term used for the scattering of light by solid particles in the flame and which erroneously increases the amount of light which appears to have been absorbed.

These three interferences can also be removed together in two ways -

i) Since molecular absorption, flame absorption, and light scatter take place over a wider wavelength than the atomic absorption then by measuring the absorbance at a near-by non-absorbing wavelength of the element a measure of the absorbance due to background can be assessed and subtracted from the absorbance of the element wavelength. This second line, however, to be effective must be within 1 or 2 nm because of the variation of molecular absorbance with wavelength.

ii) A better method is to use a deuterium background corrector. This is a continuous source which is time shared along with the hollow cathode lamp. Both beams are passed through the flame and a ratio taken. (The line absorption of the continuum source is negligible compared to the background over the bandwidth of the monochromater). However, above about 350 nm the continuum source is weak and the adjacent line correction must be used.

Interferences can also be removed in many cases by selectively extracting the metal (s) of interest into organic solvents by controlling the pH. e.g., metals can be complexed with ammonium pyrrolidine dithiocarbamate (APDC) and then extracted into methyl iso-butyl ketone (MIBK).

2.8.4 Main Advantages

i) The method is fairly rapid depending on the number of elements of interest.

ii) Detection limits in the flame are in the 10^{-6}g range and with the carbon atomiser are in the 10^{-13}g range.

iii) Equipment is relatively easy to handle with no long training period required.

2.8.5 Main Disadvantages

i) By its very method of detection this method is destructive.

ii) It does not allow for simultaneous detection of a number of elements, although a number of elements can be determined on the one sample, the limiting factor being the amount of sample.

iii) Samples must be brought into solution before analysis.

This method is best suited to the analysis of a number of samples in a batch because of the time involved in setting up equipment and fresh standards.

Atomic absorption has been used as an analytical technique in air pollution studies, both with flame atomisers (154-167) and flameless systems (168-177). Several workers devised systems whereby the air was drawn through the carbon rod which was subsequently placed directly into the spectrophometer. (170-176). Atomic absorption has also been used in the analysis of water, again using flame (178-182) and flameless systems. (183-187).

More recent advances in atomic absorption include the hydride system in which the hydrides of Se, Sb and As are produced chemically in an enclosed system, concentrated in a cold trap and aspirated directly into the flame. This removes matrix interferences and also as aspiration in the flame is 100% since it is in the form of a gas compared with 10% for solutions, the detection limits are greatly improved. (1000 times in the case of Se).

There is also now available a mercury system, similar to the above, mercury is formed chemically and the gas pumped round an enclosed system using a quartz cell in place of the flame.

CHAPTER III AIR POLLUTION

3.1 INTRODUCTION

It is difficult to judge when air pollution was first considered to be a problem. Recent years have seen a large increase in the concern for metal and/or element levels in the atmosphere as illustrated in Chapter I. However, in England as long ago as 1377, Richard III, and Henry V in 1413, regulated and restricted the use of coal in London because of the health hazards of smoke and odours.

The reason for the increased concern is two-fold -

i) The population growth of recent years had led to a larger demand for manufactured products and electrical power, increasing even low levels of pollutant output to a major problem.

ii) The enormous increase in the use of motor vehicles which has been shown to elevate lead levels in roadside vegetation and insects (188-193).

Cause for Concern

There have been numerous episodes in the past of air pollution resulting in illness and death, several examples of which are listed below.

i) Glasgow 1909 - During two periods of foggy conditions in the Autumn 1,063 deaths were attributed to the noxious conditions and the smoke (194).

ii) Meuse Valley, Belgium 1930 - which is 15 miles long and 300 feet deep - A thermal inversion confined emitted pollutants from the large number of industrial plants, killing 60 people and causing the death of many cattle (194-195).

iii) Donora, Pennsylvanie, U.S.A. 1948 - This was the site of three large industrial plants in a U-shaped valley. A thermal inversion combined with foggy weather caused 43% of the 14,000 population to be ill and killed 20 people. A subsequent study carried out in 1952 and also in 1957 found that the exposed population had a less favourable mortality rate than those not exposed in 1948. This at least indicates the possibility of long term effects from breathing polluted air (195).

iv) Poza Rica, Mexico 1950 - Hydrogen sulphide accidentally released from a sulphur recovery plant during foggy weather with weak winds and low inversion layer hospitalised 320 people of whom 22 died (194-195).

v) London, England 1952 - lying in the broad Thames valley - During a four day period of fog and temperature inversion between 3,500 and 4,000 excess deaths were recorded. The mortality rate remained elevated for several weeks after the weather improved, again implying that acutely increased pollution may start a process which could continue to operate even after conditions have returned to normal.

This latter incident caused records to be checked and further relationships between mortality and bad weather to be sought. There were excess deaths in the Winters of 1948, 1891, 1882, 1880, 1873, 1862 and 1859 (194-195).

vi) New York City, U.S.A. 1953 - Increased pollutant levels due to widespread atmospheric stagnation caused an excess of deaths compared to average (195).

The following points should be emphasised from the above incidents -

i) Most of the deaths occurred in people who were known to have heart and lung conditions and also in the old and the very young. If, however, these are the people most at risk then safety standards ought to take this into account and be set below their threshold and not based on that of the average person.

ii) Pollution incidents occurred during periods of either thermal inversion, low wind speed or fog, all of which cause the pollutants to remain concentrated round their source for longer periods than normal.

iii) In most cases SO_2 and particulate matter were shown to be involved.

iv) There is evidence to suggest that the effects of high pollutant levels remained long after the pollutant levels returned to normal.

v) There is a need for monitoring levels of pollutants and being able to predict how levels will vary under differing climatic conditions.

It is this final point which forms the basis of the work in Section 3.5 of this Chapter.

Of the two pollutants which have caused most problems (SO_2 and particulate matter) it was decided that a study of particulate matter would be more profitable as the SO_2 levels in Glasgow are already well documented by the Smoke Officer of the Environmental Health Department.

3.2 PARTICULATE MATTER

The terms, atmospheric particulate and atmospheric aerosol, are taken in this work to be synonymous, although strictly speaking an aerosol can contain either solid or liquid particles whereas particulate matter contains only solid particles. The amount of particulate matter in the atmosphere is important for several reasons -

i) As chemical species *per se* some constituents exhibit high orders of toxicity to plants and animals.

ii) As physical entities they scatter and absorb light. It has been estimated that as much as 20% of the energy available to heat the earth-atmosphere system from the sun can be lost in some cases due to back-scatter of the solar beam. Until recently both Pittsburgh and St. Louis (U.S.A.) had palls of smoke which required the street lights to be lit during the day (195).

iii) As charged particles they can lead to condensation and coalescence of other particles and gases. This has also been shown to cause an increase in the amount of rainfall due to the increased number of condensation nuclei, i.e. affect climate (196-198). Although it must be said in a similar study (199) no evidence for this was found despite the production of sufficient condensation nuclei.

iv) They are suppliers of large specific surface areas for absorption of pollutants. This can have the effect of retaining harmful substances in the respiratory tract and lungs for longer periods and also of enhancing the penetration of these substances deeper into the lungs.

It is also known that air polluted with SO_2 and particles of charcoal produce more rapid corrosion of metal surfaces than SO_2 alone.

v) They afford an opportunity for catalysis of normally slow reactions to take place. For example, in the presence of Mn, Fe or V the production of sulphuric and nitric acids from their oxides in the atmospheric aerosol is greatly accelerated.

iv) and v) above combine to give a chemical breeding ground either for more or less noxious products.

vi) They can land on the surface of leaves and interfere with light interception, respiration and transpiration, leading to stunted growth. In fact it has been suggested that particles could actually prevent the stomata closing properly thus allowing gaseous pollutants more ready access (200).

vii) They soil clothes and buildings. Although this is the most obvious effect of particulate pollution, and although offensive to the eye it is the least dangerous.

As would be expected the Smoke Officer has comprehensive records on the total particulate levels of the city of Glasgow's atmosphere and to add new information it is therefore the actual constituents of the particulate matter and their concentrations which have to be studied.

3.2.1 Metals in Particulate Matter

Metals are important constituents of particulate matter for the following reasons -

i) It is mainly metals which are the catalysts in atmospheric reactions.

ii) There are many known emitters of metals - iron and steel works, electrical power stations, coal and oil burners, smelter works, car exhausts to name but a few.

iii) Several metals exhibit low thresholds of toxicity, e.g. Pb, Cd, Ni, Sb, Be and Hg.

iv) Biochemically, metals can interfere with enzymic reactions both in animals and plants (201-207).

3.2.1.1 Choice of Metals

The choice of which metals to include in the study is a difficult one. Obviously the choice is limited to those which can be detected by the methods to be used, but even within this range a choice has to be made.

These metals which are highly toxic (see above) are of course a first priority, but the answer is not so simple, as metals can alter the biological activity of other metals or other pollutants. They can do this in four ways -

i) Potentiation - There is an enhanced response of two or more substances over and above that of additive or predicted effects and in which one substance is inactive or by itself produces a different effect, e.g. a NaCl aerosol which is normally inactive enhances the irritation caused by SO_2 (195).

ii) Addition - The effects of more than one pollutant are the sum of the individual effects.

iii) Synergism - The effect of more than one pollutant is greater than the individual effects, e.g. Pb increases the toxicity of As and vice-versa. Cu has a similar effect on Hg(1), Co increases the detoxification time of CO (208) and O_2 increases the toxicity of Pb (209).

iv) Antagonism - Pollutants work against each other to reduce the effect, e.g. As blocks the toxic action of Se (1). Several other examples are cited elsewhere (210-214).

Since there is not sufficient data available to catalogue all the effects of pollutants on each other, metals cannot therefore be chosen solely on this basis with any degree of confidence.

Another complicating factor is that certain metals have very low toxicities but are extremely valuable in determining the source of other metals, e.g. Al has been used in the calculation of enrichment factors normalised to soil. (See Section 3.5.3.3).

The safest approach would therefore be to make as few a priori judgements as possible about the importance of individual metals and to measure as many as possible. This was the approach adopted here.

Where neutron activation analysis is used several non-metallic elements can be easily determined, and based on the above reasoning should also be measured (e.g. Br in Section 3.5.2.1).

3.3 SAMPLE COLLECTION

Sample collection is one of the most important considerations for the analyst. The factors which can affect the accuracy and meaning of results are -

i) size of sample (i.e. volume of air)
ii) rate of sampling
iii) duration of sampling
iv) collecting medium
v) location.

It will become apparent that the choice of one of these in many cases automatically fixes the condition of the remainder.

3.3.1 Size of Sample

The quantity of air required must be known. This requires knowledge of the minimum pollutant concentration of interest as well as the sensitivity of the analytical technique to be employed. When information is not available the amount of air required must be determined by trial and error.

3.3.2 Rate of Sampling

The permissible rate of sampling is determined by the collection device selected and is dependent on the allowable head loss as well as the experimentally determined optimum flow rate, i.e. that flow rate permitting highest efficiency of collection. For example, a unit capable of efficient operation at high flow rates is essential where a short sample duration is desirable. Units which separate particles, e.g. a cascade impactor must be run at the quoted rate.

3.3.3 Duration of Sampling

The duration is selected which will provide the information desired. For peak concentrations and their causes, as short a sampling period as possible should be used. For background or average values weekly or monthly sampling is sufficient.

Any sampling period will only indicate the average concentration during that time period. Figure 3.1 illustrates the daily values of Se concentrations for May 1973 and the weekly and monthly averages calculated from these. The value of the average concentration for the whole year is given for comparison.

There is of course a limiting condition where very short sample duration results in a rapidly fluctuating record which may be difficult to read and perhaps uneconomical.

3.3.4 Height of Sampling

The choice of sampling height depends on the information required. If human exposure is to be measured then the ideal sampling height is at the height of the average person. If transport or area differences are being measured then rooftop or sampling towers are appropriate thus avoiding the pick-up of re-suspended particles.

Ambient sampling is usually at 5-15 metres. Table 3.1 illustrates the concentration difference at 5 and 52 metres for Zn, Fe, Mn and Cr at one site (Glasgow University). The results also illustrate the necessity of maintaining a constant sampling height for studying different areas.

FIGURE 3.1 SELENIUM CONCENTRATIONS IN THE ATMOSPHERE DURING MAY 1973 AND YEARLY AVERAGE.

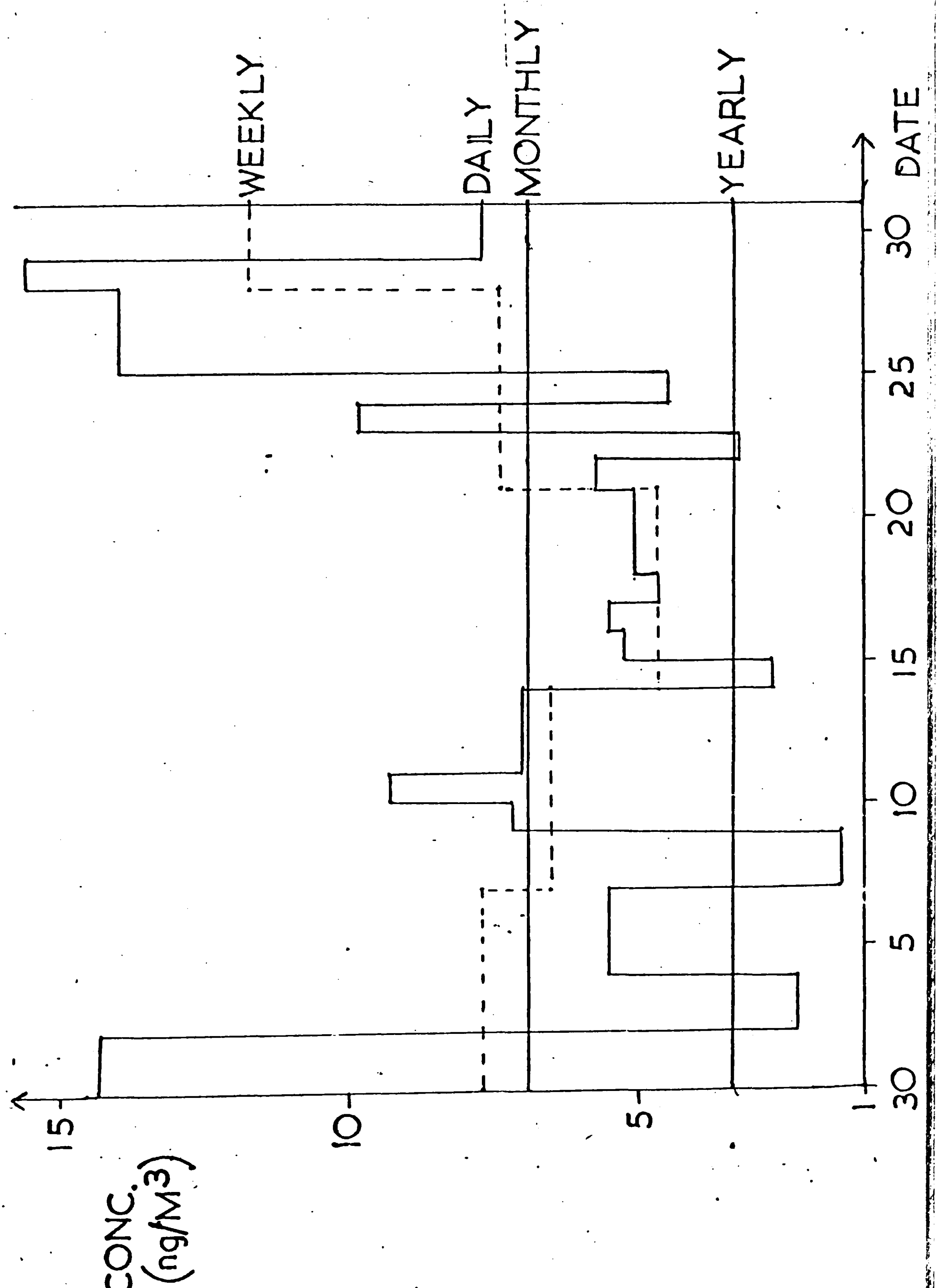


TABLE 3.1 VARIATION IN ELEMENTAL CONCENTRATION WITH HEIGHT (ng/M^3)
(ATMOSPHERIC PARTICULATES COLLECTED SIMULTANEOUSLY)

	Zinc		Iron	
SAMPLE No.	5 Metres	52 Metres	5 Metres	52 Metres
1	121.3	202.5	156.0	429.7
2	36.0	59.6	210.0	256.0
3	90.0	158.1	118.0	737.0
4	31.4	53.4	140.0	685.9
5	27.1	294.1	137.0	223.7
6	43.4	143.9	86.0	584.9
7	280.6	14.4	364.5	240.1
8	240.5	343.6	284.0	875.3
9	153.8	539.2	114.0	1026.2
10	307.9	282.3	247.5	875.3

	Manganese		Chromium	
	5 Metres	52 Metres	5 Metres	52 Metres
1	13.7	34.6	4.0	13.7
2	6.6	9.9	2.8	5.8
3	7.5	20.5	2.3	13.5
4	6.6	14.9	2.6	9.4
5	8.2	6.1	1.8	8.9
6	7.4	21.5	2.0	24.7
7	22.3	19.7	8.7	5.0
8	15.1	18.3	3.3	19.3
9	11.3	29.9	1.0	41.9
10	7.8	13.6	1.6	10.2

3.3.5 Location of Sampling

Again the location depends on what is required from the results. If a suspected source is being examined then the samples must be placed upwind of the source. If, however, ambient background levels are required then the samples must be placed such that it is representative of the area and that it is not adversely affected by a near-by pollution source. Values for different parts of Glasgow will be discussed later (see Section 3.6).

3.3.6 Collection Medium

The collection device must be suitable for the specific pollutant involved. It is not necessary that the collection be 100% efficient but it must be known and reproducible. An efficiency below about 75%, however, is generally not suitable for air pollution sampling (215).

Several collection devices have been used in air metal pollution studies.

In some cases natural collectors have been used. For example, some types of moss (e.g. Spanish Moss) are epiphytes, i.e. they derive all their nutrients from air and can therefore be used as indicators of metal levels in the surrounding air (216). Both moss growing naturally (217, 218) and suspended in nylon bags (219, 220) have been used.

In countries of heavy snowfall the snow has been used as a collector (221,222). The Pole snow profile experiments are of course well known (3, 223, 224) but snow has also been used as an indicator around factories (225, 226) and roads (227-229) and the effects of draining and dumping into rivers and lakes investigated (227, 230).

The annual growth of tree rings has been shown to be useful in gaining historical information on metal levels (231, 232). However, in a recent review article (233) this method was critically assessed in terms of metal uptake through roots and leaves and the possibility of metal movement within the rings.

City pigeons when compared to their country counterparts were found to have much higher lead contents in their hard tissues (234), and it was suggested that these might serve as indicators of pollution levels.

Finally, utilising the fact that due to the hot climate in Turin most houses have air conditioning units, it was suggested that the air filters in these units could be used as dust collectors (235).

The most common collection device is an air filter, i.e. a porous bed through which the air must pass. The filter materials most frequently used are paper, glass fibre and membrane.

Paper Filters (e.g. Whatman's) - These are mats of randomly orientated cellulose filters which force the air to change direction many times in an abrupt fashion so that inertial forces or direct collisions will bring the particles into contact with a relatively large surface area of the filter. These filters depend heavily on impaction to obtain high efficiencies for removal of small particles. (0.3 μm or less).

Glass Fibre Filters - These are similar to paper except that they are made of glass fibre rather than cellulose. They achieve high efficiencies without requiring impaction velocities due to the electrostatic nature of the matrix which tends to attract particles from the air stream.

Membrane Filters - The method of manufacture of these filters permits a uniformly controlled pore size (0.05-10 μm commonly used in air pollution). The pores constitute 80-85% of the filter volume and are made of esters of cellulose (especially cellulose acetate). These filters also tend to be electrostatic. Due to this, and by the building up of a precoat of collected particles on the surface these filters can collect particles much smaller than the pore size would suggest, e.g. 0.45 μm can collect particles down to about 0.1 μm.

These filters are also well suited for particle sizing since most of the particles are retained at or near the surface.

3.3.6.1 Choice of Filter Material

The choice of filtering material depends on what is required from the sample. Because of their high flow rates paper and glass fibre are useful for total particulate measurements, but tend to be hygroscopic and require equilibrating at constant humidity before weighing. Membrane filters on the other hand are non-hygroscopic and have extremely high collection efficiencics but also have a large resistance to air flow thus reducing the permitted sampling rate and consequently increasing the sampling time.

Another important factor when choosing a filter for elemental analysis is the impurity level in the filter paper itself. Table 3.2 illustrates the levels of impurity in glass fibre (GA - 6) Whatman (No. 1) and membrane (E.H.W.P.) as estimated by neutron activation analysis. It can be clearly seen that glass fibre is useless for analysis by this method due to the high Na content alone which masks other peaks. It can also be seen that membrane has the lowest impurity levels of all elements measured except chromium.

Considering all the above factors it was decided that membrane filters were the best choice for this work.

The advantages are -

i) low background levels of impurities

ii) non-hygroscopic nature enabling direct weighing

iii) extremely high collection efficiencies (98-99% down to an aerosol diameter of at least 0.3μm).

The disadvantages are -

i) They tend to be brittle and electrostatic especially after irradiation. This, however, was found to be less of a problem after experience and practice in handling the filters was obtained.

ii) The high collection efficiencies mean that loading and clogging takes place more rapidly than with other types of filters. This, as said previously, limits the rate of sampling and increases the minimum sampling time required and also of course decreases the maximum sampling time allowed.

TABLE 3.2 CONCENTRATIONS OF ELEMENTS IN FILTERS (ng/cm^2)
(UNLESS OTHERWISE STATED)

Element	Millipore EHWP	Glass Fibre GA-6	Whatmans No. 1
Br	8.65	+	ND
Co	0.29	1.21	0.72
Cr	20.04	35.12	2.97
Fe	376.6	1.9 *	0.31 *
Mn	4.72	+	5.80
Na	496.8	12.53 *	3.02 *
Sb	0.20	14.5	0.54
Sc	0.008	1.49	0.02
Se	8.1	ND	9.07
Zn	10.20	94.9	11.58

+ = not determined due to high sodium activity

* = μg/cm^2

ND = not detected.

MILLIPORE EHWP = 2.5 cm. diameter
GLASS FIBRE GA-6 = 15 cm. diameter
WHATMANS No. 1 = 9 cm.

For Cu - see page 56 Table 3.4

3.4 REPRODUCIBILITY OF FILTER PAPER BLANKS

The filter paper blanks for millipore in Table 3.2 were those obtained from the first box of 100 used by choosing five filter papers at random. A similar blank was carried out on the succeeding boxes as they were used. The results are given in Table 3.3 and indicate that inconsistencies exist from box to box. To determine whether these inconsistencies exist within one box the following experiment was carried out.

The boxes of 100 filters were separated into four lots of 25. In one of these lots the filters were divided into 5 sets of 5 consecutively from the top. In the remaining three, 5 filters were selected at random from each omitting the top and bottom 3 filters.

This process was repeated with another box.

The samples were analysed by atomic absorption for 9 elements. To give all the results was considered unnecessary at this stage since all nine elements showed the same pattern as depicted by Cu in Table 3.4 which was -

i) The first and last 5 filters had higher blank values than the inside filters (x20 in the case of Zinc). This indicated the wisdom of rejecting the first and last 3 filters when collecting samples.

ii) Apart from these filters the blank values within a lot of 25 were reproducible.

iii) Filter papers within one box of 100 had reproducible blank values.

iv) Filter paper blanks varied from box to box.

TABLE 3.3 VARIATION IN MILLIPORE BLANK VALUES WITH BOX (ng/cm^2) (ELEMENT LEVELS)

Element	Box 1	Box 2	Box 3	Box 4
Br	8.6	7.9	9.3	8.4
Co	0.29	0.41	1.1	0.65
Cr	20.04	18.68	14.13	10.51
Fe	376	97.8	407	133
Mn	4.72	4.95	4.0	4.28
Na	497	99.2	489	503
Sb	0.2	6.68	14.26	10.38
Sc	0.01	0.03	0.06	0.04
Zn	10.2	9.2	39.5	5.5
Se	8.1	6.2	6.5	7.4

TABLE 3.4 VARIATION IN BLANK VALUES OF COPPER IN MILLIPORE FILTER PAPER (ng/cm^2)

Filter Paper Description	Results for 5 Filter Paper Blocks	Results for 25 Filter Paper Blocks	Average for Box (100 Filter Papers)	Average for 4 Boxes
Box 1				
Lot 1				
1st 5 Filters	110.0			
2nd "	20.8			
3rd "	20.4	20.4±0.35		
4th "	20.1			
5th "	60.3		21.1±1.04	
Lot 2		20.4		
Lot 3		22.6		
Lot 4		20.9		
Box 2				
Lot 1				
1st 5 Filters	270.0			33.3 ± 12.34
2nd "	50.3			
3rd "	50.9	50.8±0.46		
4th "	51.2			
5th "	470.1		50.5±0.92	
Lot 2		49.5		
Lot 3		51.6		
Lot 4		50.0		
Used Box 1*			30.1	
Used Box 2*			30.6	

* Boxes Used for sample collection.

The average value obtained for each box with the standard deviations are given in Table 3.5 along with the values obtained from a random sample of 5 filter papers for Boxes 1 and 2 used for sample collection.

The small variations which do exist within one box are so small compared to the weight of element collected as to be insignificant.

TABLE 3.5 AVERAGE BLANK VALUES IN MILLIPORE FILTER PAPER (ng/cm^2)
(METAL LEVELS)

Element	Box 1	Box 2	Used 1	Used 2
Al	31.8±6.9	15.5±1.42	73.7	51.4
Cd	0.64±0.05	0.5±0.22	1.5	0.3
Cr	11.8±0.62	9.6±0.19	26.0	20.3
Cu	21.1±1.04	50.5±0.92	30.1	30.6
Fe	115.4±4.7	133.7±6.1	92.6	140.8
Mn	4.0±0.33	8.5±0.50	5.5	4.9
Ni	18.2±2.07	26.1±1.12	27.5	12.8
Pb	10.0±1.33	5.0±0.37	3.8	1.3
Zn	5.5±0.05	44.7±14.6	10.9	32.6

3.5 ATMOSPHERIC LEVELS OF TRACE ELEMENTS AND THEIR VARIATION WITH WEATHER

3.5.1 Sampling

As explained in the previous Section the sampling time is dependent on what is required from the results. In this case where variations in element levels were being examined and the effect of climate investigated daily samples would be ideal since the weather centre observations are on a 24 hour basis.

To summarise the previous section the factors which must be taken into account when sampling are -

i) Enough sample must be collected in order that the element can be measured.

ii) The sample must not be so large that clogging of the filter occurs.

iii) The sampling rate must be such as to take account of the filter's resistance to flow.

By trial and error it was found that 20-30M^3 of air were required for analysis and that this amount did not clog the filter. However, it was found that collecting this volume over 24 hours led to a large pressure drop across the filter with time. It was therefore necessary to collect over 48 hours. Figure 3.2 illustrates the variation of volume with time which indicates a uniform sampling rate and no clogging over this 48 hour period.

For practical reasons three samples a week were collected. Sampling was started at 9. 00 a.m. on Monday morning to coincide with the weather centre data and changed at the same time on Wednesday and again on Friday. This meant that the week-end sample was running for 72 hours but this did not clog the filter.

FIGURE 3.2 SAMPLING RATE OF MILLIPORE FILTERS WITH CHARLES AUSTIN M 361 PUMP

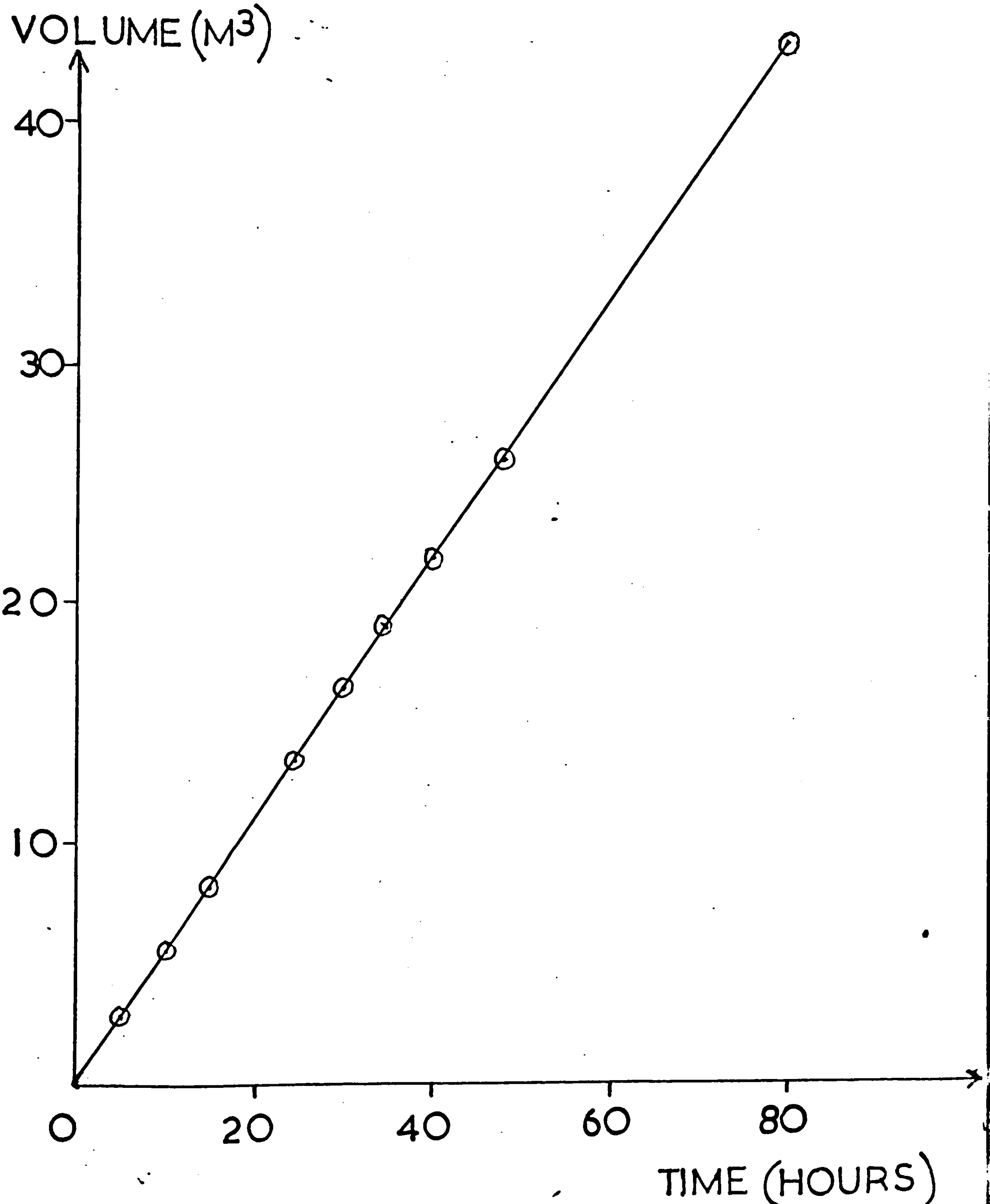


Figure 3.3 illustrates the apparatus used to collect the sample and is similar to that used by Warren Springs Laboratory (236). The pump was a Charles Austin model M 361 and was designed for continuous running. The sampling funnel was situated about 5 metres above ground level outside the Chemistry Department of Glasgow University approximately 50 metres from the nearest main road, using a 2.5cm. diameter membrane filters (E.H.W.P.)

After collection, the filter was heat sealed in clean polythene sheeting.

3.5.2 Analysis

The samples were analysed by neutron activation analysis followed by γ-ray spectroscopy.

This method is suitable for air pollution filters because -

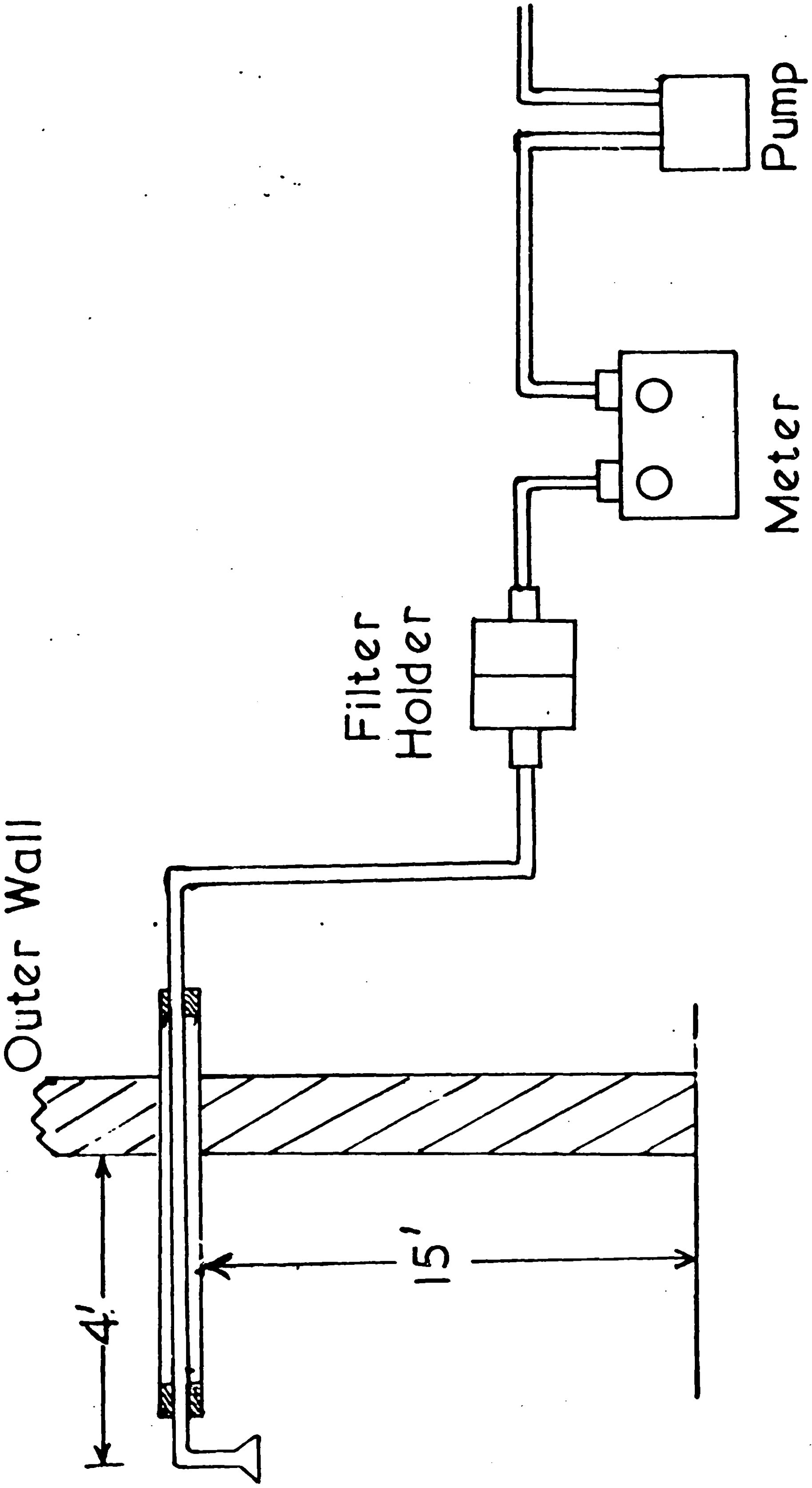
i) Carbon, nitrogen and oxygen, the major constituents in air particulates, have low neutron capture cross sections and hence do not exert matrix effects.

ii) Samples are thin and therefore there is little self absorption of γ-rays and shielding of neutrons.

3.5.2.1 Irradiations

Two irradiations of these samples were required. The first was for 15 minutes at a thermal neutron flux of 3×10^{12} n/cm^2/ sec. at the Scottish Reactor Centre at East Kilbride for the determination of Na, Mn and Br. The second was for 96 hours at 6×10^{12} n/cm^2/ sec. in the Dido Reactor, A.E.R.E., Harwell, England, for the other elements measured. For both irradiations standards were prepared by dissolving spectroscopically pure

FIGURE 3.3 APPARATUS FOR COLLECTION OF ATMOSPHERIC PARTICULATES



metals or metal oxides in suitable acids and placing 10 µl aliquots on filter discs. Each standard was prepared in triplicate and corresponded to 2-20 µg.

Standard kale whose elemental concentration is known (237) was irradiated along with the samples and standards to check the accuracy of the standards.

3.5.2.2 Counting

Table 3.6 presents the nuclear data for the elements determined (238). 1 hour after the first irradiation the samples and standards were counted with a 60 cm^3 detector (Nuclear Enterprises 2.2 KeV resolution at 1332 KeV; peak to compton ratio 24 : 1) in conjunction with a Nuclear Data 4400 system coupled to a Nuclear Data N D 812 computer. The dust samples were counted for 15 - 20 minutes for Na, Mn and Br and the standards for 1 minute. Figure 3.4 is a typical γ-ray spectrum obtained. The areas under the γ-ray peaks were calculated by the method described by Covell (239).

The longer lived isotopes produced during the 96 hour irradiation were counted 10 days and 30 days after the end of the irradiation.

These dust samples required count times of 1 - 2 hours and the standards 1 - 5 minutes. Figure 3.5 is a spectrum obtained after 10 days decay.

In an attempt to reduce manual handling the raw data from the spectrometer was punched on paper tape for processing by a KDF9 computer and peak areas, standard deviations and energy calibrations calculated (240). This, however, proved to be unsuccessful as mistakes were invariably made in punching and

TABLE 3.6 NUCLEAR DATA FOR ISOTOPES MEASURED BY NEUTRON ACTIVATION ANALYSIS

Isotopes	Half-life	Thermal neutron capture cross-section of parent isotope (Barns	Isotopic Abundance (%)	Energy of γ-ray Meausred (KeV)
^{24}Na	15h	0.40	100	1368
^{46}Sc	88.8d	25	100	889, 1120
^{51}Cr	27.8d	16	4.3	320
^{56}Mn	2.58h	13.3	100	847
^{59}Fe	45.1h	1.23	0.33	1099, 1291
^{60}Co	5.27Y	17	100	1173, 1332
^{65}Zn	243.6d	0.82	48.9	1115
^{75}Se	120.4d	55	0.87	265, 279
^{82}Br	35.5h	0.26	49.5	554, 777
^{110m}Ag	253d	4.2	48.2	937
^{124}Sb	60.3d	3.4	42.7	603, 1691
^{134}Cs	2.05Y	27.4	100	796
^{140}La	40.2h	8.8	99.9	487
^{169}Yb	32d	3200	0.14	308
^{177}Lu	6.7d	2050	2.6	208
^{181}Hf	42.4d	12.6	35.2	482
^{233}Pa from ^{232}Th	27d	7.4	100	312

FIGURE 3.4 γ-RAY SPECTRUM OF SHORT LIVED ISOTOPES DETECTED IN ATMOSPHERIC PARTICULATES IN GLASGOW.

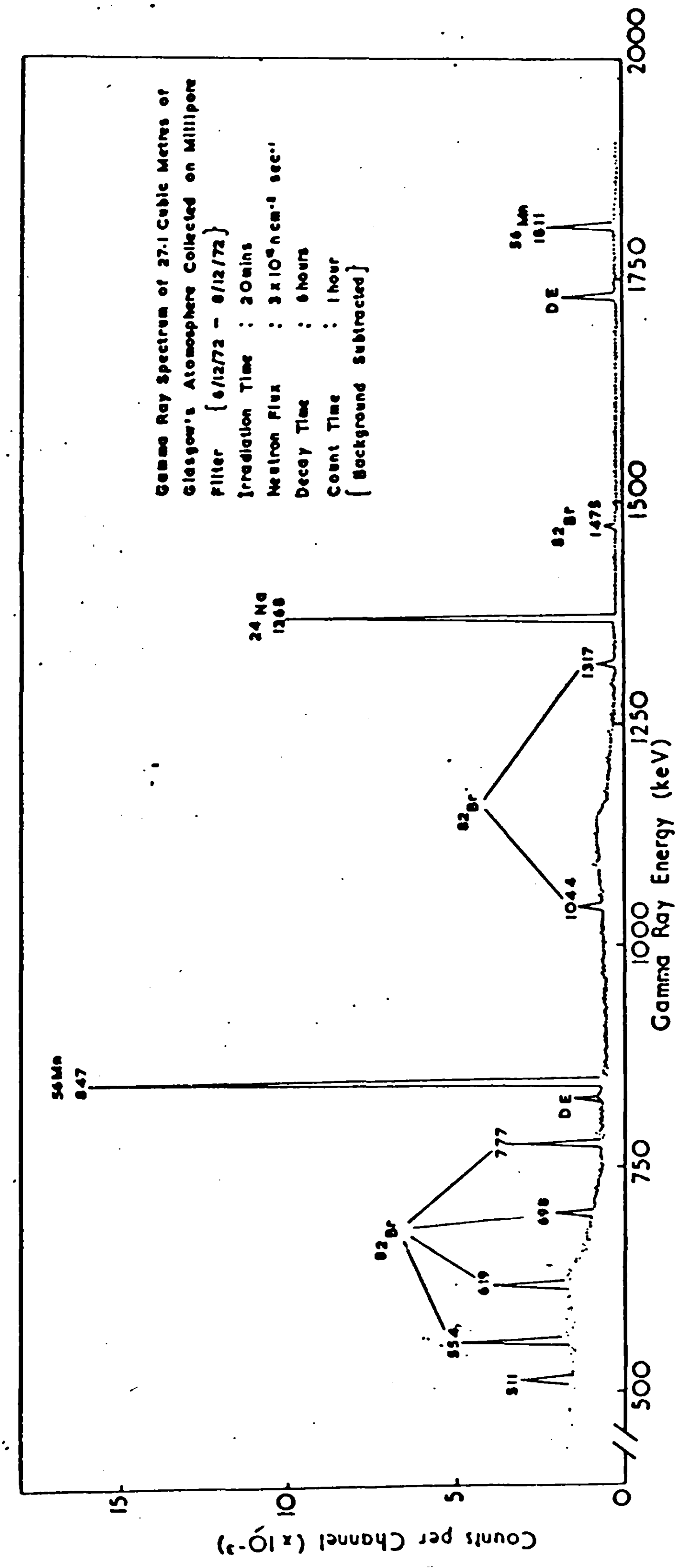
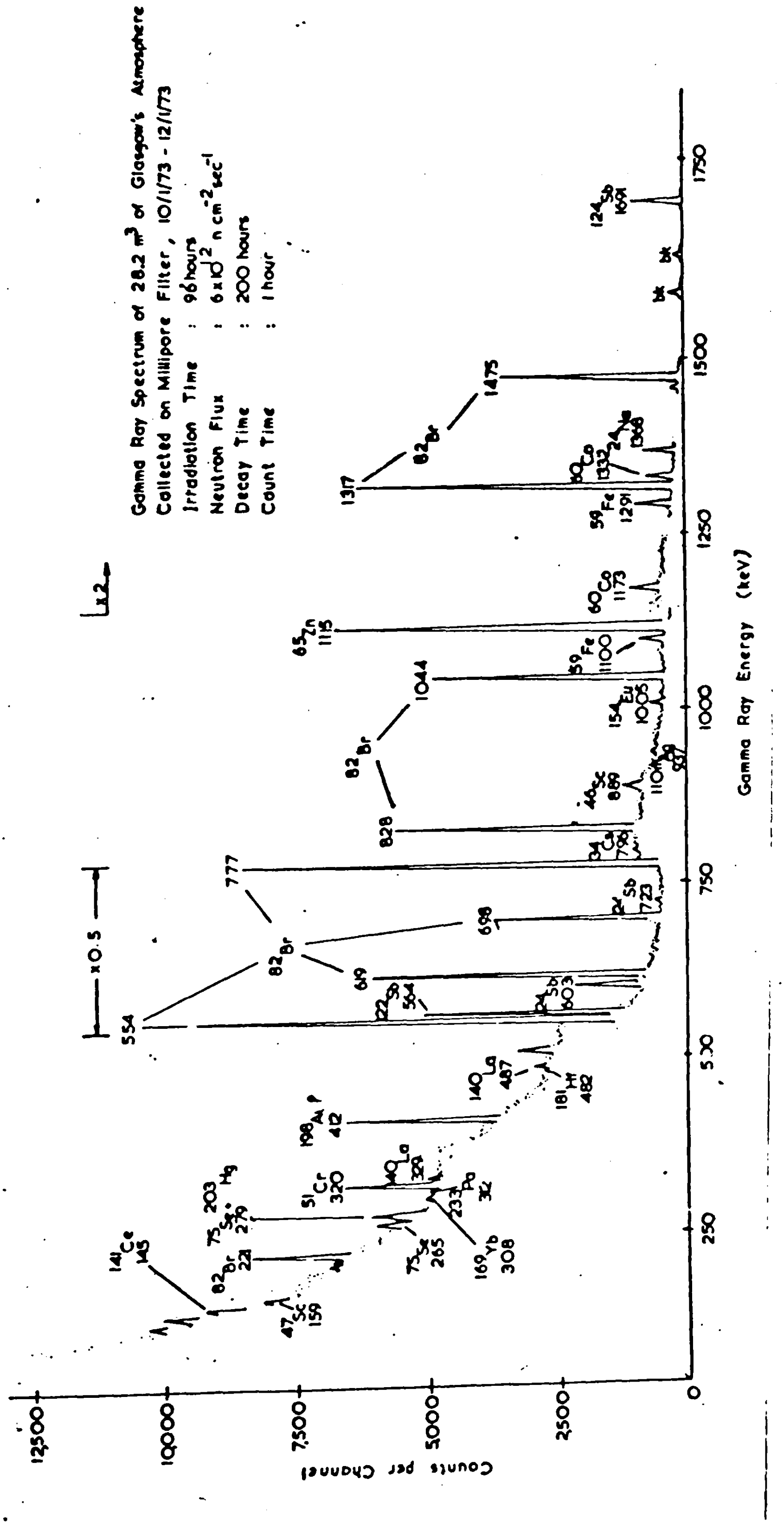


FIGURE 3.5 γ-RAY SPECTRUM OF LONG LIVED ISOTOPES DETECTED IN ATMOSPHERIC PARTICULATES IN GLASGOW.



the machine had a tendency to stick. Also small photopeaks located on the tails of neighbouring large peaks had still to be processed manually. For these reasons the programme was abandoned and the results calculated by hand.

3.5.2.3 Interferences

In instrumental neutron activation analysis where no chemical separation is carried out, interfering isotopes are removed simply by their decay or by ensuring that the energy of the reactor is such that they cannot be activated.

The first method is used when an 'interfering' isotope has a much shorter half-life than the isotope of interest. In Figure 3.5 it can be seen that ^{82}Br is still masking some peaks but after 30 days these Br peaks have virtually completely decayed, allowing the other isotopes to be measured, e.g. 554 KeV ^{82}Br masking 564 KeV ^{122}Sb.

The second method is used for isotopes with high neutron capture cross sections, e.g. ^{24}Na, ^{56}Mn and ^{82}Br.

However, despite these manipulations sometimes the most prominent photopeak of an isotope cannot be used because of interferences by neighbouring photopeaks of other isotopes, e.g. 844 KeV ^{27}Mg on 846 KeV. ^{56}Mn, and 559 KeV ^{76}As on 555KeV ^{82}Br and 564 KeV ^{122}Sb. The mono-energetic ^{803}Hg (279.1 KeV)is interferred by ^{75}Se (279.6 KeV) and vice-versa. For Hg a correction based on the pure ^{75}Se spectrum is applied and for Se determinations the alternative 265 KeV photopeak is used. Similarly there is a mutual interference effect of

^{65}Zn (1115 KeV) and ^{46}Sc (1120 KeV). Again the alternative ^{46}Sc 889 KeV peak is used and for Zn a correction based on a pure ^{46}Sc spectrum is employed.

3.5.2.4 Limitations

From Table 3.6 it can be seen that Mn with a half-life of 2.58 hours is the shortest half-life used. This is because the minimum delay time between the end of irradiation and the counting of the sample is 45 minutes and represents the travelling time from the Reactor Centre and Glasgow University. This means that such elements as Cu, As, V, S and Al all with half-lives less than 10 minutes could not be measured.

Similarly with the longer irradiation period, because of the delay in getting the samples back to Glasgow (4-5 days) the shortest half-life usable was that of ^{140}La (40.2 hours) and even this could only be determined on the first five or six in each batch before the activity was lost.

Remembering that saturation activity is reached at irradiation times greater than or equal to seven times the half-life (see Section 2.6) then activities cannot be increased to last longer for counting simply by increasing the length of time in the reactor and must be accepted as a limiting factor in this method when a nuclear reactor is not immediately at hand.

Because of this the 45 elements which can be determined under ideal conditions are reduced to the 17 elements listed in Table 3.6.

3.5.2.5 Accuracy

To test the accuracy of the method three standard filter papers obtained from the International Atomic Energy Agency in Vienna were analysed. The results are given in Table 3.7 and the "true" value and range claimed by the Agency in Table 3.8 (241). As can be seen from these two Tables the method is giving a true indication of the atmospheric levels of these elements.

From counting statistics and reproducibility of replicate analysis the accuracy of the results is estimated as follows -

Br, Co, La, Mn, Na, Sb, Sc, Zn - 10%

Cr, Fe, Se, Th - 20%

Ag, Cs, Hf, Lu, Yb - 30%.

TABLE 3.7 ELEMENTAL CONCENTRATIONS FOUND IN STANDARD FILTERS (μg) MEASURED BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS.

	Cr	Fe	Mn	Se	Zn
Filter No. 1	1.91	198.4	4.1	0.85	70.8
Filter No. 2	1.93	201.0	4.3	0.81	72.1
Filter No. 3	1.90	186.6	4.0	0.84	73.4

TABLE 3.8 "TRUE" ELEMENTAL CONCENTRATIONS SPOTTED ON STANDARD FILTERS (μg)

	"True" Value	Range
Cr	1.85	1.76-1.94
Fe	194	184.3-203.7
Mn	4.2	4.15-4.41
Se	0.85	0.81-0.89
Zn	74	70.3-77.7

3.5.3 RESULTS

The concentration of elements in dust particulates collected in Glasgow are given in Table 3.9. The results for Br, Co, Cr, Fe, Mn, Na, Sb, Se, and Zn represent 165 samples from 1st August 1972 - 31st August 1973. The results for La represent 50 samples at various times during the above period for reasons already discussed. The results for Cs, Hf, Lu, Th and Yb represent 60-70 samples again at various times during the above period (not all necessarily from the same sample). This is due to the fact that the appearance of these elements in the samples was sporadic and the range and mean were calculated from those samples in which the element was detected.

The results for similar industrial cities in other countries and also the threshold limit values for 1973 for factories in Great Britain are included for comparison. The individual results for the 10 elements collected over 13 months are illustrated in Figure 3.6, and emphasise the wide scatter of results and the need for some sort of interpretation.

The results indicate the wide variation in element content of atmospheric particulates, but in spite of these fluctuations the mean values obtained are generally in agreement with results quoted for other parts of the world.

It is immediately obvious that even the maximum values found for these elements in ambient air are in no case anywhere near the threshold values. However, it is unwise to depend upon industrial exposure data and to use industrially allowable levels as community standards because -

TABLE 3.9 ATMOSPHERIC LEVELS OF TRACE ELEMENTS (ng/M^3)

	Glasgow August '72 - August '73		Chicago U.S.A. (124)	Niles Michigan U.S.A. (124)	Heidelberg Germany (129)	Texas U.S.A. (242) (50 Stations)	San Francisco U.S.A. (121)	Paris France (243)	Glamorgan Wales (117)	Industrial Limits (mg/M^3) (244)
	Range	Mean								
Ag	0.3-12.9	2.7	2.4	1	1	-	0.05-0.2	-	-	0.01
Br	11-300	66.0	67	43	30.5	20-470	0.05-0.2	433	56	0.7
Co	0.06-14.4	0.8	2.6	0.95	2.2	-	0.46-1.6	6.67	5.8	0.1
Cr	0.1-89.8	8.0	113	9.5	4.6	50-1100	2.2-16.0	15.1	13.5	0.5
Cs	0.06-3.0	0.9	-	-	-	-	-	-	0.33	-
Fe	17-7100	294	13,800	1900	1041	100-10,000	610-3000	3500	6090	1.0
Hf	0.03-0.7	0.3	-	-	-	-	-	-	-	0.5
La	0.07-2.38	0.8	5.9	1.3	1.3	-	0.69-3.1	3.42	1	-
Lu	0.01-0.8	0.2	-	-	-	-	-	-	-	-
Mn	0.6-290	23	255	62	23.6	20-1700	5-31	82.5	24	5.0
Na	66-2075	331	455	170	224	-	2600-6300	1823	1020	2.0 (as hydroxide)
Sb	0.02-55.2	5.5	32	6.3	6.3	-	0.68-3.8	50.8	2.9	0.5
Sc	0.01-2.85	0.11	3.1	1.2	0.50	-	0.48-2.1	0.7	0.21	-
Se	0.01-27.7	3.3	3.8	2.5	-	-	0.31-1.9	-	1.7	0.2
Th	0.01-1.0	0.3	1.3	0.27	0.27	-	0.06-0.36	-	0.16	-
Yb	0.3-4.3	1.3	-	-	-	-	-	-	-	-
Zn	7.7-3646	319	1400	140	-	5-1770	27-500	-	367	5 (as oxide)

- = Not Determined

FIGURE 3.6 GRAPHICAL REPRESENTATION OF ATMOSPHERIC LEVELS OF ELEMENTS, SMOKE AND SO_2 AT GLASGOW UNIVERSITY AUGUST '72 - AUGUST '73.

FIGURE 3.6 (CONTD.)

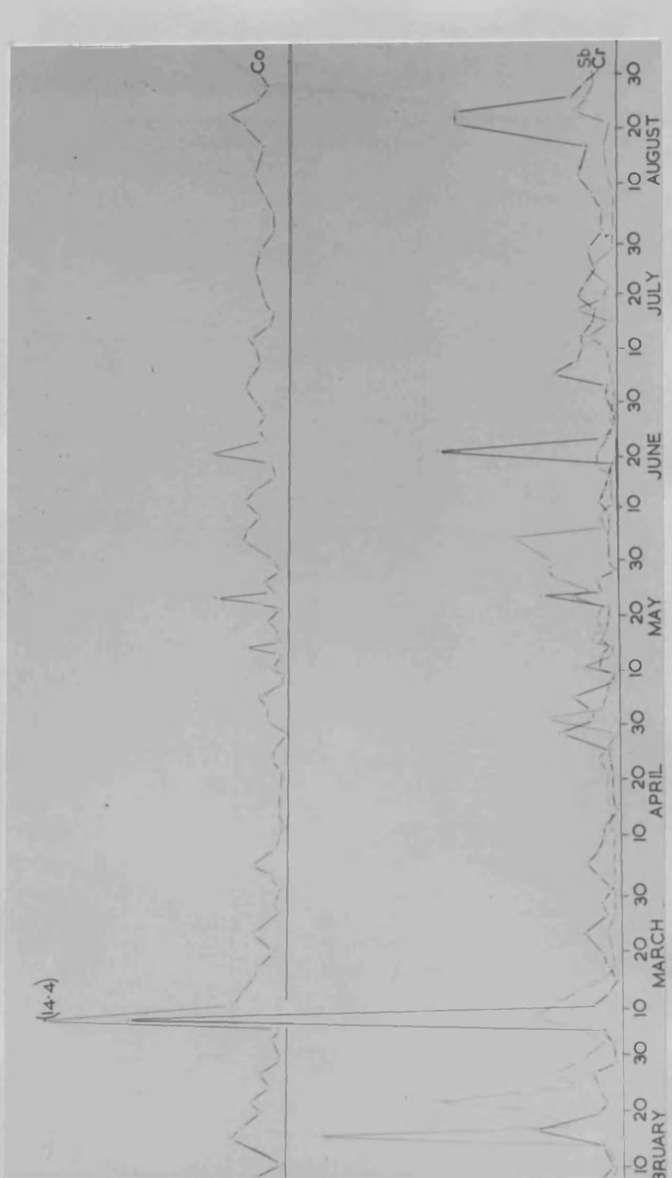


FIGURE 3.6 (CONTD.)

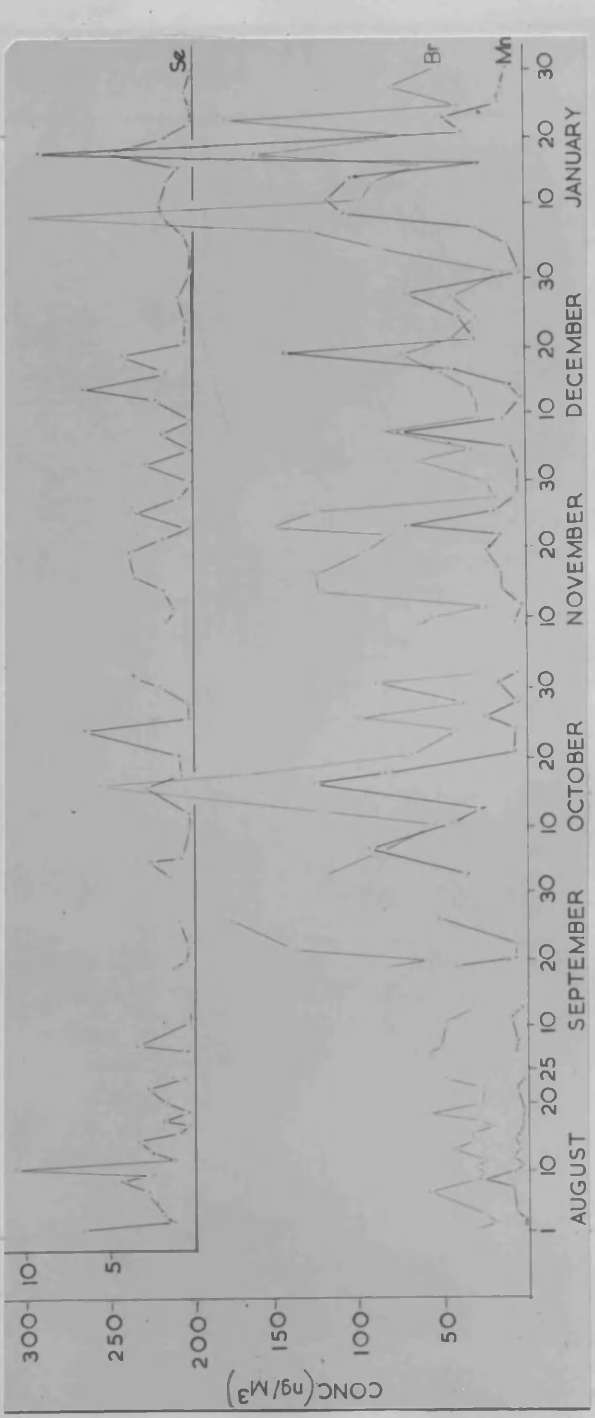


FIGURE 3.6 (CONTD.)

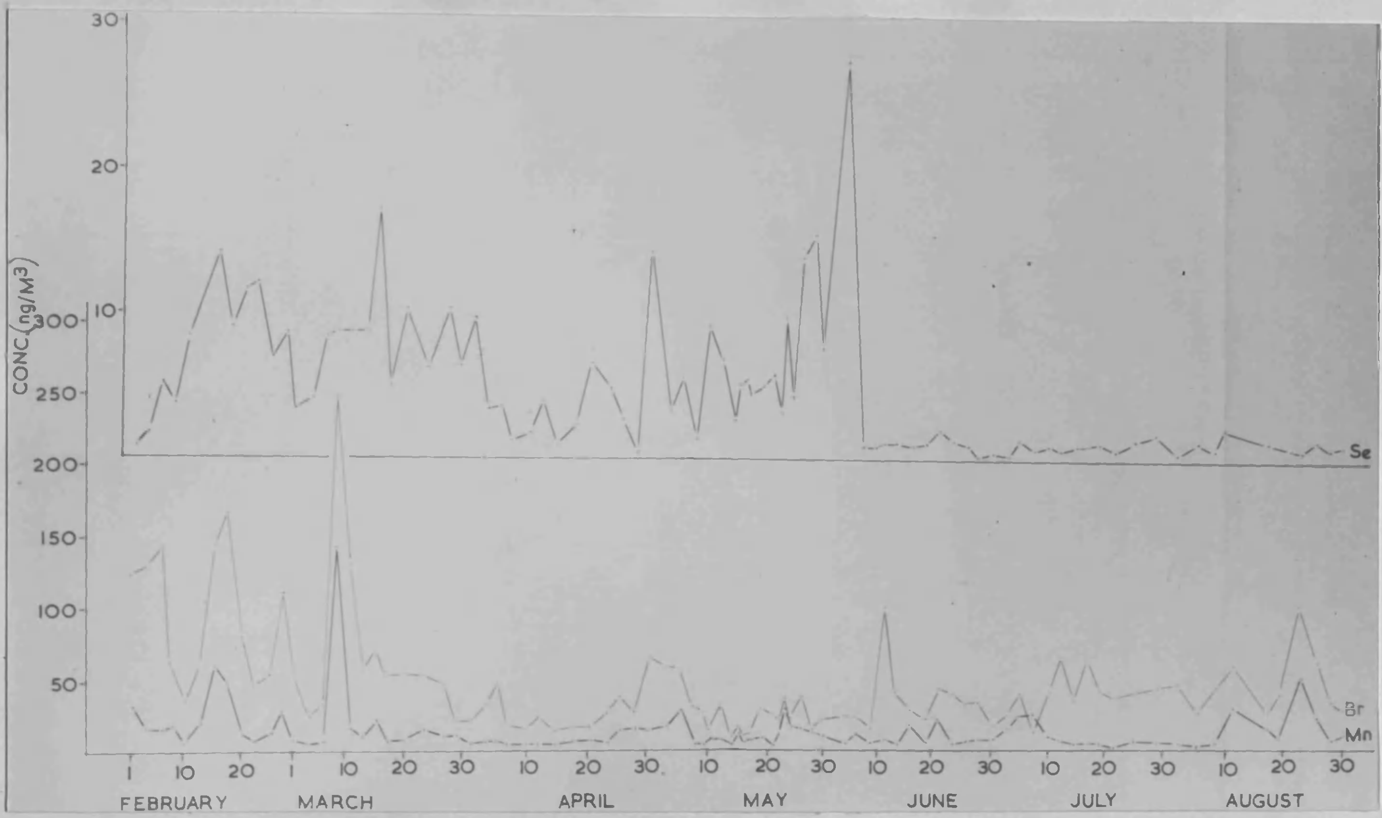


FIGURE 3.6 (CONTD.)

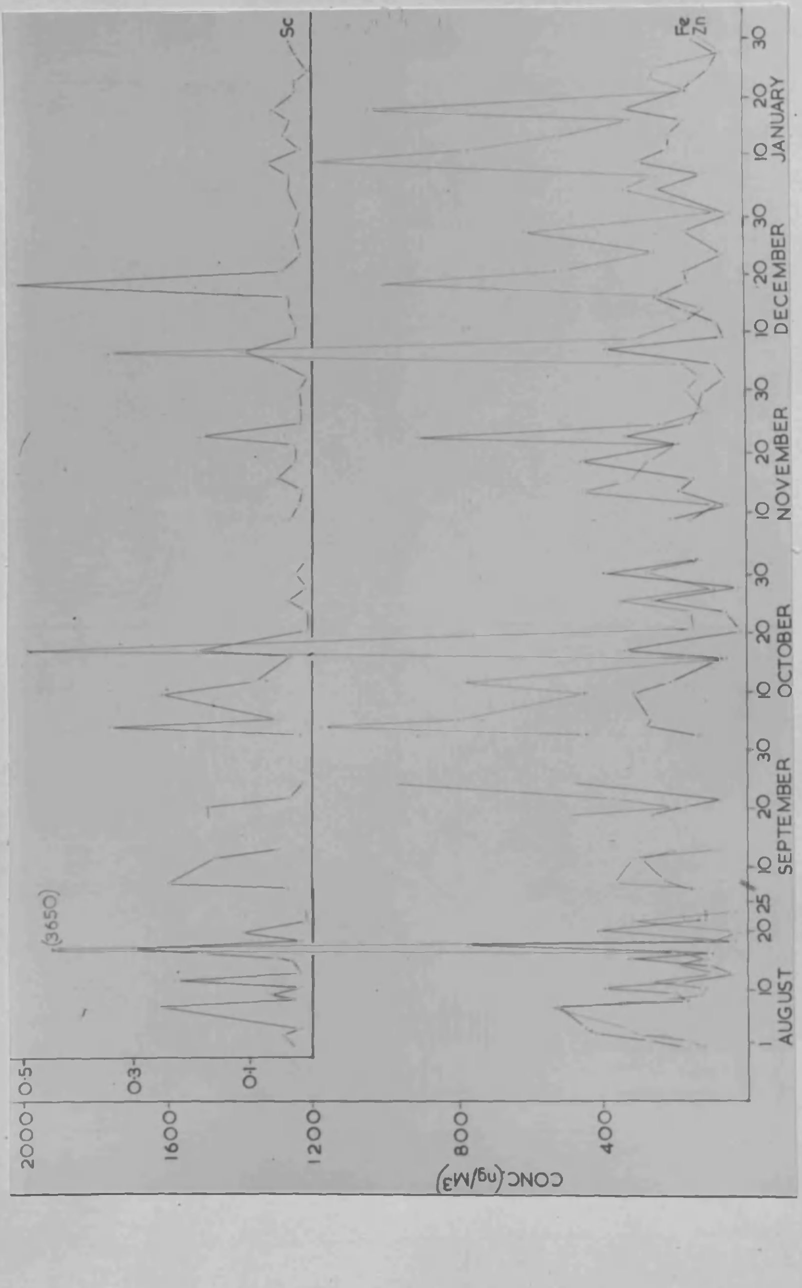


FIGURE 3.6 (CONTD.)

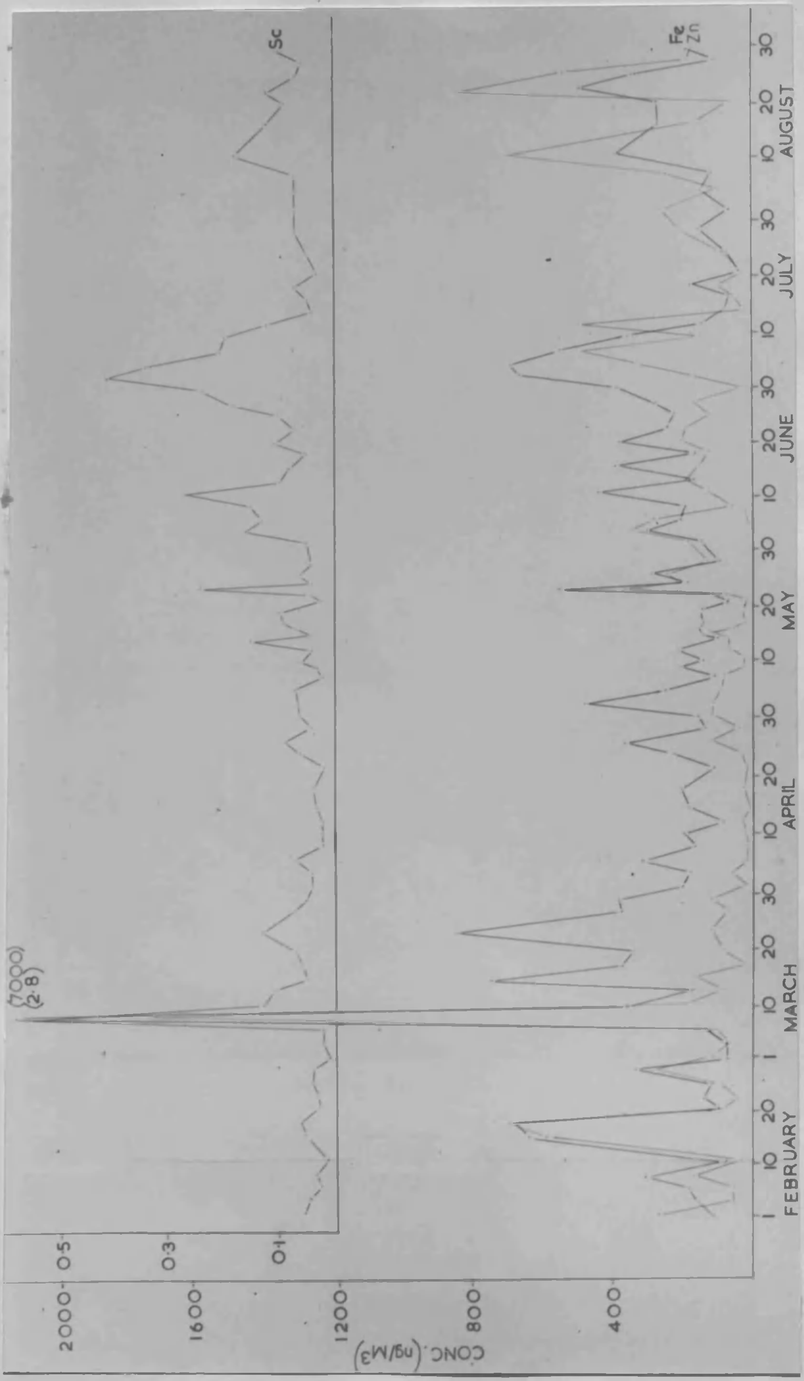


FIGURE 3.6 (CONTD.)

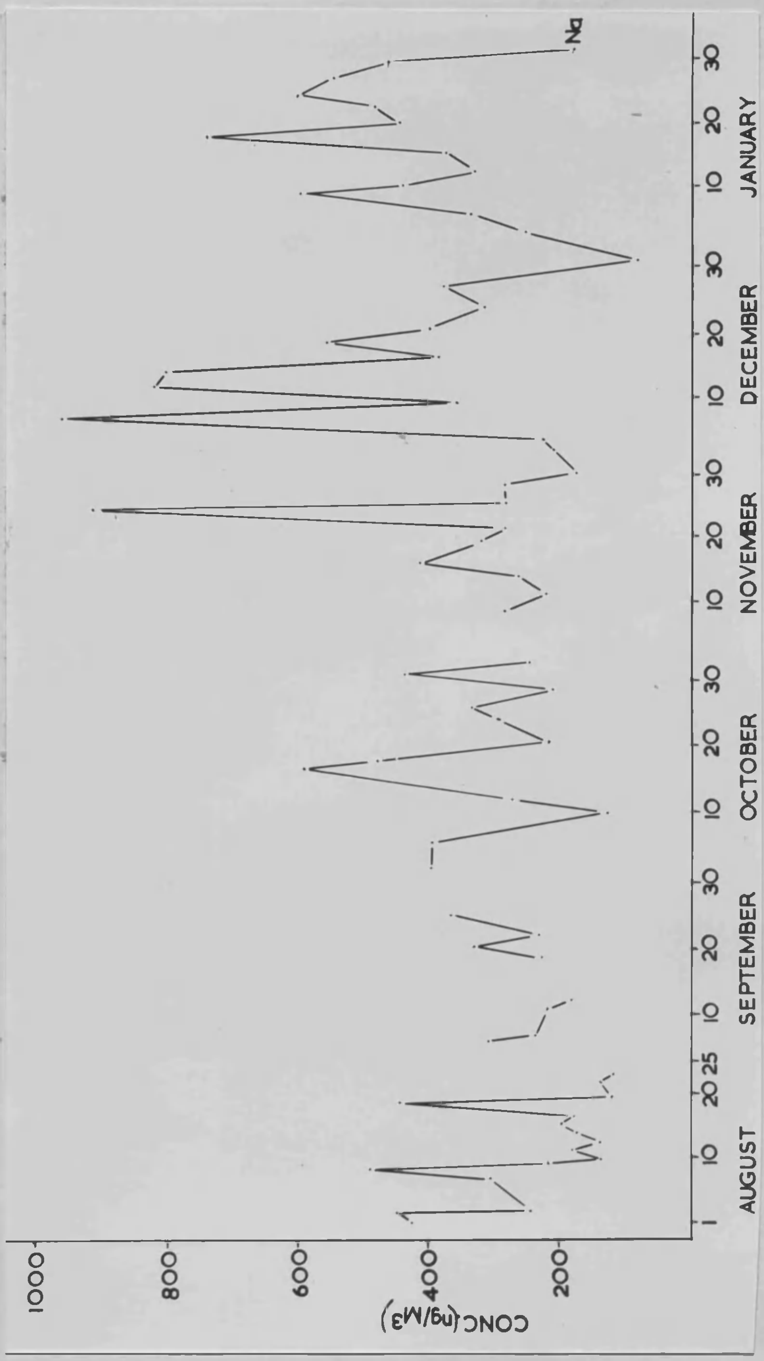


FIGURE 3.6 (CONTD.)

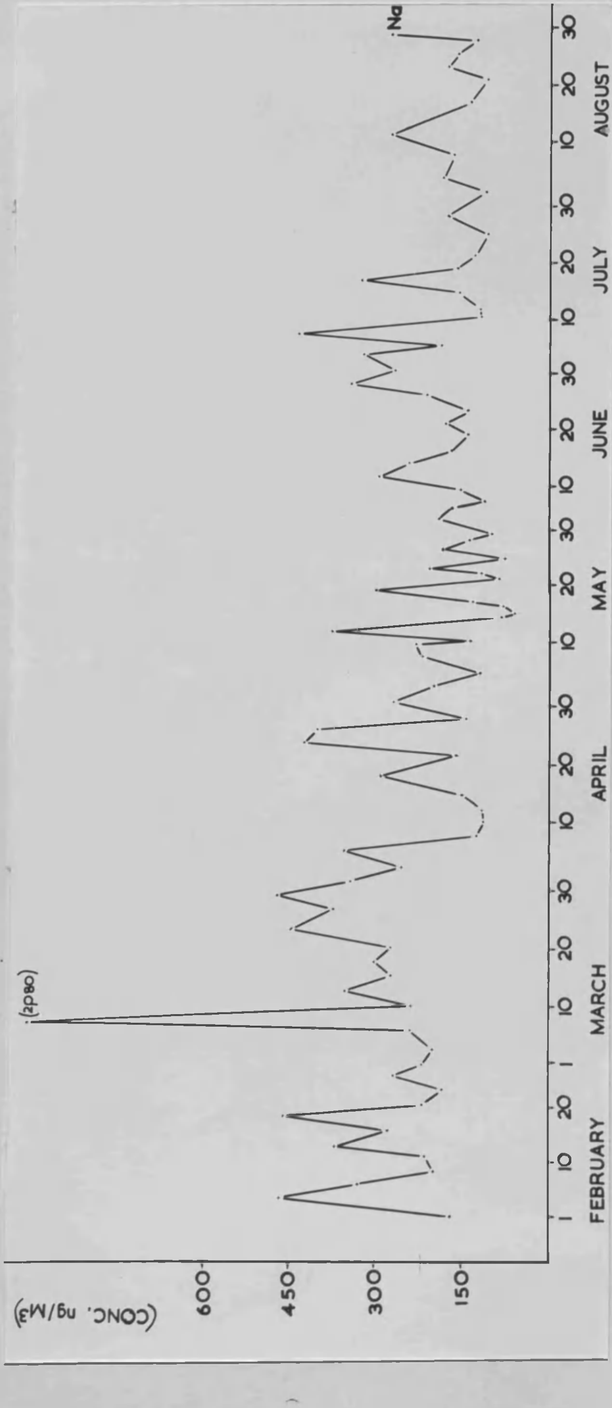


FIGURE 3.6 (CONTD.)

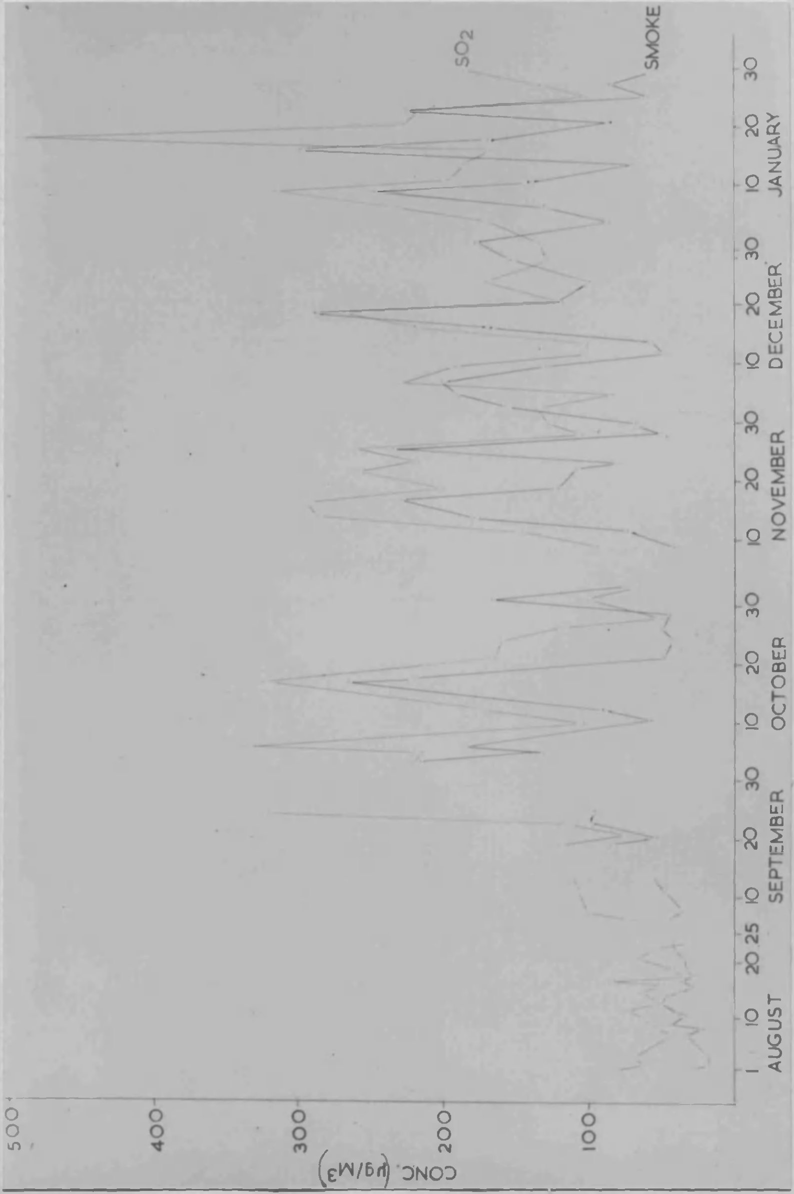
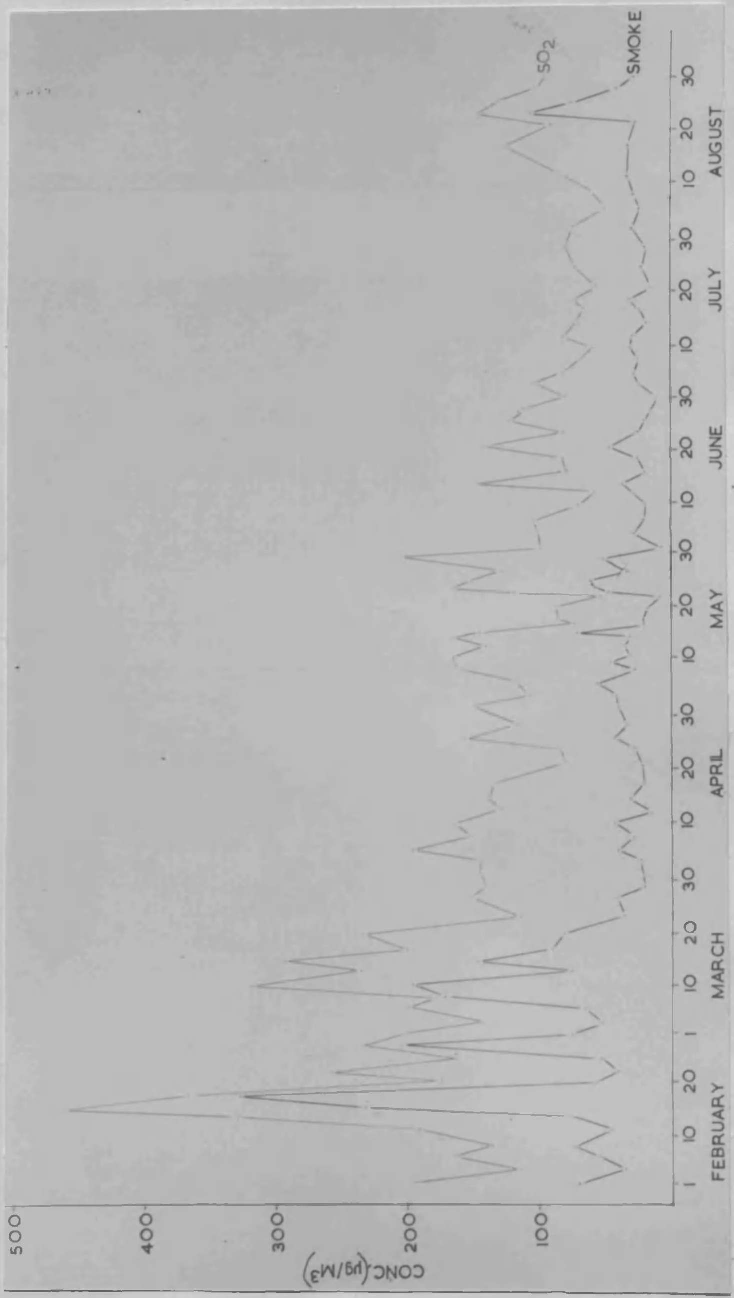


FIGURE 3.6 (CONTD.)



i) Workers are usually in a controllable occupational atmosphere which is confined in its exposure to a limited area (2).

ii) Exposed persons are usually in good health and are removed if they show idiosyncracies to a particular pollutant (2).

iii) They are usually younger and healthier than the general population (2).

iv) In the normal working week of 40 hours they have 180 hours of non-exposure (2).

v) They are usually exposed to a single pollutant. (However, it must be pointed out that these workers are probably more at risk generally since they are also exposed to general urban environment outside working hours) (2).

vi) Threshold limit values for industrial exposure reflect the capacity for detoxification of pollutants by the body and may be inapplicable to air pollution since continuous exposures do not give the same possibilities for excretion or detoxification of pollutants during times when more are being absorbed (195).

3.5.3.1 Correlation of Elements

As can be seen from Figure 3.6 in general the elements, smoke, and SO_2 trends follow each other. However, in order to attempt to place these results on a mathematical basis, straight line correlation coefficients were calculated by computer programme on the 158 samples. The results are given in Table 3.10 and all are significant at the 95% level or greater (30 out of 36 being at the 99.9% level). Total smoke and SO_2 levels were calculated for the

TABLE 3.10 CORRELATION COEFFICIENTS OF ELEMENTS WITH EACH OTHER AND SMOKE AND SO_2

(ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY 1973-1975.)

Cr	Cr									
Co	0.61	Co								
Br	0.23	0.44	Br							
Fe	0.58	0.93	0.34	Fe						
Mn	0.27	0.42	0.62	0.30	Mn					
Na	0.43	0.73	0.52	0.66	0.54	Na				
Sb		0.22	0.27	0.17	0.23	0.12	Sb			
Sc	0.56	0.91	0.27	0.93	0.30	0.61	0.19	Sc		
Se				0.16			0.41		Se	
Zn	0.43	0.55	0.61	0.44	0.69	0.56	0.36	0.44		Zn
Smoke		0.26	0.64	0.14	0.54	0.35	0.26			0.39
SO_2		0.12	0.61		0.59	0.31	0.33		0.28	0.25

sampling periods from daily levels at the Glasgow Art Gallery's site of the Smoke Officer. This was the most suitable site being adjacent to the University. The missing values (Table 3.10) were deliberately omitted as their coefficients of significance were less than 95%.

Some very good correlations are evident, namely, Fe/Sc, Fe/Co, Co/Sc and to a lesser extent Co/Cr, Na/Sc, Mn/Zn, Co/Na and Fe/Na. Many more are in the moderate correlation coefficient bracket and taking into consideration the dynamic nature of the atmosphere they are probably quite meaningful.

Three of the results are in extremely good agreement with those of John _et al_ (121) namely, Fe/Sc, Fe/Co and Co/Sc. John _et al_ also had correlation coefficients of 0.9 and greater for the combinations of Co, Cr, Mn, Sb and Sc. Their samples were, however, taken in a rural setting (San Fransciso Bay area) and were thus mainly soil derived. (See Section 3.5.3.3).

Another interesting point is the relationship between Sb and Se, the two most volatile elements in the group. It will be noted that apart from Fe, Sb is the only element which bears any relationship to Se and that in the case of Sb the relationship with Se is the best of all elements measured.

In these results Br and Mn display the best relationships with total smoke and SO_2 but why this should be so is difficult to understand.

The Se/SO_2 coefficient is disappointing since Se and S are recognised as being isomorphic. Most of the natural sources of Se are from S bearing minerals. The Se/S ratio was calculated from monthly averages (S being calculated from SO_2) and the results are given in Table 3.11, together with those for Buffalo and Cambridge, U.S.A., and also values for coal and crude oil used in U.S.A. (140). As can be seen the average value for Glasgow is an order of magnitude lower than the other two although the range lies within that of Cambridge. The difference between Buffalo and Cambridge is explained in terms of differing fuel consumption habits. This may well be the explanation for the difference in the Glasgow situation as well. There will almost certainly also be a difference in the Se/S ratio of Scottish fossil fuels compared to those employed in the U.S.A. study.

3.5.3.2 Seasonal Variations

Monthly averages were calculated from daily values and are plotted in Figure 3.7.

The following points can be made about the graphs -

i) Apart from Cr there is good agreement between the results for August 1972 and August 1973.

ii) The good correlations noted earlier between Br, smoke and SO_2 are evident. Br has two definite peaks: September/October/November and January/February/March, i.e. the Autumn and Winter months. The December result is curious in that there is a definite reduction in level despite being the middle of Winter.

iii) The trends for Zn and Mn are obscured by peaks in October. However, by removing two peak values well in excess of the remaining values occurring during 4-5/10/72 and 17-18/10/72 when there were 11 hours of calm winds with 4 hours of fog

TABLE 3.11 SELENIUM - SULPHUR RATIO IN ATMOSPHERIC PARTICULATES AT GLASGOW UNIVERSITY 1972-73.

	Range	Average
Glasgow	$0.1\text{x}10^{-4}$ - $1.1\text{x}10^{-4}$	$0.04\text{x}10^{-3}$
Buffalo	$0.5\text{x}10^{-3}$ - $1.6\text{x}10^{-3}$	$0.9\text{x}10^{-3}$
Cambridge	$0.1\text{x}10^{-4}$ - $4.4\text{x}10^{-4}$	$0.1\text{x}10^{-3}$
Crude Oil (U.S.A.)	$0.1\text{x}10^{-4}$ - $0.6\text{x}10^{-4}$	$0.5\text{x}10^{-4}$
Coal (U.S.A.)	$0.5\text{x}10^{-4}$ - $5.0\text{x}10^{-4}$	$2.9\text{x}10^{-4}$

FIGURE 3.7 MONTHLY AVERAGES OF ATMOSPHERIC LEVELS OF ELEMENTS, SMOKE AND SO_2 AT GLASGOW UNIVERSITY 72-73

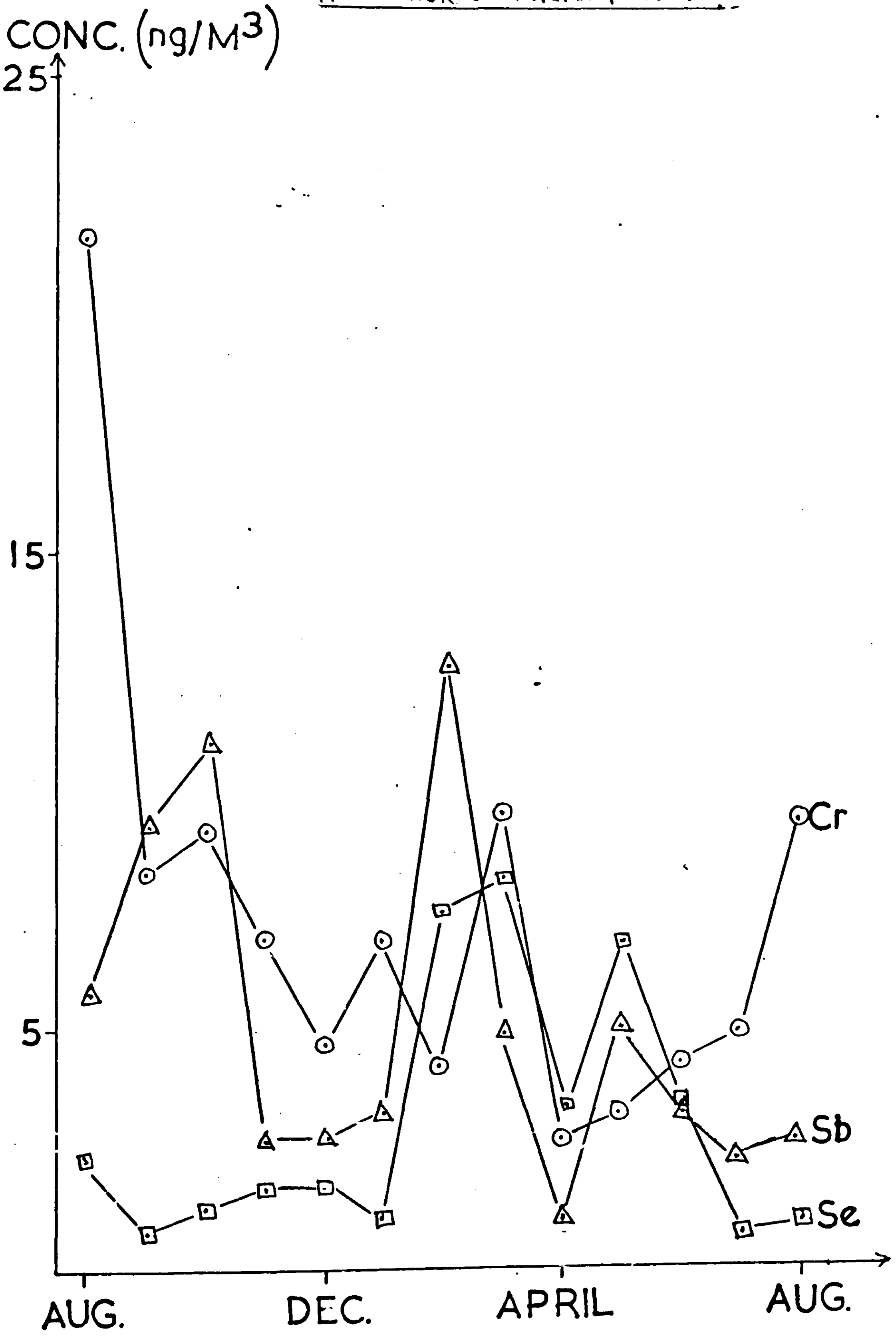


FIGURE 3.7 (CONTD.)

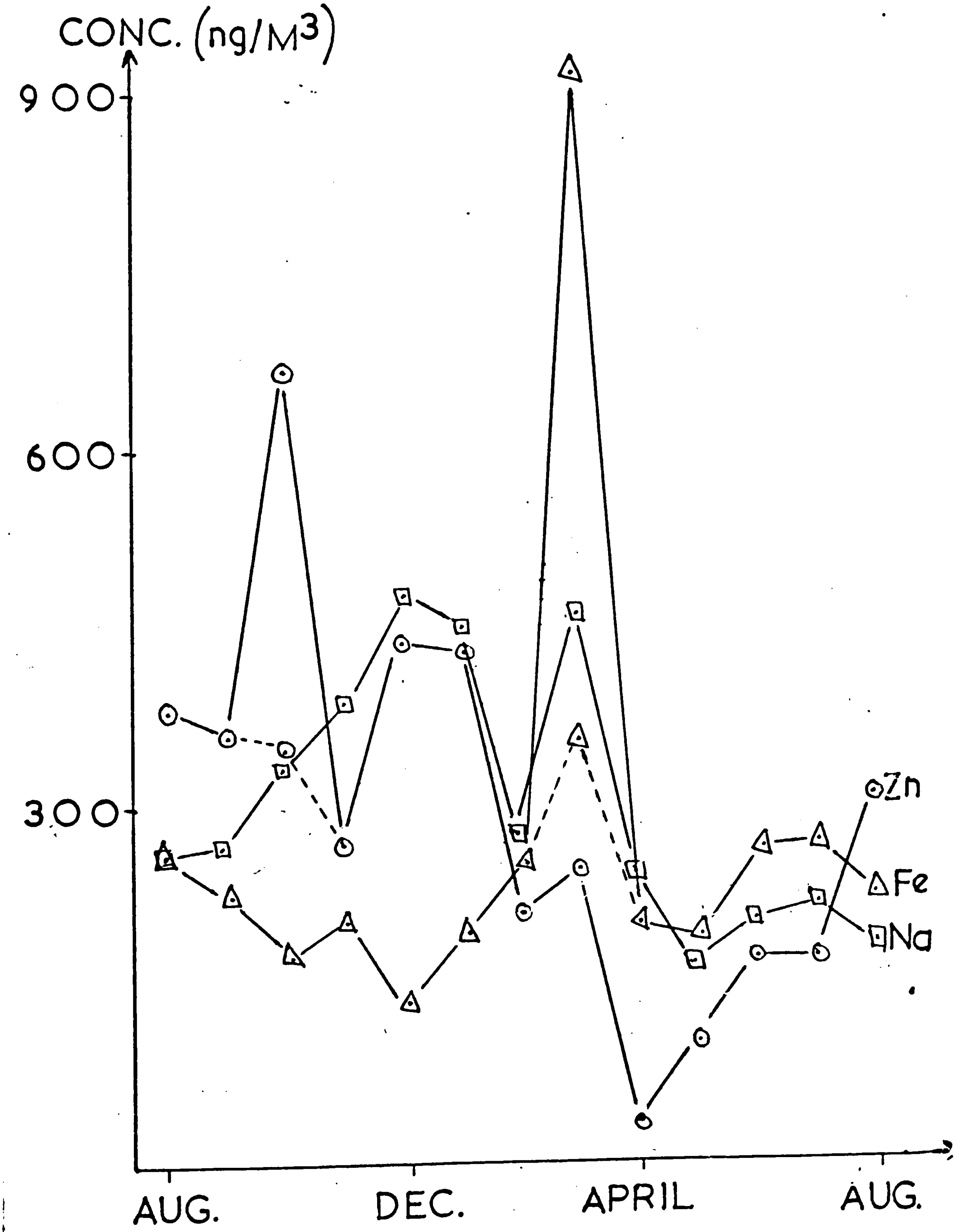


FIGURE 3.7 (CONTD.)

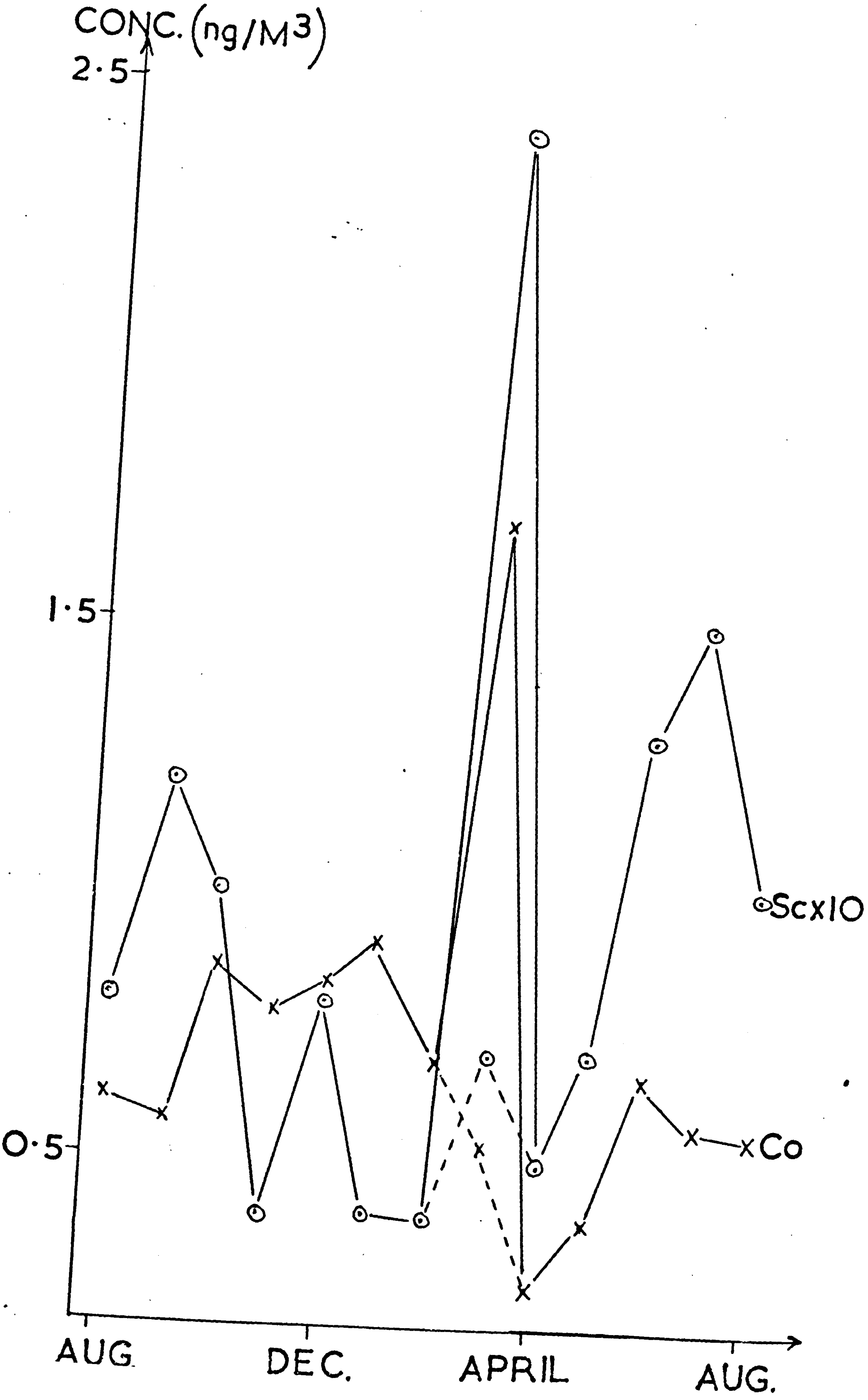
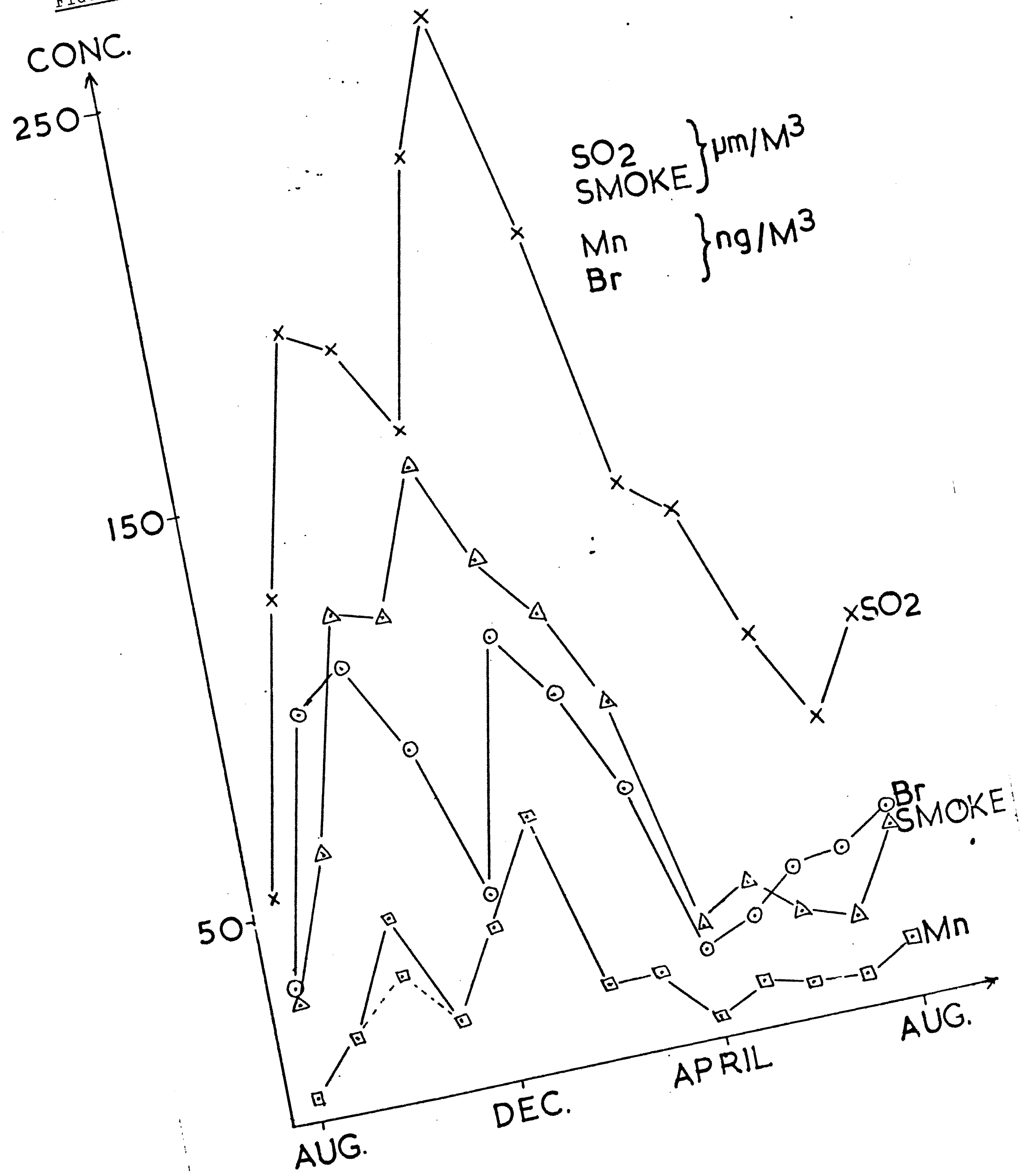


FIGURE 3.7 (CONTD.)



and 13 hours of calm winds with 6 hours of fog respectively, the trend becomes more evident. Peak values occur during December and January and lower values during the Summer.

The justification for removing these two peaks will be discussed later. (See Section 3.5.3.4.7).

iv) Similarly be removing 1 peak value for Na and Co during 7-9/3/73 with 20 hours of calm winds with 10 hours of fog again gives a trend of peak levels covering the October/January period and lower values during the Summer months.

v) The patterns of the two volatile elements Se and Sb after October are in good agreement as far as peaking and troughing are concerned, although the graphs intersect twice. This would also help to explain why the correlation coefficient is not as high as might be expected. The peaks are also moved slightly to the right and occur more in Spring and Summer. Whether this is a reflection of temperature affecting the residence times of these volatile elements is an open question at this stage.

vi) Fe does not vary much throughout the seasons. The large value for March is reduced drastically by removing the same sample as for Na and Co. (7-9/3/73).

vii) For Cr and Sc there are no apparent trends with random fluctuations throughout the year.

To summarise, after removing peaks for the reasons given above there is a general trend of higher levels during Winter months reflecting perhaps more fuel consumption.

The exceptions are Se and Sb the volatile elements which tend to peak during Spring and Summer and their results are in better agreement than might be suggested by their correlation coefficient. Fe is relatively stable throughout the year as might be expected from the continuous processes involved in iron and steel works. Finally Cr and Sc seem to be independent of season and fluctuate randomly.

Although these results by and large are what would be expected it must be said that they are based on one year's sampling and although the August 1972 and August 1973 results are in good agreement a further year's results would have strengthened or refuted the conclusions made and could also improve the Cr and Sc seasonal dependency. (In fact the Cr results for August 1972 (21.6ng/M^3) and August 1973 (9.4ng/M^3) are the only ones which are not in agreement.

3.5.3.3 Enrichment Factors

Several workers have attempted to explain the source of atmospheric elements by comparing the ratio of the elements to some standard in the aerosol with that of a reference material (121, 127, 129, 245-251). The two main reference materials which have been used are soil or crustal rock and the sea. These of course are obvious choices - once thought of - the sea being more relevant to coastal aerosols and soil to inland sites. The standard is usually an element which is relatively abundant in both the reference material and in the aerosol, e.g. Na would be used when the sea is the reference material while Al or Fe would be used when soil is the reference material. Any element which is present in both the reference material and in the aerosol can, however, be used and in one study (245) Sc which is a relatively minor constituent of aerosols was used.

The enrichment factor, E(x), is defined as -

$$E(x) = \frac{\text{Conc. X aerosol}}{\text{Conc. R aerosol}} \bigg/ \frac{\text{Conc. X reference}}{\text{Conc. R reference}}$$

Where Conc. X aerosol and Conc. X reference are the concentrations of element X in the aerosol and reference material respectively. Similarly Conc. R aerosol and Conc. R. reference are the concentrations of the normalising element in the aerosol and reference material respectively.

If E = 1 for element X, the ratio of it to the normalising element is the same in the aerosol as in the reference material. If E = 2, the ratio of it to the normalising element is twice as high in the aerosol as in the reference material, i.e. the element X is enriched by a factor of 2 in the aerosol. If all the elements in the aerosol have E = 1 the composition of the aerosol and the reference material are exactly the same.

In the present study enrichment factors were calculated with reference to soil and to crustal rock where soil figures were not available. The levels used were those of Bowen (252). The factors were calculated using Fe as the normalising element and based on the yearly average value of each element as has been done elsewhere (249). The results are given in Table 3.12, together with those of Rahn for Liege (Belgium) based on Al as the normalising element (251).

TABLE 3.12 ENRICHMENT FACTORS OF ELEMENTS IN ATMOSPHERIC PARTICULATES

	Glasgow (72-73)	Liege
Ag^{+}	3490	910
Br^{+}	1706	2200
Co^{+}	13	5.8
Cr^{+}	11	
Cs^{+}	19	20
Fe^{+}	1	2.9
Hf*	13	
La^{+}	3	3.8
Lu*	52	
Mn^{+}	4	5.1
Na^{+}	7	1.2
Sb*	118	2500
Sc^{+}	2	1.2
Se^{+}	2133	4300
Th^{+}	8	
Yb*	56	
Zn^{+}	822	2100

* = BASED ON ROCK

+ = BASED ON SOIL

As can be seen -

i) The Glasgow values for Cs, Fe, La, Mn and Sc are in extremely good agreement with those of Liege.

ii) Se, Br and Na are of the same order.

iii) Ag and Co are respectively 4 and 2 times higher for Glasgow while Zn is 3 times smaller.

iv) Only for Sb is there any great difference between the two sets of results, Glasgow being 21 times lower.

In the study with Sc as the reference element it was found that Zn, Se, Sb and Pb were enriched by several orders of magnitude (Pb as will be seen later is also highly enriched in Glasgow's atmosphere) and that La, Fe, Hf and Th ratios were comparable with an earth crust origin. This again is the same pattern as was found in Glasgow's atmosphere.

It is clear that Ag, Br, Sb, Se and Zn are greatly enriched compared to soil and Lu and Yb moderately so. However, the fact that the other elements have about soil proportions does not necessarily mean that they indeed originate from soil or rock (although of course wind-raised soil does exist and in rural areas will contribute to atmospheric levels it is difficult to imagine enough wind-raised soil entering the city to be solely responsible for the high levels of elements found). In fact in the Liege study it was estimated that between 70-98% of the masses of the elements were from local pollution. Also Dams et al (247) showed that for industrial N.W. Indiana Fe, Mn, Zn. Sb, Cr, W, Co, Sc, La, Ce, Th, Ca, and Mg were linked to local steel production and supporting activities. The reason for this anomaly (soil proportions but not soil derived) is said by Rahn (251) to be the presence of fly ash in the atmosphere from fuel burning and other activities. Rahn has suggested (with evidence) that there are two distinct inorganic fractions in coal one of which is the rock fraction consisting of Na, Mg, Al K, Ca, Ti, Cr, Mn, Fe, Zn, Th, La and Ce and this is confirmed by Masson (253). This mineral fraction was deposited at the same time as the original organic material. The second fraction consisting of V, Co, I, Se, As and Sb is not present in the mineral fraction and was probably precipitated from ground water by absorption or chemical reaction as the coal was being formed.

It will be noted that most of the elements in the first fraction are those which are closest to soil or rock proportions; and this fly ash is an alternative source of large quanitites of material which has rock proportions; material which is actually rock particles released nearly unchanged by pollution sources. Zn which has a larger enrichment factor must have additional sources.

As part of the same study Rahn analysed various fuels and emissions from industry and found -

i) Coal is the largest source of Al, As, Ba, Cd, Cr, Mo, S, Si, Sn, and Ti and contributes important amounts of Ca, Co, Mg, Se and V.

ii) Fuel oil is most important for Co, Ni, Se and V.

iii) The iron and steel industry contributes most importantly to Cu, Fe, Mg, Mn and Zn.

iv) Burning gasoline is most significant for Br, Cl and Pb.

By studying this list the additional sources of enriched elements can be seen.

A further explanation of the enrichment of the volatile elements is by volatilisation of these elements during combustion and preferential condensation on to the smallest particles which will have a longer residence time in the atmosphere compared to the larger fly ash particles.

When considering the emissions inventory above which by no means covers the whole industrial spectrum it is probably surprising that the correlation coefficients were as good as they were rather that a disappointment.

3.5.3.4 Climatic Variations

Similar to the question of which elements to study the question of which weather parameters to study arises, and again the best approach is to utilise all the data available and reject, if not appropriate, after use.

3.5.3.4.1 Wind

Wind is the most important climatic aspect of air pollution, acting as a transporter and hence as a diluter. The direction in which the wind is blowing is of course important in determining in which direction the pollution will be carried as is also the wind speed since low winds will allow the pollution to remain concentrated for longer periods.

It has been shown that wind observations taken at local airports are suitable for air pollution studies in the neighbouring city (194). Subsequently Glasgow Airport observations were used in this work. Observations are taken hourly and these values were averaged over the sampling period in the eight compass directions to give a total time for which the wind was blowing in any one direction, together with the average wind speed during that time. The following is the type of result arrived at -

Sampling Period	Direction from which wind is blowing	Average speed (m.p.h)	Duration (Hours)
15/ 9 a.m. 17/11/72 9 a.m.	N	2.0	1
	NE	3.0	1
	E	-	-
	SE	2.5	2
	S	2.0	1
	SW	5.3	10
	W	5.9	15
	NW	7.0	8
	Calm Winds		10

The elements were plotted against (i) Wind Speed and (ii) Wind Duration for each direction individually, the assumption being that if an element has a strong source then this should show in the wind speed and duration for that particular direction relative to the sampling position. Straight line correlation coefficients were calculated by computer, but the association in all cases was found to be very weak, r-values of second and even third decimal place being frequent.

Correlation coefficients greater than 0.1 and confidence limits greater than 95% are given in Table 3.13. In each case only about half of the results were even in the low correlation bracket (0.20 - 0.40) with the remainder in the bracket usually reserved for no correlation (0.00 - 0.20). However, the

TABLE 3.13 CORRELATION COEFFICIENTS OF ELEMENTS WITH WIND SPEED, DURATION AND DISTANCE

(ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY 72-73)

Element/Direction	Wind Speed	Duration	Wind Distance
Br/SW	- 0.19		- 0.14
Br/W	- 0.26	- 0.20	- 0.28
Br/NW	- 0.21	- 0.18	- 0.20
Co/W	- 0.16	- 0.11	- 0.15
Cr/SW		- 0.19	- 0.18
Cr/W			- 0.14
Mn/NE	0.14	0.13	
Mn/E	0.23	0.20	0.15
Mn/SE	0.19	0.31	0.20
Mn/SW	- 0.31	- 0.25	- 0.24
Mn/W	- 0.37	- 0.28	- 0.29
Mn/NW	- 0.21	0.16	- 0.17
Na/SE		0.17	
Na/W	- 0.16	-0.20	- 0.17
Se/SE	- 0.14		- 0.13
Sb/S	- 0.16	- 0.14	- 0.17
Sb/SW	- 0.18	- 0.35	- 0.28
Sb/W	- 0.13		
Sb/NW		- 0.14	
Zn/SW	- 0.16	- 0.27	- 0.24
Zn/W	- 0.23	- 0.18	- 0.20

reported values were at least 10 times higher than the omitted values and are at least indicative of trends which should be further investigated. The sign is probably meaningless being negative in most cases and caused by the large number of concentrations of the various elements when no wind was blowing in that particular direction.

As said previously the concentration of a pollutant is related to both the length of time and also the speed of the wind in a particular direction. The next step therefore was to combine these two variables into one and this was achieved by using the "Wind Distance", i.e. speed x time and is a measure of the amount of air passing over the sampler in any given direction. These values were again computer plotted against the elements and correlation coefficients calculated. The results are given in Table 3.13 again for values greater than 0.1 only. It will be clear that the results are comparable with those for wind speed and duration and therefore add nothing new in terms of understanding.

Since the elemental value was an average for the sampling period it was thought that an average wind speed and duration for the same period would show a closer relationship. To be meaningful this average must allow weight to be added to the varying influences of duration and speed in the eight directions. This was achieved through the use of vectors using the formula -

$$R = \sqrt{X^2 + Y^2}$$

where R = resultant force

X = the component of the force acting along the X - axis

Y = the component of the force acting along the Y - axis

and in the direction given by $\tan\theta = Y/x$.

X is given by $A_1 \text{ Cos}\alpha_1 + A_2 \text{ Cos}\alpha_2 + \cdots + A_n \text{ Cos}\alpha_n$

and Y is given by $A_1 \text{ Sin}\alpha_1 + A_2 \text{ Sin}\alpha_2 + \cdots + A_n \text{ sin}\alpha_n$

where A is the magnitude of the force and α is the angle which the line of action of that force makes with the X - axis.

Obviously with different numerical values for speed and duration the angles of action of the resultant forces are going to be different. To obtain an angle which included components of speed and duration therefore "Vector Distances" were also calculated. The zero degree point was taken as East and all angles calculated relative to this direction. For example, for the sampling period given earlier this process gave -

Vector Speed (VS) = 10.8 m.p.h.; Vector Angle for Speed (VAS) = 352°
(i.e. 8° below east)

Vector Time (VT) = 25.7 hours: Vector Angle for Time (VAT) = 4°

Vector Distance (VD) = 160 miles; Vector Angle for Distance (VAD) = 0°

These again were plotted against the elements and correlation coefficients calculated. The results are given in Table 3.14 and again have confidence level of 95% or more. Again all three sets are comparable and in some cases slightly more encouraging than previously.

With vector angles it is the shape of the graph which is important rather than the correlation coefficient, pockets of points being desired rather than straight lines. Figure 3.8 illustrates the plots obtained for Se and are typical of all the

TABLE 3.14 CORRELATION COEFFICIENTS OF ELEMENTS* WITH VECTORS OF WIND PARAMETERS

	Vector Speed	Vector Time	Vector Distance
Br	- 0.35	- 0.31	- 0.31
Co	- 0.14	- 0.16	- 0.16
Cr		- 0.22	- 0.22
Fe			
Mn	- 0.28	- 0.23	- 0.27
Na			
Sb	- 0.19	- 0.38	- 0.31
Sc			
Se			
Zn	- 0.18	- 0.31	- 0.30

TABLE 3.15 CORRELATION COEFFICIENTS OF ELEMENTS* WITH CALM HOURS

Br	0.42
Co	0.31
Cr	
Fe	
Mn	0.27
Na	
Sb	0.32
Se	
Sc	
Zn	0.29

* ATMOSPHERIC PARTICULATES- GLASGOW '72-'73.

FIGURE 3.8 COMPUTER PLOT OF SELENIUM V WIND PARAMETERS
(ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY '72-73.)

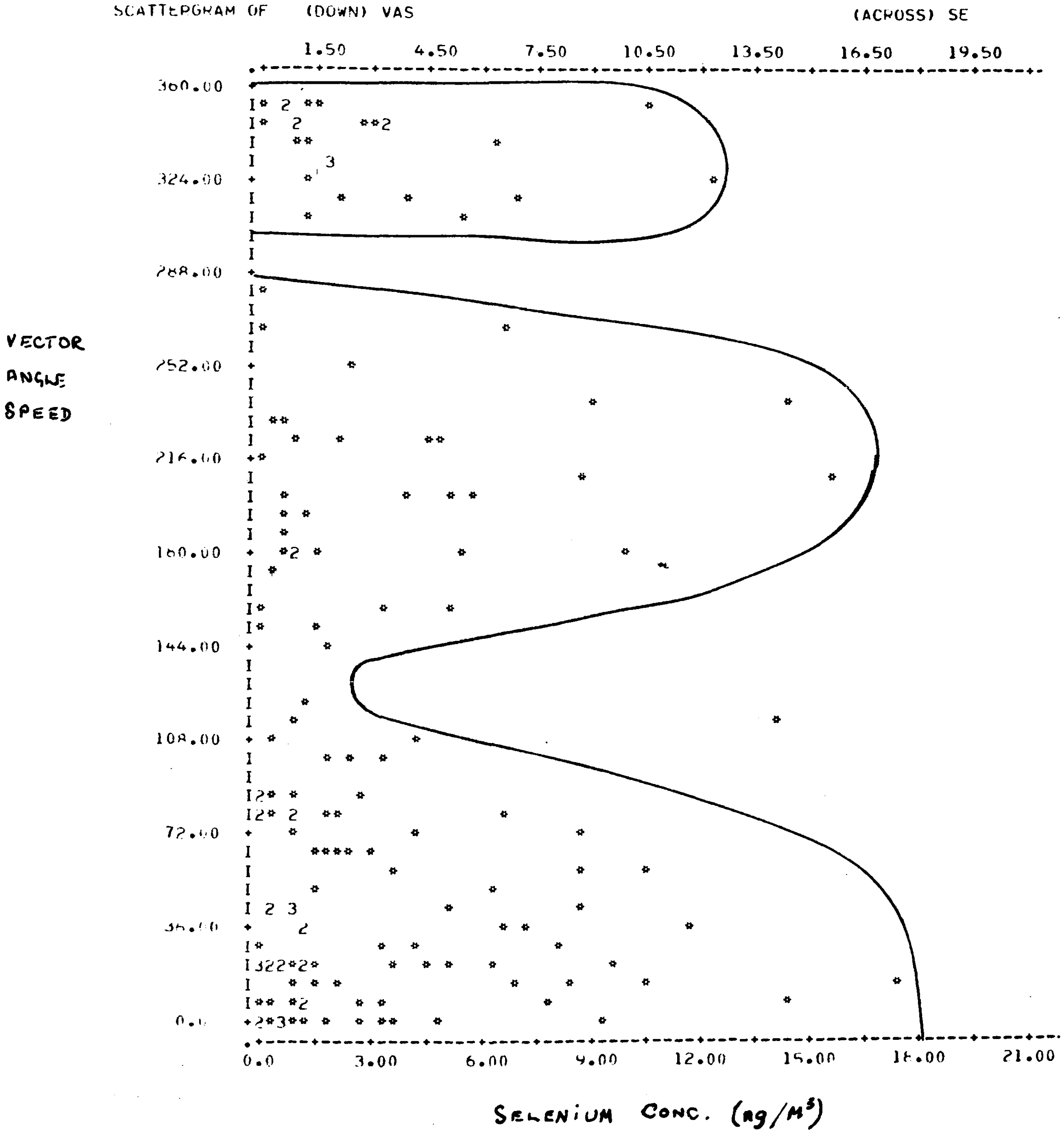
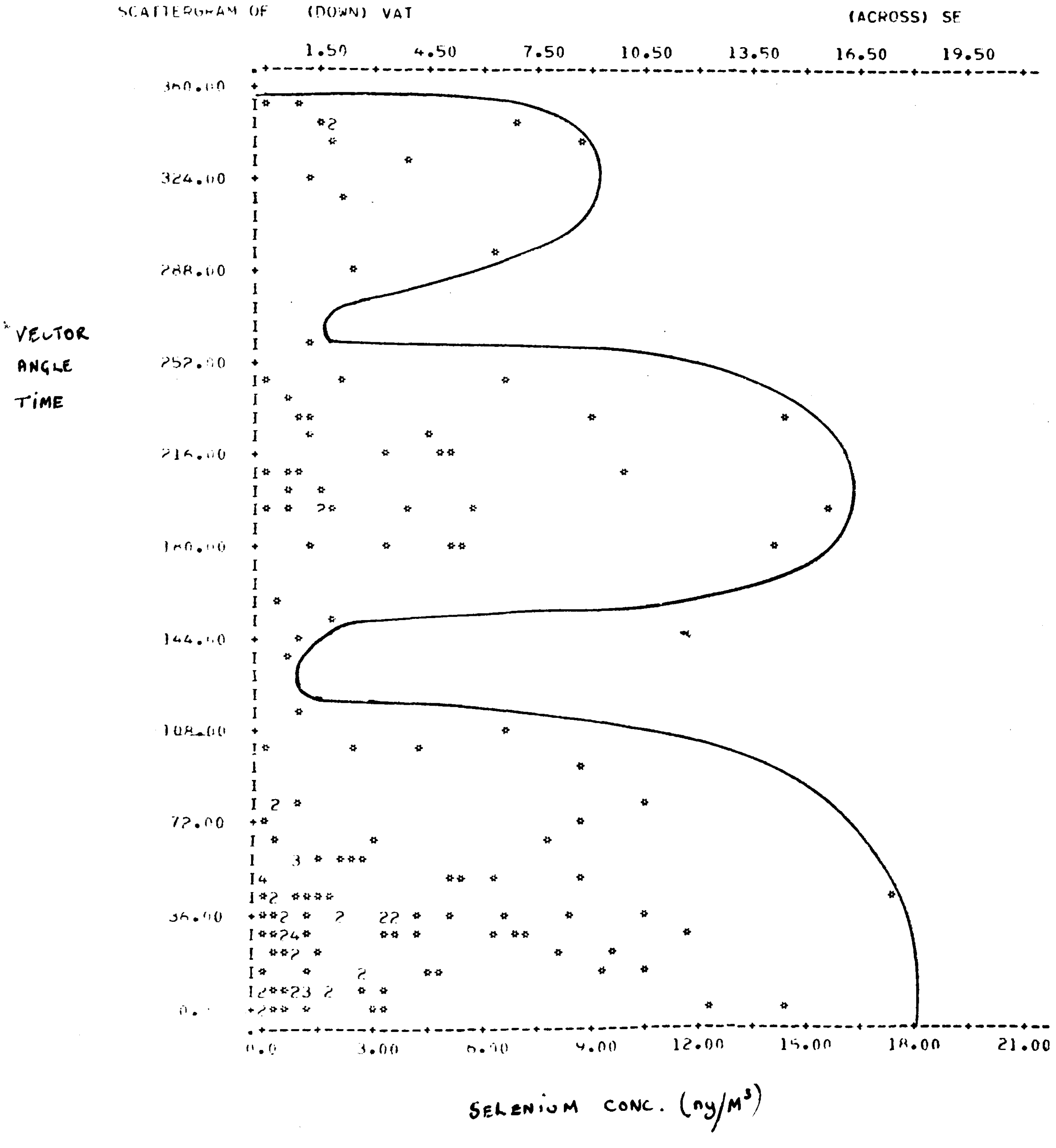
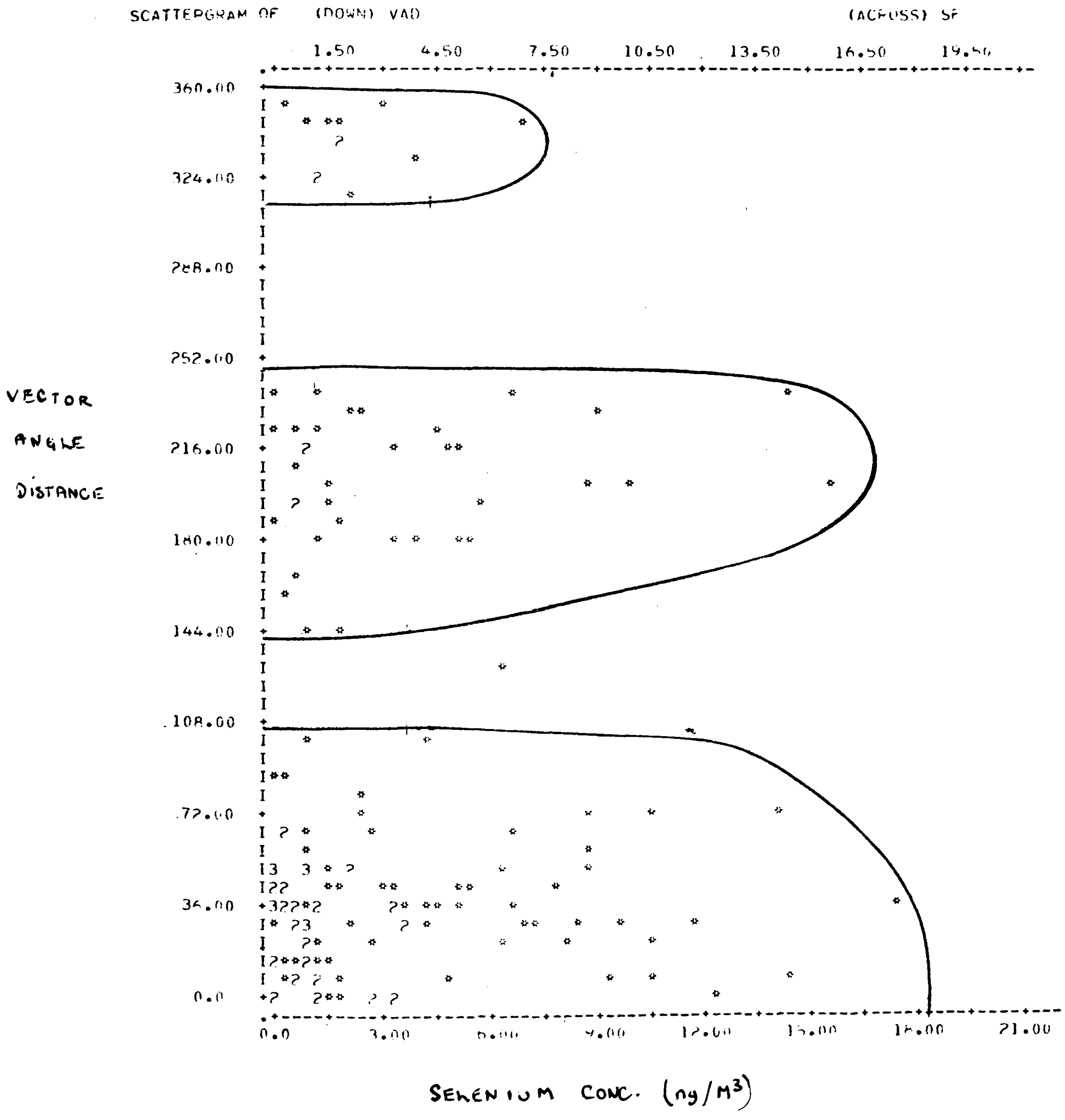


FIGURE 3.8 (CONTD.)



4.8 (contd.)


SCATTERGRAM OF (DOWN) VAD (ACROSS) SE
1.50
4.50
7.50
10.50
13.50
16.50
19.50
360.00
324.00
288.00
252.00
216.00
180.00
144.00
108.00
72.00
36.00
0.0
0.0
3.00
6.00
9.00
12.00
15.00
18.00
21.00
VECTOR ANGLE DISTANCE
SELENIUM CONC. (ng/M³)

elements. As can be seen in the speed and time plots it is tempting to divide the points into three groups but it is not until the distance plot is studied that this can be done with justification. The three groups are:-

i) 0° - 108° which is the largest group and corresponds to W-SSE winds

ii) 144° - 250° which is the middle group and corresponds to SE- NE winds

iii) 310° - 360° which is the smallest group and corresponds to W-NW winds.

This does not mean that the elements are derived from these directions, although they all correspond to industrial complexes, since by the very way in which the vector angles were calculated, a direction may be obtained which did not appear in the sampling period. It does at last show that there is a relationship between elemental concentration and wind, speed and duration both being important.

As mentioned previously periods of low wind speeds lead to a build up of pollutants. To investigate this, elemental concentrations were plotted against the total number of calm hours per sample. The correlation coefficients are given in Table 3.15. The sign of the elements given are all positive, i.e. as the number of calm hours increase the concentration of elements increase.

3.5.3.4.2 Rain

Rain is said to be the most important scavenger of the atmosphere. Uniform rain falling at 1 mm/hr for 15 minutes will scavenge 28% of 10µm particles. The efficiency decreases with particle size and becomes negligible at 2µm and smaller (194). There are two modes of action -

i) Washout where particles impact on water droplets.

ii) Rainout or condensation around the particles to form a droplet. There can be up to 25 particles/drop of rain for normal dust concentrations(194).

Rain is measured on a 24-hour basis at the weather centre giving total rain in mililitres and total time for whch rain was falling.

These were totalled for the sampling periods to give -

i) Total rain which fell in mililitres.

ii) Time for which rain was falling in hours.

iii) Rate at which rain was falling (by dividing i) by ii) in mililitres/hour.

These values were plotted against the elements and straight line correlation coefficients calculated. The results are given in Table 3.16. As can be seen the results were extremely disappointing, it being expected that during periods of rain the levels of the elements would be reduced. The omitted values were an order of magnitude less than these given.

Three samples of rain water were collected on 10-11/12/74, 2-3/6/75 and 21-22/8/75 in a previously acid washed plastic container placed on the roof of Glasgow University chemistry building. The samples were acidified with "Aristar" nitric

TABLE 3.16 CORRELATION COEFFICIENTS OF ELEMENTS WITH RAIN
(ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY '72-'73)

	Duration of Rain	Amount of Rain	Rate of Rain
Br		- 0.13	- 0.14
Sb	- 0.17		
Zn	- 0.15	- 0.14	

TABLE 3.17 CONCENTRATIONS OF ELEMENTS IN RAINWATER (ppm)
COLLECTED AT GLASGOW UNIVERSITY.

Sample	Al	Cd	Co	Cr	Cu	Fe	Mn	Na	Ni	Pb	Zn
1	0.21	ND	ND	ND	0.08	0.05	0.01	7.5	ND	0.04	0.14
2	0.15	ND	ND	ND	0.03	0.03	0.02	0.4	ND	0.04	0.08
3	0.28	ND	ND	ND	0.05	0.08	0.01	1.5	ND	0.03	0.04

ND = Not Detected

acid and filtered through a 0.45 μm membrane filter and then analysed by atomic absorption spectroscopy using the method of standard additions. The results are given in Table 3.17. It can be seen that some of the elements at least are being washed/rained out although the amount is not in linear relationship to the amount, time and rate of precipitation of rain.

3.5.3.4.3 Fog

Fog is defined as the suspension of water droplets in the atmosphere, with or without particulate matter. Fog with a smoke combination was the original "smog" before American workers extended the meaning to cover photochemical pollution.

In a city atmosphere fog will consist of particulate matter and hence it would be expected that periods of fog would exhibit elevated levels of elements due to their being held in the atmosphere under stagnating conditions for a longer period.

At the weather centre visibility distances are measured every hour. When visibility is less than 1 mile the distance is given in yards. These latter readings were taken as foggy conditions and were averaged out over the sampling periods to give the average visibility during foggy conditions and the duration. These values were plotted against the elements and correlation coefficients calculated. The results are given in Table 3.18. The samples which had no foggy conditions were given a visibility of 4,000 yards and as the programme limits were set at 3,900 yards these samples were omitted. For this reason the signs are meaningful and reflect what would be expected, i.e. as visibility decreases the concentration

TABLE 3.18 CORRELATION COEFFICIENTS OF ELEMENTS WITH FOG

(ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY 72-73.)

	Visibility	Duration
Br	- 0.36	0.42
Mn	- 0.29	0.39
Sb	- 0.28	0.18
Zn	- 0.26	0.29

increases and as duration increases the concentration increases. The actual values are also more promising than previously with values as high as 0.42 being recorded. The fact that both factors are varying at the same time will also tend to obscure any relationship and the correlation may even be better than is suggested here.

3.5.3.4.4 Temperature

Environmental temperature is important due to its effect on the uptake of pollutants by plants, and in modifying the toxic response of inhaled substances in animals with high and low temperatures increasing the undesirable effect. It is also an important factor in the formation of photochemical air pollution together with sunshine.

Kneip et al (254) studying 8 elements in New York City found that V was inversely correlated to temperature and Pb, Cu and Cd were directly correlated with temperature. The effect of temperature was investigated on these results. Readings at the weather centre are taken every hour. However, the hourly variation was not significant and values at 1200, 1800, 0000 and 0600 hours and the daily maximum and minimum values were found to be enough to give an accurate average temperature for the sampling periods. The values were plotted against the elements and correlation coefficients calculated. The results are given in Table 3.19. Again the sign is meaningful and the relationship is inverse. Of the elements in common, Kneip et al found no correlation of temperature with Zn, Mn, or Cr. This was also found to be the case here for Zn and Cr but there was a weak correlation with Mn.

TABLE 3.19 CORRELATION COEFFICIENTS OF ELEMENTS WITH VARIOUS WEATHER PARAMETERS

ATMOSPHERIC PARTICULATES - GLASGOW UNVERSITY (79-73)

	Temperature	C.C.	C.H.	SH.	VP.	RH.	AP.
Br	- 0.24	0.16		- 0.28	- 0.21	0.34	0.27
Co							0.17
Cr							
Fe							0.15
Mn	- 0.25	0.17		- 0.25	- 0.21	0.23	0.16
Na	- 0.27			- 0.14	- 0.28	0.13	
Sb		0.15	-0.21				
Se	- 0.20				- 0.27		
Sc							0.19
Zn				- 0.18			0.17

C.C. = Amount of Sky covered by clouds

C.H. = Height of clouds

SH. = Hours of sunshine

VP. = Vapour pressure

RH. = Relative humidity

AP. = Atmospheric pressure

3.5.3.4.5 Cloud Cover

It would be expected that low clouds would elevate concentrations due to enclosing pollution in the lower atmosphere.

At the weather centre cloud cover is recorded in terms of eighths of the sky covered and also the height of that cloud, on an hourly basis. These were averaged over the sampling period to give the average sky covered and average height of cloud. The results of plotting these values against the elements are given in Table 3.19. Again for these elements given, the association is very weak but the signs are as would be expected. As the amount of sky covered increases the concentration increases and as the height increases the concentration decreases.

3.5.3.4.6 Miscellaneous

Other parameters which are measured at the weather centre are sunshine hours, relative humidity, atmospheric pressure and vapour pressure. Sunshine hours are recorded as a total per day and were simply added to give a total number for the sampling period. For the others, which are recorded hourly, it was found necessary only to treat them similarly to temperature readings to obtain an average value. The results of correlating these with the elements are given in Table 3.19.

Although some correlation exists it must be remembered that climatic conditions are inter-related, e.g. relative humidity is related to fog; low atmospheric pressure leads to stagnating conditions, etc., and hence some relationship might be expected.

However, Lininger et al (50) did find that some Br concentrations in Cambridge, Mass. "seem to be related to relative humidity".

On the whole this computer approach was disappointing as manifested in the correlation coefficients. One reason for this, as already stated, is trying to cope with more than one variable at a time. In all, including the eight wind directions 30 variables have been studied. Two different approaches were adopted -

i) Visual inspection where samples were selected to correspond with weather conditions of rain, fog, etc. This approach is of course empirical but does allow an element of choice to account for the varying factors, e.g. rain and fog during the same sampling period might cancel out each other's effect on the average elemental level measured. On this empirical basis an element was said to increase or decrease if it was larger or smaller respectively than the samples on either side by more than the experimental error.

ii) Use of a computer programme capable of handling more than one variable at a time, i.e. obtain a multiple regression coefficient for the elements plotted simultaneously against the 30 variables.

3.5.3.4.7 Visual Inspection

3.5.3.4.7.1 Wind:- From the data as set out in the example previously given samples were sub-divided into wind directions, with no set criteria but simply by judging the most predominant direction. On this basis 48% of the samples had predominantly the prevailing W/SW winds and 13% had E/NE winds. The remainder were mixed.

Trying to contribute any element to E/NE winds can be seen from Table 3.20 to be impossible due to the other weather conditions prevailing at that time and emphasises what was said previously. No further attempts were made with this approach.

Samples were also collected which occurred during periods of calm. In the majority of cases it was found that these periods of calm were accompanied by haze, i.e. visibility greater than 1,000 yards but less than 1 mile. The cases where there was no accompanying haze can be attributed to two causes.

i) The hours of calm were scattered throughout the sampling period although giving a high total.

ii) To the wind measuring instrument calm means a wind speed less than 3 m.p.h. This speed is probably enough to prevent haze forming but low enough to be recorded as calm.

The haze is probably due to the collection of pollution during the stagnating calm periods.

In all cases except three where there was an appreciable amount of calm or haze (greater than 5 hours) at least one element was elevated. In the three exceptions there was an appreciable amount of rain (at least 13.6 mililitres) which would tend to nullify the elevating effect of calm conditions. The results are given in Table 3.21.

(ATMOSPHERIC PARTICULATES GLASGOW UNIVERSITY 72-73)

TABLE 3.20 ELEMENTS AFFECTED BY E/NE WINDS

Date	Elements Elevated	Elements Decreased	Other Parameters
4/5/10/72	Se, Cr, Zn, Co, Fe, Mn, Na		Haze
9/11/10/72	Sc, Sb, Fe	Se, Zn, Co, Na, Br	Rain
6/8/12/72	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br		Haze
15/18/12/72	Sb, Zn, Co, Fe, Mn, Br	Se, Na	Haze
27/29/12/72	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br		Haze
12/15/1/73	Cr, Sc, Co	Na	
17/19/1/73	Se, Cr, Zn, Sb, Co, Fe, Mn, Na, Br		Haze
12/14/3/73	Br	Zn, Fe, Mn	
20/23/4/73	Se	Sc, Sb, Zn, Co, Fe, Na	
23/25/4/73	Na	Cr	
2/4/5/73	Fe	Se	
16/17/5/73	Se, Fe		
17/18/5/73		Se, Cr, Sb, Zn, Br	
18/21/5/73	Sb, Zn, Co, Mn, Na, Br		
21/22/5/73	Se	Zn, Co, Fe, Mn, Na	Rain
		Cr, Sc, Br	Low Cloud Cover
22/23/5/73	Se	Sb, Br	
23/24/5/73	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br		Haze

TABLE 3.20 (CONTD.)

Date	Elements Elevated	Elements Decreased	Other Parameters
28/ 29/5/73	Sb	Cr, Zn, Fe, Br	
16/ 18/7/73	Se, Cr, Sb, Zn, Fe, Br		Haze
20/ 22/8/73	Cr	Sc, Sb, Zn, Mn, Na	
22/ 24/8/73	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br		Haze
24/ 27/8/73	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br		Haze

TABLE 3.21 ELEMENTS AFFECTED BY NUMBER OF CALM HOURS

(ATMOSPHERIC PARTICULATES GLASGOW UNIVERSITY 72-73

Date	Hours of Calm	Hours of Fog		Elements Elevated
		Slight	Dense	
18/ 20/9/72	14	1		Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
26/ 28/9/72	29	11	4	Se, Cr, Zn, Co, Fe, Mn, Na, Br
2/ 4/10/72	23	32	5	Se, Cr, Sc, Sb, Zn, Co, Fe
4/ 5/10/72	16	17		Se, Cr, Zn, Co, Fe, Mn, Na
5/ 6/10/72	8	2	2	Se, Sb, Zn, Co, Fe, Mn, Na
11/ 13/10/72	21	2		Cr, Zn, Co, Na, Br
16/ 17/10/72	15			Se, Co, Mn, Br, Na
17/ 18/10/72	9	13	6	Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
19/ 21/10/72	10	6		Br
30/10/ 1/11/72	14	4		Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
13/ 15/11/72	9	4		Se, Cr, Sb, Zn, Co, Mn, Br, Fe
15/ 17/11/72	10	9	3	Se, Sc, Sb, Zn, Co, Na, Br
17/ 20/11/72	12	12		Se, Sc, Zn, Fe, Mn, Na, Br
24/ 27/11/72	15	10		Se
1/ 4/12/72	22	16	9	Se, Cr, Br
6/ 8/12/72	17	11		Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
8/ 11/12/72	10	5		Cr, Sb, Zn, Co, Mn
15/ 18/12/72	6	22		Sb, Zn, Co, Fe, Mn, Br
18/ 20/12/72	16	15		Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br

TABLE 3.21 (CONTD.)

Date	Hours of Calm	Hours of Fog		Elements Elevated
		Slight	Dense	
20/ 22/12/72	4	4		Sb, Zn, Fe, Na, Br
27/ 29/12/72	2	9		Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
30/12/72 2/1/73	14	5		None
3/ 5/1/73	6	15		Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
5/ 8/1/73	32	21		Sc, Sb, Zn, Co, Fe, Mn, Na, Br
8/ 10/1/73	28	8		Se, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
15/ 17/1/73	9	3		None
17/ 19/1/73	15	6		Se, Cr, Zn, Sb, Co, Fe, Mn, Na, Br
22/ 24/1/73	8	4	10	Sb, Zn, Co, Mn, Br
26/ 29/1/73	5			Se, Br
7/ 9/2/73	6			Cr, Se, Sb, Zn, Co, Fe, Mn
14/ 16/2/73	31	10	1	Se, Cr, Sc, Sb, Zn, Fe, Mn, Na, Br, Co
16/ 19/2/73	26	23	11	Cr, Sc, Zn, Fe, Mn, Br
23/ 26/2/73	4	3		Cr, Sc, Zn, Mn, Br
26/ 28/2/73	18	14		Se, Cr, Sc, Zn, Sb, Co, Fe, Mn, Na, Br
7/ 9/3/73	10	2		Cr, Sc, Sb, Zn, Co, Fe, Mn
9/ 12/3/73	37	20	10	Cr, Sb, Zn, Co, Fe, Mn, Br
14/ 16/3/73	11	9	4	Se, Zn, Fe, Mn, Br

TABLE 3.21 (CONTD.)

		Hours of Fog		
Date	Hours of Calm	Slight	Dense	Elements Elevated
19/ 21/3/73	6			Se, Cr, Sb, Zn, Mn, Br
27/ 30/4/73	5	1	1	Cr
30/4 2/5/73	6	4		Se, Sb, Zn, Co, Br
23/ 24/5/73	6	3		Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
25/ 28/5/73	12	12		Se, Sb, Sc, Cr, Zn, Co, Fe, Na, Br
29/ 30/5/73	5	10		Cr, Sc, Zn, Fe, Br
20/ 22/6/73	11	6		Se, Cr, Sc, Zn, Co, Fe, Mn, Na, Br
22/ 25/6/73	9			Se, Cr, Zn, Fe, Br
2/ 4/7/73	13			Sc, Sb, Zn, Co, Fe, Mn, Na, Br
4/ 6/7/73	8			Se, Cr, Sc, Zn, Co, Fe, Mn, Br
6/ 9/7/73	6			Cr, Zn, Fe, Mn, Na
13/ 16/7/73	14	4		Se, Cr, Co, Fe, Na
16/ 18/7/73	5	3		Se, Cr, Sb, Zn, Fe, Br
20/ 23/7/73	8			None
23/ 27/7/73	19			Se, Sc, Sb, Zn, Co, Fe, Mn
31/7 3/8/73	11			Sb, Zn, Br
9/ 14/8/73	28	13		Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
22/ 24/8/73	12	20		Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
24/ 27/8/73	17	42		Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br

The frequency of elevation of the elements is given in Table 3.22. The results can be seen to be more encouraging than previously especially in the case of Se which only appeared once in the whole of the computer programme results.

3.5.3.4.7.2 Rain:- Samples were selected during which there was 5 mililitres or more of rain. The results are given in Table 3.23. There are 4 samples which increased during rain. In three of these (6-8/12/72, 14-16/2/73 and 30/4-2/5/73 there was either foggy or calm conditions during the sampling period.

In general the number of elements which decrease tends to be shorter in samples in which haze or fog occurred. The frequency of reduction is given in Table 3.22.

Again the results are much more encouraging with the lowest percentage of 36 for Sc.

3.5.3.4.7.3 Fog:- Only 14 samples during the year had fog conditions. The results are given in Table 3.24. In only 1 sample was there no elevation of any element. The number of elements elevated was reduced in samples where rain also occurred. The frequency of elevation is given in Table 3.22 and again this is impressive.

3.5.3.4.7.4 Cloud Cover:- Cloud cover is probably an effect/ no effect variable, i.e. only full cloud cover at a low level will exhibit an effect. Samples with total cloud cover below a nominal 4,500 feet were studied. This amounted to 9 samples and

TABLE 3.22 FREQUENCY OF INCREASE OR DECREASE OF ELEMTNTS (%)

(ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY 72-73)

Element	Calm	Rain	Fog	Cloud Cover
Br	75	46	71	78
Co	66	51	64	78
Cr	64	41	56	55
Fe	70	46	57	67
Mn	66	54	71	67
Na	52	54	43	55
Sb	61	51	57	55
Sc	48	36	21	67
Se	59	41	50	33
Zn	82	56	86	78

TABLE 3.23 ELEMENTS AFFECTED BY AMOUNT OF RAIN
(ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY 72-73)

Date	Amount of Rain (mili itres)	Elements Decreased
3/ 4/8/72	5.7	Sc, Na
7/ 8/8/72	12.6	None
9/ 11/10/72	9.4	Se, Zn, Co, Na, Br
19/ 21/10/72	6.4	Cr, Sb, Zn, Co, Fe, Na
27/ 30/10/72	6.6	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
10/ 13/11/72	23.1	Se, Cr, Sb, Zn, Co, Fe, Mn, Na, Br
17/ 20/11/72	17.0	Co, Br
29/11/ 1/12/72	8.6	Se, Cr, Mn, Na
1/ 4/12/72	12.1	Sc, Sb, Zn, Co, Fe, Na
4/ 6/12/72	9.1	Se, Cr, Co, Fe, Na, Br
6/ 8/12/72	10.5	None
11/ 13/12/72	23.2	Cr, Sb, Zn, Co. Mn
13/ 15/12/72	10.4	Cr, Sb, Zn, Co, Mn
30/12/72 2/1/73	14.3	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
15/ 17/1/73	16.5	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Br
19/ 22/1/73	24.8	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
22/ 24/1/73	7.1	Se, Cr, Fe
26/ 29/1/73	9.9	Zn, Co, Fe

TABLE 3.23 (CONTD.)

Date	Amount of Rain (mililitres)	Elements Decreased
7/ 9/2/73	7.0	Se, Na, Br
9/ 12/2/73	7.3	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
14/ 16/2/73	6.8	None
23/ 26/2/73	7.1	Se, Sb, Co, Fe, Na
2/ 5/3/73	6.9	Sb, Zn, Fe, Mn, Na, Br
30/3 2/4/73	12.8	Cr, Zn, Co, Mn
4/ 6/4/73	15.0	Zn, Fe, Mn
6/ 9/4/73	4.9	Se, Sc, Sb, Zn, Mn, Na, Br
30/4 2/5/73	19.6	Cr, Mn
4/ 7/5/73	19.8	Na, Br
11/ 14/5/73	8.6	Sc, Sb, Co
21/ 22/5/73	5.9	Cr, Sc, Zn, Co, Fe, Mn, Na, Br
18/ 20/7/73	30.4	Cr, Sc, Zn, Fe, Mn, Na, Br
4/ 6/7/73	10.7	Sb, Na
13/ 16/7/73	19.4	Sc, Sb, Zn, Mn, Br
18/ 20/7/73	11.3	Sb, Mn, Na, Br
20/ 23/7/73	13.6	Se, Sc, Zn, Fe, Mn, Br
3/ 7/8/73	17.1	Sb, Zn, Co, Mn, Br
7/ 9/8/73	10.6	Se, Sb, Zn
9/ 14/8/73	7.0	None
27/ 29/8/73	7.4	Se, Sc, Sb, Co, Fe, Mn, Na

TABLE 3.24 ELEMENTS AFFECTED BY FOG (ATMOSPHERIC PARTICULATES GLASGOW UNIVERSITY 72-73)

Date	Visibility (yards)	Duration (hours)	Elements Elevated
21/23/9/72	666	3	Zn, Br
26/28/9/72	800	4	Se, Cr, Zn, Co, Fe, Mn, Na, Br
2/4/10/72	420	5	Se, Cr, Sc, Sb, Zn, Co, Fe
5/6/10/72	235	2	Se, Sb, Zn, Co, Fe, Mn, Na
17/18/10/72	332	6	Cr, Sc, Sb, Zn, Co, Fe Mn, Na, Br
15/17/11/72	716	3	Se, Sc, Sb, Zn, Co, Na, Br
8/11/12/72	337	9	Cr, Sb, Zn, Co, Mn
17/19/1/73	220	19	Se, Cr, Zn, Sb, Co, Fe, Mn, Na, Br
19/22/1/73	900	2	Se, Mn, Na, Br
22/24/1/73	443	10	Sb, Zn, Co, Mn, Br
16/19/2/73	609	11	Cr, Sc, Zn, Fe, Mn, Br
9/12/3/73	281	10	Cr, Sb, Zn, Co, Fe, Mn, Br
14/16/3/73	413	4	Se, Zn, Fe, Mn, Br
24/25/5/73	640	4	None

the results are given in Table 3.25. The effect, however, is obscured by calm, haze and foggy conditions prevailing during most of these samples and over the small number leaves little in the way of samples to be studied. However, the results are given and the frequency of elevation in Table 3.22.

On the whole this exercise was much more rewarding than the previous attempts, the expected trends being found. However, it was noted during the exercise that the trends were not linear and hence it was not thought prudent to subject these sub-samples to the computer programme previously used.

3.5.3.4.8 Multiple Regression Coefficient

The programme used was capable of handling all 30 variables simultaneously. The results obtained are (i) a multiple regression coefficient, i.e. the best straight line fit of a 31 dimensional graph; (ii) the number of values which lie on this line, i.e. the number of samples which can be explained by the variables; and (iii) an equation of the form:

$$y = m_1 x_1 + m_2 x_2 + \text{-----} m_{30} x_{30} + C$$

where y = elemental concentration

x_1 - - - x_{30} = value of variables 1 - - - 30 corresponding to y.

m_1 - - - m_{30} = constant multiplication factor for that variable.

C = intercept on y axis

The correlation coefficients in general are much improved over the single variable approach and again Se which only appeared once in the whole of that section now has a regression

TABLE 3.25 ELEMENTS AFFECTED BY CLOUD COVER

(ATMOSPHERIC PARTICULATES
GLASGOW UNIVERSITY 72-73)

Date	Cloud Height (feet)	Elements Elevated
3/4/8/72	4300	Cr, Co
17/18/10/72	3200	Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
27/29/12/72	3140	Se, Cr, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
5/8/1/73	1375	Sc, Sb, Zn, Co, Fe, Mn, Na, Br
8/10/1/73	3840	Se, Sc, Sb, Zn, Co, Fe, Mn, Na, Br
22/24/1/73	3015	Sb, Zn, Co, Mn, Br
21/22/5/73	2525	Se
22/23/5/73	1575	Cr, Se, Zn, Co, Fe, Mn, Na
29/30/5/73	2600	Cr, Sc, Zn, Fe, Br

TABLE 3.26 RESULTS OF MULTIPLE REGRESSION COEFFICIENT PROGRAMME

Manganese

multiple regression coefficient = 0.72

number of samples explained = 52%

Most Effect	Least Effect
Speed of East Winds	Duration of East Winds
Temperature	Duration of NW Winds
Speed of SW Winds	Duration of Fog
Visibility	Duration of Rain
Duration of SE Winds	Duration of NE Winds
Number of Calm hours	Speed of NW Winds

Bromine

multiple regression coefficient = 0.78

number of samples explained = 60%

Most Effect	Least Effect
Relative Humidity	Speed of W Winds
Number of Calm hours	Duration of W Winds
Atmospheric Pressure	Speed of SW Winds
Duration of fog	Rate of rain
Duration of SE Winds	Speed of East Winds
Duration of NW Winds	Speed of NE Winds
(Speed of NW Winds)	

TABLE 3.26 (CONTD:)

Zinc

multiple regression coefficient = 0.82

number of samples explained = 68%

Most Effect	Least Effect
Relative Humidity	Temperature
Visibility	Duration of East Winds
Atmospheric Pressure	Duration of NE Winds
Speed of North Winds	Duration of SE Winds
Number of Calm hours	Vapour Pressure
Duration of Fog	Speed of South Winds

Cobalt

multiple regression coefficient = 0.42

number of samples explained = 18%

Most Effect	Least Effect
Duration of Fog	Vapour Pressure
Visibility	Relative Humidity
Atmospheric Pressure	Number of Calm hours
Duration of NE Winds	Speed of SE Winds
Duration of S Winds	Speed of N Winds
Duration of Rain	Duration of NW Winds

TABLE 3.26 (CONTD.)

Iron

multiple regression coefficient = 0.39

number of samples explained = 15%

Most Effect	Least Effect
Visibility	Duration of N Winds
Duration of Fog	Speed of N Winds
Duration of S Winds	Relative Humidity
Duration of NE Winds	Speed of S Winds
Atmospheric Pressure	Rate of Rain
Duration of Rain	Duration of NW Winds

Sodium

multiple regression coefficient = 0.61

number of samples explained = 37%

Most Effect	Least Effect
Duration of Fog	Duration of SE Winds
Speed of SW Winds	Duration of W Winds
Duration of NE Winds	Vapour Pressure
Atmospheric Pressure	Speed of N Winds
Visibility	Speed of East Winds
Duration of Rain	Speed of NE Winds

TABLE 3.26 (CONTD.)

Selenium

multiple regression coefficient = 0.49

number of samples explained = 21%

Most Effect	Least Effect
Duration of Rain	Speed of S Winds
Rate of Rain	Speed of SW Winds
Duration of NW Wunds	Temperature
Duration of S Winds	Relative Humidity
Duration of SE Winds	Duration of E Winds
Visibility	Duration of NE Winds

Chromium

multiple regression coefficient = 0.54

number of samples explained = 29%

Most Effect	Least Effect
Atmospheric Pressure	Amount of Rain
Duration of SE Winds	Duration of W Winds
Duration of Fog	Duration of SW Winds
Speed of SW Winds	Speed of S Winds
Duration of Calm	Speed of SE Winds
Visibility	Duration of N Winds

TABLE 3.26 (CONTD.)

Scandium

multiple regression coefficient = 0.39

number of samples explained = 15%

Most Effect	Least Effect
Duration of Fog	Speed of N Winds
Visibility	Duration of Calm
Atmospheric Pressure	Temperature
Duration of S Winds	Vapour Pressure
Duration of NE Winds	Duration of N Winds
Speed of W Winds	Duration of NW Winds
(Speed of NE Winds)	

Antimony

multiple regression coefficient = 0.60

number of samples explained = 36%

Most Effect	Least Effect
Speed of N Winds	Speed of NW Winds
Duration of NW Winds	Rate of Rain
Visibility	Speed of W Winds
Duration of N Winds	Relative Humidity
Duration of Calm	Duration of W Winds
Duration of Fog	Speed of W Winds

coefficient of 0.49. The coefficients range from 0.39 for Fe, to 0.82 for Zn. Mn and Br have coefficients of 0.72 and 0.78 respectively. This would be expected due to their frequency of appearance in the single variable approach.

The programme also computes errors in the estimation of the m values and in the majority of cases these were so high as to make these m values meaningless. This is due to the variables which are not affecting the levels and by elimination of these variables even higher coefficiences would be obtained. Unfortunately time did not allow this. However, from the student - T values calculated in the programme what can be stated is the variables which are having most and least effects. The 6 most and least effective are given in order in Table 3.26, together with the regression coefficients and the percentage of samples explained. It will be noted that 9 out of the 10 elements have visibility in the first 6, and 7 out of 10 have duration of fog. Surprisingly only 4 out of 10 have rain and 5 out of 10 have the number of calm hours, 4 of which had the best correlation previously (Sb, Zn, Mn, Br). It is also interesting to note that relative humidity is the main factor in the case of Br. (See Section 3.5.3.4.6).

3.5.4 Conclusions

The atmospheric system is so dynamic that no sensible conclusions can be drawn by simply examining the variables individually as if they were independent of each other.

There are two approaches which might be adopted -

i) By making an empirical study of the data and selecting samples to suit chosen weather conditions. This allows human judgement to reject samples which have "interfering" conditions, but great care must be taken to remain as unbiased as possible.

The results of this study were extremely encouraging and supported what would have been expected, i.e. rain decreased levels while fog and periods of calm winds increased levels.

ii) By using a multiple regression programme to vary all the variables at once. This is a more scientific approach but does not allow for the intrinsic variability of atmospheric levels. The results, however, were extremely encouraging with correlation values much higher than in the single variable approach.

These correlation values could probably be further improved by a process of continually rejecting those parameters which are having least effect and eventually arriving at the precise conditions under which an element level will tend to rise or fall thus making predictions of possibly hazardous conditions much easier.

3.6 VARIATION IN ELEMENTAL CONCENTATION WITH LOCATION

An important part of air pollution monitoring is local fluctuations within a city and how these compare with sites outwith the city.

3.6.1 Sampling

The first problem in sampling is of course finding a site or in this case suitable sites throughout the city. Schools are an obvious choice and with the permission of the Education Authority several schools throughout the area were chosen. The city sites are illustrated in Figrue 3.9 and described in Table 3.27.

Ideally a number of sites should be set up and samples taken simultaneously to enable direct comparisons to be made. The Glasgow Smoke Officer has 15 permanent sampling sites for total particulate determination but unfortunately the samples were unsuitable for use in elemental determinations for the reasons -

i) The particulates were measured by a staining technique and therefore very dark stains were not desired, i.e. insufficient material.

ii) Glass fibre filter papers were used for sample collection.

Because of the two combinations, viz:- small sample size (about $0.34M^3$) and high filter blanks these samples had regrettably to be discarded.

The task of setting up 10-15 sites for simultaneous sampling was prohibitive and a three site comparison had to be used. One site was fixed (University) and the other two moved around at one month intervals.

FIGURE 3.9 GRAPHICAL REPRESENTATION OF CITY SITES USED FOR COLLECTING ATMOSPHERIC PARTICULATES)

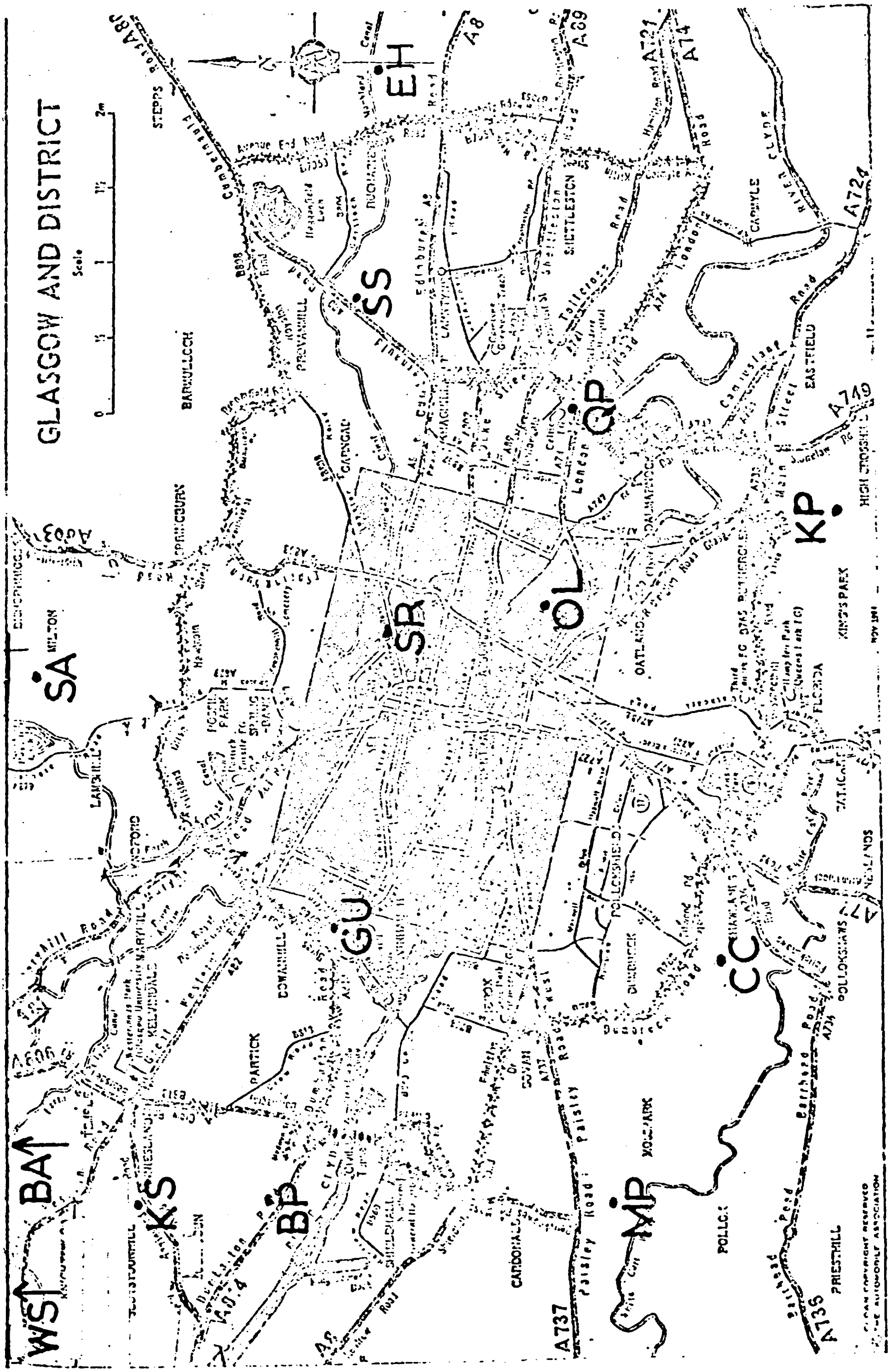


TABLE 3.27 DESCRIPTION OF SITES THROUGHOUT THE CITY USED FOR COLLECTING ATMOSPHERIC PARTICULATES.

G.U.	This is the site at Glasgow University used as the reference site.
MP., CC.	These sites were chosen because they are in residential areas and lying on the south-west side of the City they should be least affected by City pollutants since prevailing winds blow from the south-west.
B.A.	This site is also residential but lies on the north side of the river and should therefore be more affected by City pollutants than MP or CC.
WS. KS, BP	These sites lie to the north of the Clyde and were chosen to study the effect of the various industries (ship-building, iron works, engine works, etc.) along this section of the river on atmospheric levels of elements. BP also lies across the river from the large coal burning Braehead Power Station.
EH, KP	These sites were chosen to study the effect of the large Clydebridge Steelworks/Clyde Iron Works complex on the atmospheric levels of elements. KP lies to the south-west and EH to the north-east of the complex.

TABLE 3.27 (CONTD.)

SS, SR, OL	All these sites lie on main arterial roads into the City centre and were chosen for this reason. SR and OL are nearer the City centre than SS. SR is also close to six different metal works.
QP	This site lies on the same road as OL but further away from the City centre. It also lies to the north of the iron and steel complex mentioned above.
S.A.	This site lies on the north edge of the City and should reflect the accumulation of elements from the prevailing south-west winds as they blow over the City.

Since fluctuations in different areas were being studied, weekly samples were taken at roof top height. This was best achieved using a Charles Austin Capex Mark II pump which gave samples of approximately $45M^3$ over the 7 day period. Although this is a larger volume than used in Section 3.5 the slower sampling rate prevented the filters from clogging. This is illustrated in Figure 3.10 which indicates a uniform sampling rate over the sampling period.

Filter papers were changed every Monday morning.

3.6.2 Analysis

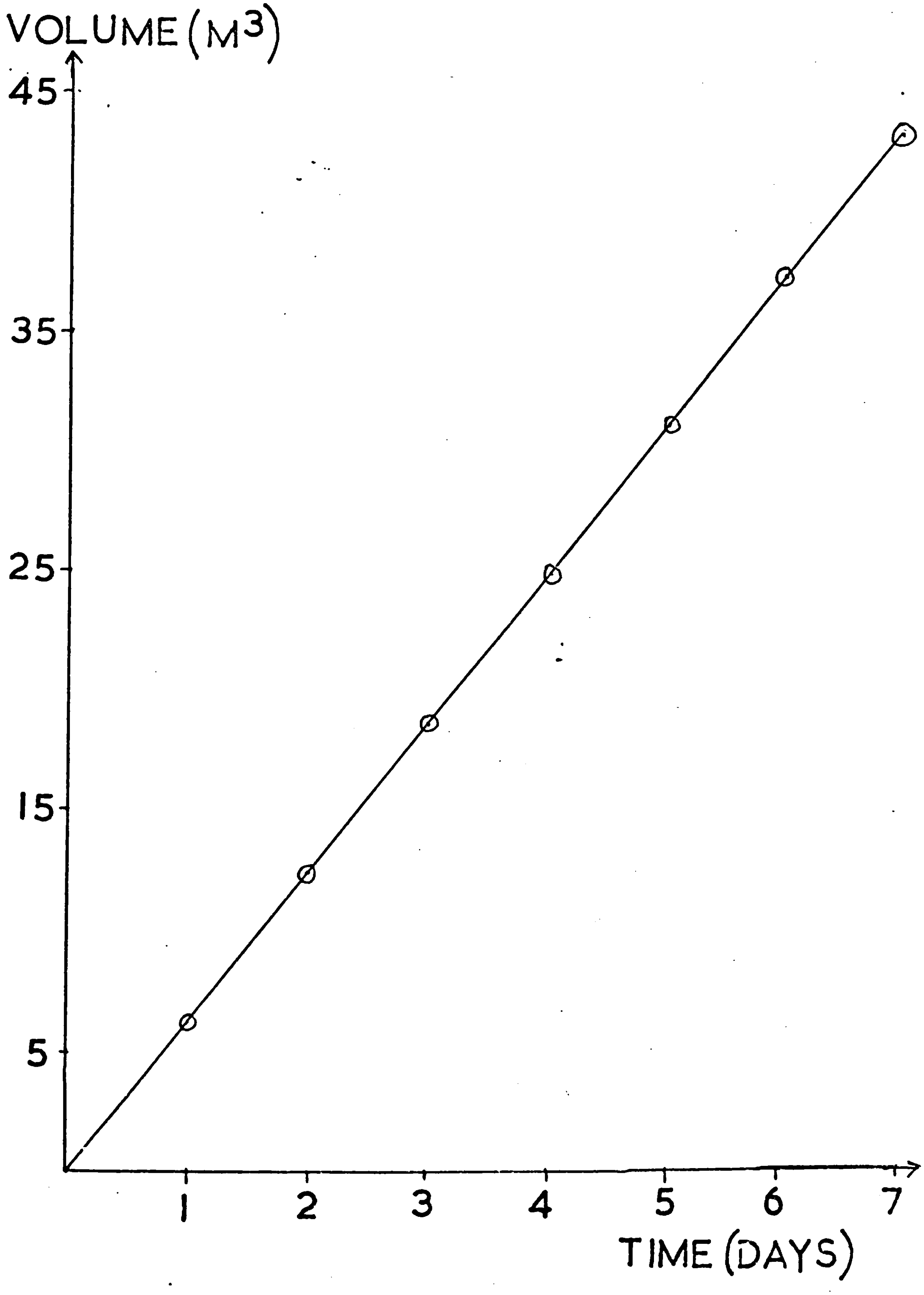
To extend the range of elements studied these samples were analysed by atomic absorption spectroscopy using a Perkin Elmer double beam 306 atomic absorption spectrophotometer with deuterium background corrector with attachments for both flame and HGA - 74 flameless systems. 11 elements were detected.

When dissolving samples for atomic absorption care must be taken to prevent the loss of volatile elements such as Pb and Cd. The two methods are wet and dry ashing.

Dry ashing at 500-600°C can result in severe loss of some metals (255). However, low-temperature ashers are now available which oxidise the carbonaceous matter at 100-120°C using an excited oxygen plasma, but this was not available for this work although it has been used elsewhere (53, 58, 73, 155, 159, 255).

Although wet ashing can also result in losses on a smaller scale it was used in this case. However, to reduce the risk of loss the filters were dissolved under pressure in teflon dissolution bombs with screw caps. A mixture of HNO_3 and H_2SO_4 was used as sulphates

FIGURE 3.10 SAMPLING RATE OF MILLIPORE FILTERS WITH CHARLES AUSTIN CAPEX MARK II PUMP



are generally less volatile than nitrates, thus reducing the risk of loss of volatile elements. HF was also added to dissolve the silicaceous material which has been shown to be present in atmospheric particulates (115). Also Kronborg et al (116) found that atomic absorption results for Fe in air particulates gave systematic low results compared to neutron activation analysis when filter papers were leached only with nitric acid since some of the Fe was in the silicate matrix.

An oven was found to be unsuccessful as the bottom of the bomb resting on the shelf and therefore receiving direct heat tended to expand out. This was overcome by using a sand bath and building the sand up round the sides of the bomb.

3.6.2.1 Procedure

The whole filter paper was placed in the previously acid washed teflon bomb, together with 5 mililitres concentrated Aristar H_2SO_4 and 3 mililitres concentrated Aristar HNO_3 and heated on a sand bath at 250°C for 30 minutes to destroy all organic matter. The bomb was thoroughly cooled, 1 mililitre of concentrated Analar HF added and again heated for 30 minutes. After being thoroughly cooled the sample was transferred to a 25 mililitre volumetric flask, made up to the mark with deionised water and stored in acid cleaned plastic bottles.

Standard solutions were prepared daily from stock solutions and in the same acid matrix as the samples.

3.6.2.2 Accuracy

The accuracy of this method was tested by analysing three standard air filters (241). Where the concentration range allowed, flame techniques were employed as it is the quicker of the two methods.

The values and range due to error are given in Table 3.28 and those obtained by analysis in Table 3.29. The results illustrate that Cu, Mn, Ni, Zn can be analysed with confidence by direct flame techniques, and Cd and Cr by direct HGA injection. However, Fe and Pb when prepared in this way gave low results by direct flame but when diluted 10 times for Pb and 100 times for Fe and analysed by HGA accurate results were obtained. This can only be explained by the dilution removing a suppression interference on these elements. This is in agreement with Quickert <u>et al</u> (256) who found severe interferences in the determination of V by flame due to Al, Si, Zn, K and Na but no interference at all when analysing by HGA.

The ninth element determined, Al was not spotted on the filters and presented a problem as to whether or not it could be determined by flame techniques. To be safe therefore samples were diluted 1,000 times and analysed by HGA.

It was found in the analysis of the samples that in fact only Zn could be determined by flame techniques, Ni, Mn and Cu being too low in concentration. These last 3 elements were therefore analysed by HGA which will in general add 5% on to the error. The accuracy of the determinations was therefore -

TABLE 3.28 "TRUE" VALUES OF ELEMENTS SPOTTED ON STANDARD FILTERS

	"True Value (µg)	Range (µg)
Cd	3.06	2.91-3.21
Cr	1.85	1.76-1.94
Cu	3.04	2.89-3.19
Fe	194	184.3-203.7
Mn	4.2	4.15-4.41
Ni	5.30	5.04-5.56
Pb	153	145.4-160.6
Zn	74	70.3-77.7

TABLE 3.29 ELEMENTAL CONCENTRATIONS FOUND IN STANDARD FILTERS (μg) BY ATOMIC ABSORPTION SPECTROSCOPY.

	Flame		H.G.A.	
Cu	3.00			
	3.25	3.08±0.14		
	3.00			
Mn	4.25			
	4.50	4.33±0.14		
	4.25			
Ni	5.3			
	5.1	5.17±0.12		
	5.1			
Zn	75			
	75	74.7±0.58		
	74			
Cd			3.17	
			3.02	3.10±0.08
			3.12	
Cr			1.77	
			1.87	1.85±0.08
			1.92	
Fe	150		192	
	147.5	148.3±1.44	190	192.3±2.52
	147.5		195	
Pb	125		153.7	
	122.5	124.2±1.44	153.7	152.5±2.14
	125		150.0	

Cd, Cr, Zn	-	5%
Ni	-	10%
Cu, Mn	-	14%
Fe, Pb, Al	-	18%

The Al was estimated to be of the same order as Fe.

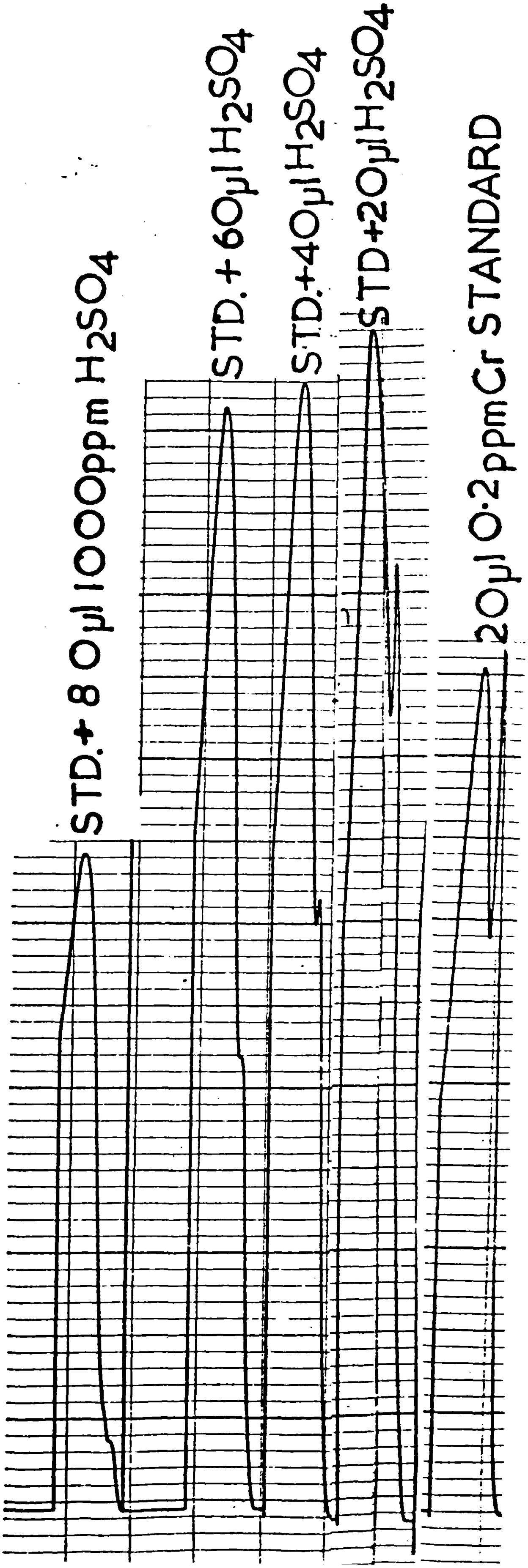
3.6.2.3 Multiple Peaks

During the analysis of elements by HGA a problem of split peaks arose. Figure 3.11 illustrates a 20 µl injection of 0.2 ppm Cr when in an acid mixture of 3 ml H_2SO_4/3ml HNO_3. This problem was encountered with most elements.

Because of the greater volatility of nitrates it was considered that the two peaks illustrated the differing volatilities of the sulphate and nitrate compounds which would be deposited on the carbon rod as the sample was dried. This is in agreement with Matowsek et al (174) who when analysing for Pb in air particulates ashed the filter paper directly in the especially designed collection cup, and obtained multiple peaks due to the different forms of Pb in the atmosphere, e.g. bromide and oxide. Matowsek et al found that by adding 1000 ppm orthophosphoric acid to the samples single peaks were produced. They interpreted this as being due to the formation of the more stable phosphates.

Figure 3.11 illustrates the effect of adding 20, 40, 60 and 80 µl of 1000 ppm H_2SO_4 to 20 µl of 0.2 ppm Cr solution. It can be seen that the first peak (nitrate) is becoming smaller as excess sulphate is added. At 60 µl the peak is single except for a small shoulder. The 80 µl peak is smaller probably because the suppression of the signal by the sulphate is now severe.

FIGURE 3.11 MULTIPLE PEAKS OBTAINED WITH CHROMIUM BY ATOMIC ABSORPTION USING HGA-74 ATOMISER.



This method, however, proved to be very expensive in terms of carbon rods and was therefore not suitable for routine analysis. In order to ensure an excess of sulphate in the sample the acid mixture was changed to 5 ml H_2SO_4 and 3 ml HNO_3. Also two drying stages were used -

i) just above the boiling point of HNO_3 which ensured that all nitrates had been removed.

ii) just above the boiling point of H_2SO_4 the excess sulphate ensuring that only the sulphate of the element was present.

It must be said that this argument does not agree with the theory given previously where sulphate and nitrate are said to decompose to oxide and then reduction by carbon to metal and carbon monoxide. By this theory, even in a mixture of nitric and sulphuric acids, both should decompose to the oxide and then to the metal hence giving only one peak.

3.6.3 Results

The results are given in Table 3.30, together with results from other industrial sites in the world. The Glasgow results represent the average of 96 samples taken over 14 sites. The Sn and V figures are based on the analysis of 12 samples chosen at random.

It will be noted that the levels of Cr, Fe, Mn and to a lesser extent Zn in this section are higher than the previous levels. However, it is not strictly fair to compare the two sets of results directly due to the latter being the average of 14 sites. Moreover these latter results represent mainly winter months which will tend to elevate the levels.

3.6.3.1 Correlation Between Elements

The samples taken at Glasgow University were used to avoid variability of site and amounted to 37 samples. Using the same programme as previously (Section 3.5) the elements were plotted against each other and straight line correlation coefficients calculated. The results at the 95% and greater confidence level are given in Table 3.31. Corresponding results from Section 3.5 are also given for comparison. The Fe/Mn coefficient is much improved, Fe/Cr is about the same and the rest are all lower. The Zn/Mn coefficient in Section 3.5 was the highest correlation with other elements and here, although reduced is the only Zn coefficient above the 95% level, maintaining at least the position of Mn as being the best correlation with Zn.

There could be several reasons for these differences -

TABLE 3.30 ATMOSPHERIC LEVELS OF TRACE ELEMENTS (ng/M^3)

	Glasgow (14 Sites)		Chicago U.S.A. (124)	Niles Michigan U.S.A. (124)	Heidelberg Germany (129)	Texas U.S.A. (242) (50 Stations)	San Francisco U.S.A. (121)	Paris France (243)	Glamorgan Wales (117)	Industrial Limits (mg/M^3) (244)
	Range	Mean								
Al	1300-18000	6588	2175	1200	-	-	250-2000	-	364	None
Cd	0.2-407	13.6	-	-	26.8	-	-	19.5	22	0.02
Cr	2.7-163	35.2	113	9.5	4.6	50-1100	2.2-16	15.1	13.5	0.1
Cu	0.7-665	63.5	1150	270	-	10-960	27-100	-	48.6	1.0
Fe	233-6680	1209	13800	1900	1041	100-10,000	610-3000	3500	609	10
Mn	17.5-829	109	255	62	23.6	20-1700	5-31	82.5	24	5
Ni	1.4-581	128	60	-	-	10	-	-	65.6	1.0
Pb	73-1060	260	-	-	-	20-2560	-	-	253	0.2
Zn	5-2400	388	1400	140	-	5-1770	27-500	-	367	1.0
Sn		<0.7	-	-	71.6	-	0.08	-	-	0.1
V		<7.0	18.1	5.0	-	4	1.5-11.0	-	24	0.5

- = Not Determined

TABLE 3.31 CORRELATION COEFFICIENTS OF ELEMENTS WITH EACH OTHER
(ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY SITE.)

Al	Al							
Cd	-	Cd						
Cr	0.56	0.59	Cr					
Cu	-	0.50	-	Cu				
Fe	0.83	-	0.67	-	Fe			
Mn	0.67	-	0.56	-	0.84	Mn		
Ni	0.67	0.29	-	-	0.34	-	Ni	
Pb	0.28	0.43	0.46	-	-	0.45	0.50	Pb
Zn	-	-	-	-	-	0.42	-	-

Correlation Coefficients of Elements in Section 3.5 (p.94 T3.10)
(ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY '72-73)

Cr	Cr		
Fe	0.58	Fe	
Mn	0.27	0.30	Mn
Zn	0.43	0.44	0.69

i) As was shown in Section 3.5 there is a relationship between elemental levels and weather conditions although this is not linear. Over the longer sampling period used in Section 3.6 therefore the levels will represent the average effect of weather conditions, some elements being more affected than others.

ii) A smaller number of samples was used in Section 3.6 (37) compared with Section 3.5 (158). Therefore small discrepancies will carry more weight in the correlation coefficient of Sec tion 3.6.

The most curious result in Section 3.6 is the total lack of relationship between Zn and Cd as they are closely related in their natural minerals. The correlation coefficient is 0.00047 with a confidence level well outside the 95% level. This could of course be explained by the reasons given above but the total lack of relationship is still striking.

Cr, Fe, Mn and Ni all have good relationships with Al and this is consistent with the fly-ash source theory of Section 3.5. Pb, Zn, Cd and to a lesser extent Cu represent those elements with the highest enrichment factors (see next section). Again the lack of relationship to Al is consistent with these elements having additional sources.

3.6.3.2 Enrichment Factors

Enrichment factors were calculated on each individual sample based on Fe to allow comparison with Section 3.5. The results, averaged for each site, are given in Table 3.32. The Glasgow average (14 sites), the range from individual samples, and those of Dams <u>et al</u> for Liege (Belgium)(251) are given in Table 3.33.

TABLE 3.32 ENRICHMENT FACTORS FOR GLASGOW SITES
(ATMOSPHERIC PARTICULATES) (BASED ON SOIL)

Site	Cu	Ni	Zn	Al	Cd	Mn	Pb	Cr
GU	135	76	337	2	11050	4	880	12
BA	133	232	123	5	7930	5	1790	9
QP	78	171	439	3	3630	5	1080	9
KS	14	293	227	5	1920	3	1570	8
BP	363	146	233	6	13990	7	1830	20
CC	4	323	126	3	12360	8	2730	15
KP	2	87	335	3	3700	4	1330	10
SS	5	80	427	2	3150	5	700	8
SR	26	43	205	2	2460	2	820	6
EH	39	61	243	2	5060	3	520	15
OL	23	52	147	4	1710	5	270	5
WS	83	222	134	4	34290	2	910	11
SA	405	146	232	5	29180	3	940	14
MP	42	181	219	4	10890	4	1440	17

TABLE 3.33 AVERAGE ENRICHMENT FACTORS FOR GLASGOW AND LIEGE
(ATMOSPHERIC PARTICULATES.)

	Glasgow		Liege (Based on Al)
	Range	Average	
Al	0.3-7	4	1
Cd	250-82870	10100	41000
Cr	5-46	12	-
Cu	1-2005	96	200
Fe		1	3
Mn	0.4-20	4	5
Ni	2-528	151	-
Pb	80-5500	1200	-
Zn	5-954	245	2100

From Table 3.33 the first point which must be made is that for Mn and Cr normalised to Fe enrichment factors are basically the same as in Section 3.5, although the actual levels were higher in Section 3.6. Zn although of the same order tended to be higher in Section 3.5, although the value does lie within the Section 3.6. range. These results are encouraging in that they should allay fears of there being an unknown factor involved which basically alters the aerosol collected and analysed from Section 3.5 to that from Section 3.6.

The results are again in good agreement with Liege which apart from Zn lie within the range of Glasgow.

The first striking feature about Table 3.32 is the uniformity of enrichment factors for Mn, Al, (Fe), and to a lesser extent Cr and Zn throughout the city. The first four elements are again those which are found in the inorganic fraction of coal and as already said Zn is also in this group but has additional industrial sources which tend to raise the enrichment factor. Cu and Ni tend to be more variable. In at least four cases with Cu (CC, KP, SS, KS) the enrichment factors are not so very far from soil ratios and another six (QP, SR, EH, OL, WS, MP) have enrichment factors below 100. Ni tends to be higher with only six below 100 and none below 50. It is probable therefore that Ni is predominantly from pollution sources other than coal burning but that Cu is in some cases purely fly-ash in origin.

An attempt at explaining the variation in Cd, Pb, Cu and Ni with respect to the area was soon abandoned. The difficulty is that the samples were not taken simultaneously and the variation could reflect wind direction at time of sampling or variability of output, and is one of the disadvantages of this type of sampling.

3.6.3.3 Variation of Elements with Sites

As said previously samples were taken around the city and referred back to Glasgow University as a reference site.

It is safe to say that there is no statistical difference between areas but a dynamic system was being studied with no two samples from the same site giving the same reading. Statistics in this context are therefore meaningless and only general trends can be concluded. The average levels are given in Table 3.34 and the order of ratios to Glasgow University, together with the ratio at the sites in Table 3.35. It is here that a lack of statistics is a hindrance, e.g. with Zn the ratio starts at 0.2 and progresses through to 1.0 with only 0.6 absent, making it difficult to judge which if any are truly different. However, certain points can still be made.

i) No site is consistently lower or higher than G.U. for all 9 elements.

ii) WS which lies in the direct flight path of the airport has the greatest ratios for Cu, Ni, Cd and Cr, and is well up the list for Al, while Pb is not much different from G.U. Klein <u>et at</u> (6) when studying metals in soils found that Cd, Cr, Cu, Ni, Fe and Zn were higher around an airport but Pb was not. Five of the elements from WS agree with this, while Zn is the lowest of all sites at WS and Fe is about the same as G.U. General trends of agreement can be noted.

iii) Areas which were thought to have no pollution sources (CC, MP) are not consistently low. Only for Cu at CC is the ratio the lowest of the sites. In fact MP-Fe, Ni, Al and Cr ratios are the second highest and Pb and Cd the third highest.

TABLE 3.34 AVERAGE LEVELS OF ELEMENTS AT CITY SITES (ng/M^3)

(ATMOSPHERIC PARTICULATES)

Site	Cu	Ni	Zn	Fe	Al(μg)	Cd	Mn	Pb	Cr
BA	41	158	95	600	5.6	6.6	63	298	14
QP	43	178	507	1084	6.8	5.2	111	297	23
KS	15	395	131	1391	14	3.2	90	481	29
WS	23	199	127	876	5.6	26	59	211	31
MP	27	236	411	1270	9.7	18	116	434	101
SA	201	144	297	953	7.8	40	48	230	35
BP	189	89	114	416	4.2	8.5	68	65	21
CC	0.9	152	113	586	3.6	12	148	261	22
KP	0.7	55	211	681	3.3	4.0	66	286	23
SS	2.0	94	240	839	3.8	3.7	87	156	18
SR	15	68	301	950	4.0	8.8	42	191	16
EH	28	61	339	930	3.0	3.9	72	124	41
OL	72	109	377	1980	12	5.0	142	680	38

TABLE 3.35 ORDER OF SITE TO GLASGOW UNIVERSITY RATIOS (OF ELEMENTAL CONCENTRATIONS IN ATMOSPHERIC PARTICULATES)

Fe EH = SR = OL = BP CC SA = BA = QP KP WS = SS GU MP KS
0.4 0.6 0.7 0.8 0.9 1.1 1.6

Cu CC QP KS SS BA = KP GU = MP BP = OL SR EH SA WS
0.03 0.1 0.2 0.3 0.5 1 1.5 1.6 3.1 3.3 21

Ni EH = OL = KP SR = BP CC = SS GU BA QP KS SA MP WS
0.5 0.7 0.9 1.3 2.1 2.5 8.0 26 95

Zn WS = BA KS = BP = OL SA = CC QP MP = KP SS SR GU = EH
0.2 0.3 0.4 0.5 0.7 0.8 0.9 1

Al EH OL = SR CC BP BA GU SS KP QP SA WS MP KS
0.3 0.4 0.6 0.7 0.9 1.1 1.2 1.5 1.8 2.1 2.9 3.4

Cd BP = QP OL = KS BA = KP = EH = SS GU = CC SR MP SA WS
0.1 0.4 0.6 1 1.4 4.4 5.3 19

Mn OL = SR SA = EH BA BP MP GU = QP = WS = KP SS CC KS
0.2 0.4 0.6 0.8 0.9 1 1.1 2.5 3.3

Pb BP SS = EH SA SR KP GU BA = QP WS CC MP KS OL
0.4 0.5 0.7 0.8 0.9 1.1 1.3 1.4 1.9 2.0 5.0

Cr SS BP = SR SA BA = OL QP CC EH GU KP KS MP WS
0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.6 2.0 2.3 2.6

iv) OL is near the centre of the city and lies on a main arterial road. This is reflected by being highest on the list for Pb. Conversely BP is probably the most residential of the sites and has the lowest Pb ratio.

3.6.3.4 Effect of Wind

As in Section 3.5 wind direction was calculated from hourly observations at Glasgow Airport to give the total hours the wind was blowing from the eight compass points. Samples were then selected such that the wind was blowing from one site over another. Some sites could not be used at all since the wind direction was never in the right direction, especially the less common winds, e.g. east winds. The lack of wind in this direction disallowed the use of the G.U.-SR-EH system. The results are given in Table 3.36. The following points can be made -

(a) There is a general rise in all elements from CC to G.U. except Pb and Mn. Pb was generally lower at G.U., but with Mn three out of four samples were higher at G.U. than at CC maintaining the same trend as other elements.

(b) All G.U. results are higher than SS.

(c) All SS results are higher except for Pb and Cu, and Al and Cd are about the same at both sites. The two Cu readings for KP were 0.8 and 23.6 and an average for such is not reliable.

(d) All MP results are higher due to NE winds and this is a part explanation of why MP levels were higher than expected.

(e) All WS results are higher except for Zn (Zn had the smallest ratio of all sites) and Mn which is about the same at both sites.

TABLE 3.36 EFFECT OF WIND DIRECTION ON ELEMENTAL LEVELS (ng/M^3)
(ATMOSPHERIC PARTICULATES).

(a) CC - GU - Average of four SW wind Samples

	Cu	Ni	Zn	Fe	Al	Cd	Mn	Pb	Cr
CC	0.9	152	113	586	3.6	11.8	148	261	22.5
GU	34.4	165	258	918	6.4	12.0	60	185	26.5

(b) GU - SS - Average of two E wind Samples

GU	19.0	110	309	1035	4.2	6.3	93	309	19.7
SS	2.7	87	184	770	3.9	3.9	80	139	17.1

(c) KP - SS - Average of two SW wind Samples

SS	1.0	88	802	931	3.9	4.5	94	194	19.5
KP	12.2	64	242	806	4.0	4.3	75	226	17.3

(d) GU - MP - Average of two NE wind Samples

GU	0.7	1.5	267	620	2.0	2.0	34	98	6.0
NP	13.0	142	316	962	6.3	16.9	68	363	46.7

(e) GU - WS - Average of two SE wind Samples

GU	0.7	1.5	267	620	2.0	2.0	34	98	6.0
WS	8.7	240	175	743	5.8	7.6	36	197	16.4

(f) GU - BA - One NW wind Sample

GU	89	76	301	715	5.3	11.7	66	200	17.6
BA	61	92	63	483	3.2	13.7	36	177	14.6

(g) Gu - QP - Average of two E/SE wind Samples

GU	192	110	1038	1740	5.3	242	14.9	320	41.8
QP	36	164	654	935	4.8	6.4	10.5	225	25.4

(f) All results except Ni and Cd are higher at G.U.

(g) All results except Ni are higher at G.U.

From these tables, as expected, in general the elements are increasing in concentration as the wind blows over the city and eventually out into the surrounding countryside.

3.6.3.4 Comparison of City with Rural Areas

Sites were set up at Ayr Academy (AA) which is one street removed from the West coast and at Loudon Academy, Galston, (LA) about 12 miles from the coast and half-way between Ayr and Glasgow.

The average results for 4 weekly samples are given in Table 3.37.

As expected Ayr levels are much lower than Glasgow except for Fe and Al which are about the same. LA tends to be more variable. However, after sampling it was discovered that due to the shape of the surrounding hills there was a funnelling effect carrying pollutants from Kilmarnock - a semi industrial town. This tends to obscure any trends, although, except for Cu and Al the levels are still lower than Glasgow. Al is about the same but Cu is much higher.

Enrichment factors were calculated for AA, LA, and the corresponding G.U. samples. The results are given in Table 3.38. Ayr enrichment factors are much closer to soil levels indicating the rural setting of this holiday resort. There is some light industry and this is probably responsible for the slight elevation of Zn and Cd. As would be expected Pb is also elevated but not so much as Glasgow thus reflecting the lower density of traffic in Ayr.

TABLE 3.37 ATMOSPHERIC LEVELS OF ELEMENTS IN RURAL SITES (ng/M^3)

	Al(μg)	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
GU	2.3	9.6	63.4	16.0	1220	216	68.7	398	703
LA	2.6	3.7	11.8	70.0	621	44	36.6	122	123
AA	2.5	4.0	11.2	2.6	911	33	21.3	107	153

TABLE 3.38 ENRICHMENT FACTORS FOR RURAL SITES
(ELEMENTS IN ATMOSPHERIC PARTICULATES)

	Ayr	Galston	Glasgow
Al	1	2	1
Cd	2870	4336	5744
Cr	5	8	20
Cu	5	171	25
Fe	1	1	1
Mn	2	3	8
Ni	21	52	53
Pb	450	778	1250
Zn	130	147	427

Galston shows the same trends as Ayr except for Cu which is more enriched than Glasgow and Ni which is the same. Enrichment factors at Galston tend to be higher than Ayr probably reflecting the effect of industry at Kilmarnock.

3.6.4 Conclusions

Because of financial restrictions simultaneous samples could not be taken and a system of reference sampling based on the University was adopted. This of course complicates any deductions which may be made from the results but does not entirely invalidate them.

The levels of elements, as expected, show a wide range of values throughout the city but no area is consistently below or above the University level. The enrichment factors do, however, remain relatively constant for Mn, Al, Fe, Cr and Zn, i.e. the elements found in the inorganic fraction of coal and are close to the soil ratios with the exception of Zn. The reasons for this have already been discussed. Cd, Pb, Cu and Ni have generally higher enrichment factors and fluctuate throughout the city. These elements represent additional industrial sources.

On comparison with rural settings, as expected, Glasgow levels tend to be higher with the enrichment factors of the rural sites closer to the soil ratios.

Finally from a wind study it can be seen that the atmospheric levels generally increase as the air blows over the city and as was pointed out in Chapter I this could lead to problems in agricultural land by the settling out of particles as the wind speed drops.

3.7 PARTICLE SIZE DISTRIBUTION OF ELEMENTS IN THE ATMOSPHERE

The size of particulate matter in the atmosphere is important to both plants and animals. The smaller the particle the easier it will be for it to enter leaves directly through the stomata and to penetrate further into the human lung.

Inhalation and retention of particles in the lung in general induces a physiologic response reflected in a slowing of the ciliary beat. The clearing action of the lungs depends on the beating action of the cilia to sweep foreign particles upwards and out of the respiratory tract into the back of the throat where they are automatically swallowed (i.e. the pollutant will then act as if swallowed). Decrease in efficiency of activity of the cilia can cause pollutants to become fixed at a particular point in the tract thus increasing the likelihood of them creating a toxic effect. Also the slower the beating action the slower the upward sweep of matter. In time this would increase the residence time of foreign matter and therefore increase its ability to exert a toxic effect on the respiratory tract lining.

Not only is this a problem with the particles as chemical species but as physical entities they adsorb and absorb gases and solutes therefore increasing their effect by holding them more focally in deeper parts of the lung for longer periods.

Particle deposition within the respiratory tract is affected by

i) Size of particle.

ii) Air velocities and transit times of air within the system.

iii) Obstructions and baffles encountered thus changing the direction of air flow.

iv) The forces necessary to displace the particles sufficiently to make them impinge on to the surfaces of the respiratory tract lining.

The size believed to cause the most injury is the particle with an effective diameter of less than 1µm. Smaller particles seem to be less readily removed from the lungs therefore adding additional dosage and residence time. Figure 3.12 illustrates the positions in the respiratory tract at which particles of various diameters are retained (2).

3.7.1 Sample Collection

In order to investigate the size distribution of atmospheric particles the sample must be fractionated. This can be achieved through the use of a cascade impactor. A four stage impactor with a back up filter was used in this work and is illustrated in Figure 3.13. However, impactors with up to nine stages are also commercially available. Millipore filter papers were used as the collection medium since the blank values were already known.

As the sample is now effectively collected over five filter papers a large sample volume is required. Since 20 M^3 was required for the analysis of the total sample, 100 M^3 was collected over a period of 15 days in July 1975 at a flow rate of 17.5 litres/minute.

3.7.2 Principles of Impaction

Impaction may be defined as the process whereby, under suitable conditions, an aerosol particle in an air flow collides with a surface and sticks.

FIGURES 3.12 PARTICLE SIZE PENETRATION INTO RESPIRATORY TRACT

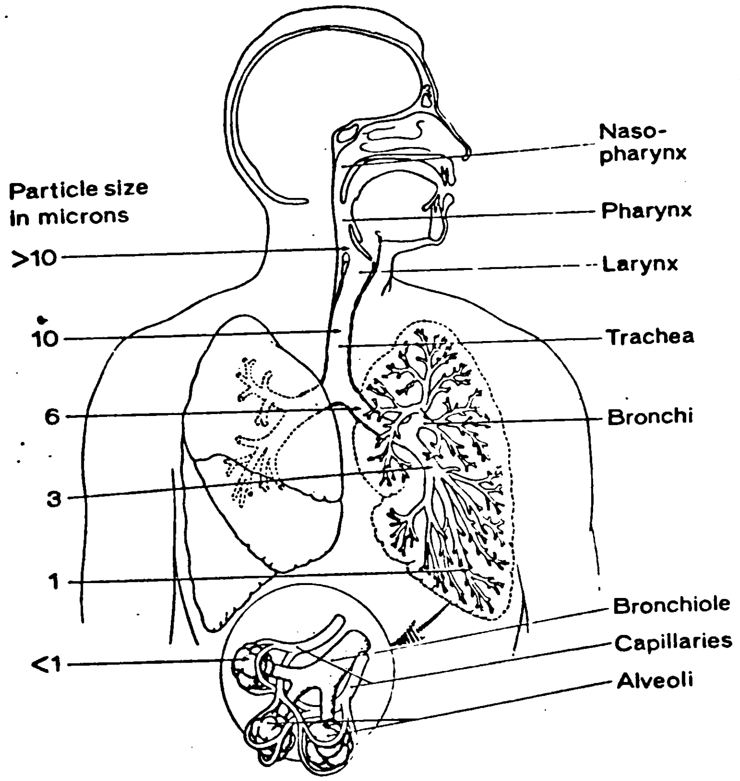
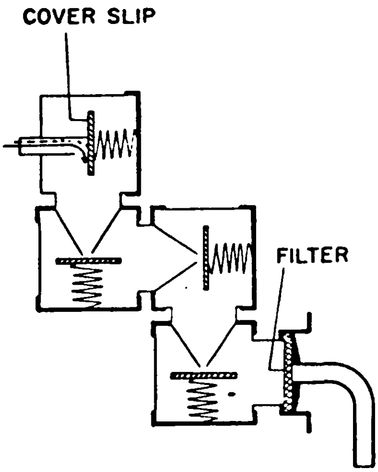


FIGURE 3.13 GRAPHIC ILLUSTRATION OF CASCADE IMPACTOR



One way to cause a particle to impact is to make the air stream bend sharply. If the bend is sharp enough the inertia of the particle causes it to continue in a straight line so that it leaves the air stream and impacts on the filter paper. This process is shown in Figure 3.14. In order to keep the particle moving with a curved streamline a radial force of $F_r = \frac{mV^2}{r}$ must be exerted on the particle (m and V are the mass and velocity respectively and r is the radius of curvature of the streamline). This force arises from collisions with the surrounding air molecules, which are more densely packed nearer the impaction surface and thus exerts a net force away from it.

It is easy to see that large particles must impact more easily than the small particles. The radial force needed to keep a particle in the streamline varies with m or with R^3 (R = radius of particle) but the number of collisions of the particles with air molecules varies with the cross-sectional area of the particle or only with R^2. Thus the larger the particle the more efficiently it will impact. This and all the other factors controlling impaction have been combined into an inertial impaction parameter K -

$$K = \frac{\sigma d^2 V}{18 \mu D}$$

where σ = particle density

d = particle diameter

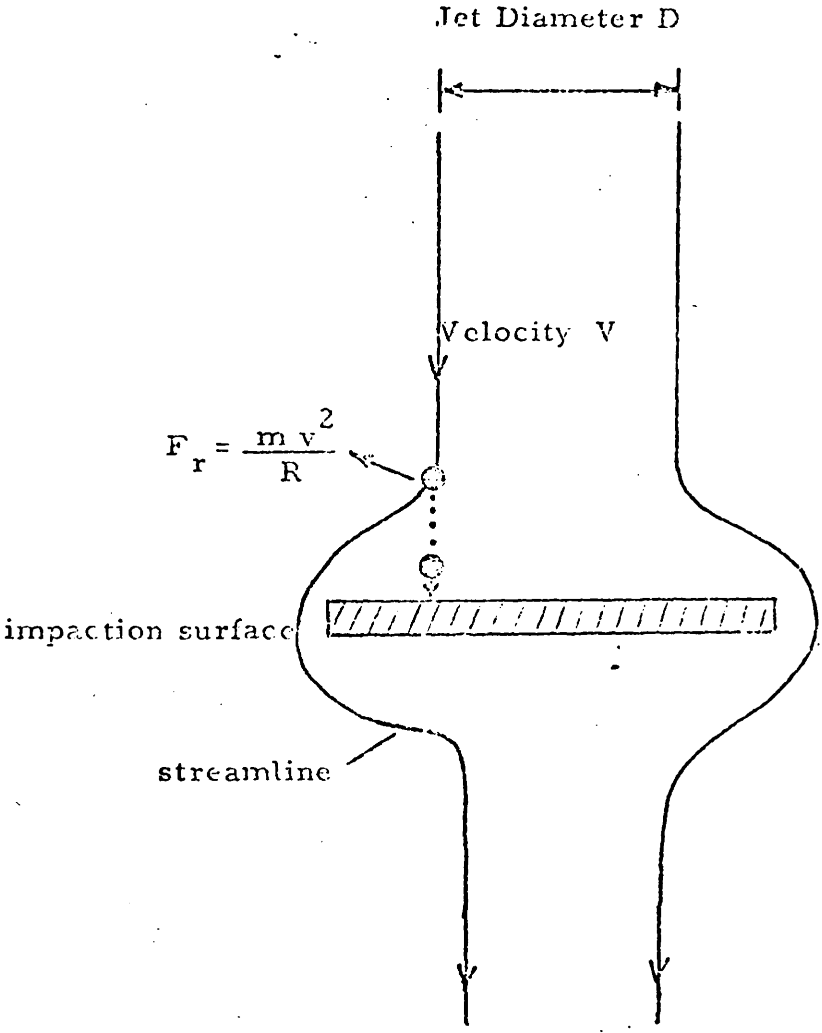
V = particle velocity

μ = air viscosity

D = jet diameter.

Large values of K indicate efficient impaction.

FIGURE 3.14 PRINCIPLES OF IMPACTION



Another impaction parameter is the cut-off diameter, or the size for which 50% of the particles will be impacted on to a surface. It is usually considered as the minimum collection diameter and may be calculated from the formula -

$$d^2_{min} = \frac{36\mu D}{\pi \sigma V}$$

where d_{min} = the cut-off diameter.

Because the largest particles are most effectively impacted it is easy to see that by subjecting an air stream to a series of impactions progressively smaller particles may be removed. To do this it is only necessary to increase the velocity of the air stream and/or decrease the diameter of the jet with each successive stage. This means that these instruments must be operated at the flow rate stipulated to achieve the size of separation quoted.

3.7.3 Analysis

The samples were digested in the acid mixture and analysed by atomic absorption spectrometry for 9 elements as described in Section 3.6.

3.7.4 Results

On visual inspection stage 1 carried virtually no particulate matter and was not analysed. The general order of staining was $5 > 4 \approx 3 > 2 > 1$ although 5 may be misleading due to the collection area being larger.

Table 3.39 illustrates the cut-off diameter, range and amount of each element collected at each stage. In each case the total concentration collected lies within the reported range of elements collected routinely in Section 3.6 (see Table 3.30). The results are also shown graphically in Figure 3.15.

3.7.4.1 Inhalation

The amounts of each element collected at each stage are illustrated as a percentage of the total element collected over all stages in Table 3.40.

With reference to Figure 3.12 it can be seen that the more toxic elements have large proportions below 1 μm diameter and therefore will pass easily into the alveoli. These are - Ni (88%), Cd (77%) and Pb (71%). The other element fractions which will enter the alveoli are Zn (83%), Cr (54%), Mn (53%), Fe (43%), Cu (35%) and Al (29%).

The remainder of each element will penetrate at least as far as the bronchi and some as far as the bronchiole.

The implications of these results are clear - any process which is installed to reduce the emission of elements into the atmosphere must be able to remove the smallest particles as a large portion of the elements are concentrated in this size range. Two recent

TABLE 3.39 CONCENTRATIONS OF ELEMENTS AS A FUNCTION OF PARTICLE SIZE (ng/M^3)

(ATMOSPHERIC PARTICULATES- GLASGOW UNIVERSITY.)

	Cut off Diameter (µm)	Range (µm)	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Stage 1	12.0	6.3 - 17.0	-	-	-	-	-	-	-	-	-
Stage 2	4.4	2.0 - 6.3	847.1	0.3	3.3	5.8	147.3	2.7	3.4	54.6	147.6
Stage 3	1.5	0.7 - 2.0	786.0	0.2	3.6	7.1	176.8	2.8	5.2	98.0	88.8
Stage 4	0.45	0.43- 0.7	252.3	1.1	1.5	3.3	87.4	2.9	42.9	172.8	1036.0
Stage 5	-	0.43	418.0	0.6	6.6	3.5	159.3	3.3	22.8	203.1	76.4
Total			2303.4	2.2	15.0	19.7	570.8	11.7	74.3	528.5	1348.8

TABLE 3.40 CONCENTRATIONS OF ELEMENTS* COLLECTED AT EACH STAGE AS PERCENTAGE OF TOTAL

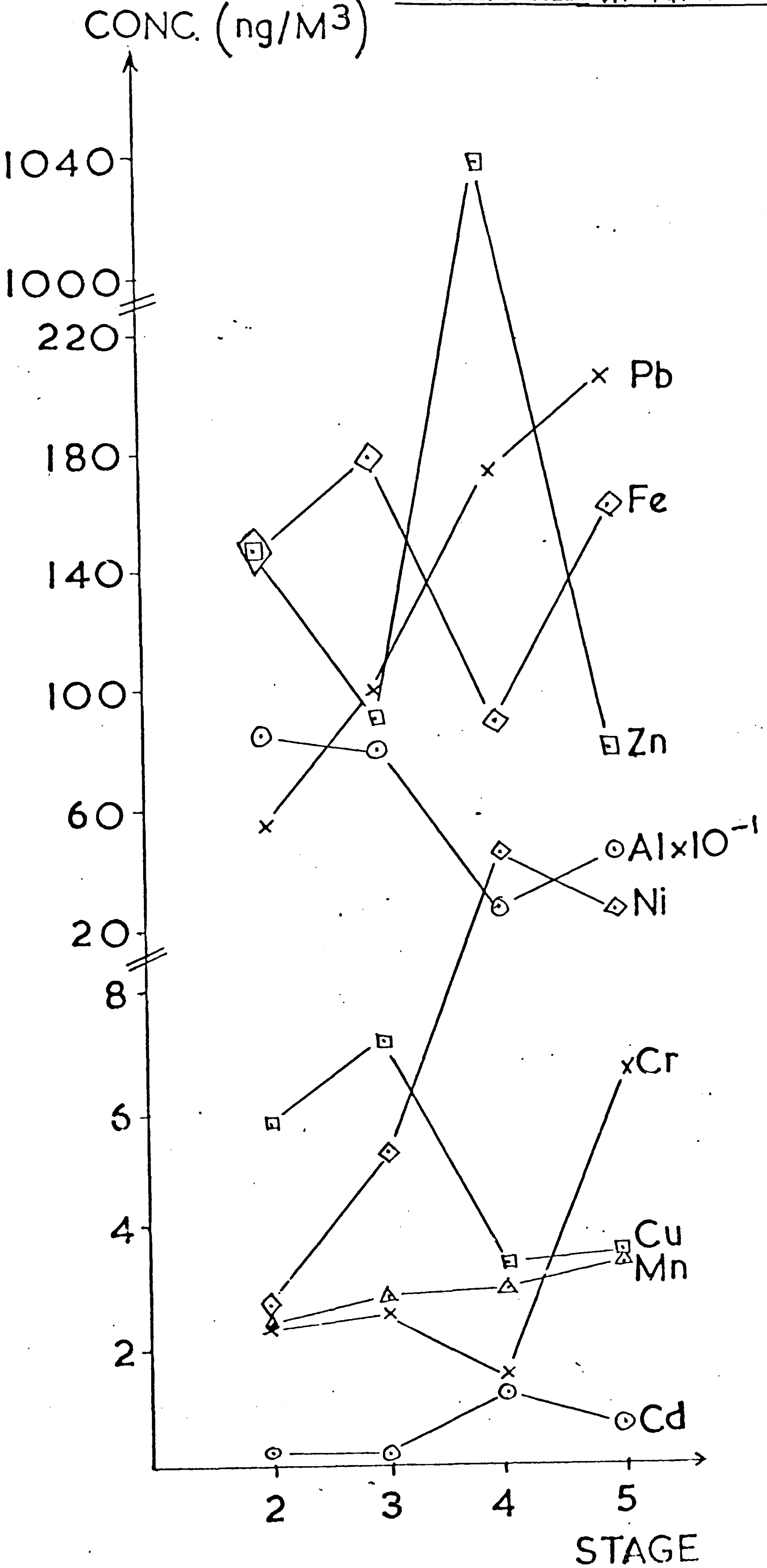
	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Stage 2	37	14	22	29	26	23	5	10	11
Stage 3	34	9	24	36	31	24	7	19	6
Stage 4	11	50	10	17	15	25	58	33	77
Stage 5	18	27	44	18	28	28	30	38	6

TABLE 3.41 MASS-MEDIAN DIAMETERS OF ELEMENTS* AND REPORTED RANGES

Element	MMD(μm)	Range(μm) (± 15%) (REPORTED)
Al	2.1	4 - 7.0
Cu	2.0	0.6 - 7.0
Fe	1.7	1.5 - 6.0
Cr	1.4	1.5 - 7.0
Mn	1.4	1 - 7.0
Zn	0.8	0.7 - 7.0
Cd	0.6	1.5 - 10.0
Ni	0.6	1.0 - 1.5
Pb	0.5	0.2 - 0.7

* ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY.

FIGURE 3.15 GRAPHICAL REPRESENTATION OF CASCADE IMPACTOR RESULTS AT GLASGOW UNIVERSITY



studies have investigated the trace element emission from coal fired boilers (257-258). In one (257) it was found that the highest concentrations of Pb and Cd appeared in the respirable size range and that the concentrations increased with decreasing particle size. This was found to be the case in this work for Pb. In the second study (258) it was found that the most toxic elements (As, Sb, Cd, Pb, Se and Tl) were concentrated in the smallest respirable particles. It was said that these are volatilised during combustion and preferentially adsorbed or condensed on to the small particles which can most easily pass through conventional control equipment.

3.7.4.2 Mass-Median Diameter (M.M.D.)

Another way of expressing cascade impactor results is by means of the mass-median diameter. This is the particle size above which 50% of the mass of that element is found. The results are given in Table 3.41, together with the reported range found elsewhere (259). Only Al, Cd and Ni lie outwith the reported ranges and of these Ni is reasonably close. Both Al and Cd are well below the minimum reported ranges. Why this should be so is not clear. As this is the first study of its kind in Glasgow there are no criteria for comparisons and the low values may reflect different industrial activity.

3.7.4.3 Size Types

Using an Anderson Cascade Impactor with nine stages Rahn (251) divided the elements into five classes depending on the mass of the element associated with each size range. These are -

1) L-type - mass associated with largest particles.
2) M-type - mass associated with medium sized particles.
3) S-type - mass associated with smallest sized particles.
4) F-type - mass divided equally among various size ranges.
5) Mixed patterns where two or more of the first three types are present to approximately the same extent.

The elements measured here were placed in one of these classes and the results are given in Table 3.42, together with those for Rahn for Liege in Belgium.

The partitioning of elements into different size ranges is of course arbitrary and borderline cases will exist. However, the results are in extremely good agreement with those of Rahn. Fe as can be seen from Table 3.39 has 57% on and above stage 3 and 28% on the back-up filter. Does this place Fe as an L-type or is 28% considered a large enough fraction to class Fe as an LS-type? Similarly Cd has 77% of its mass in the small size range but of this, 50% is on stage 4 and is extremely borderline. Cd can arguably be in either the S or M-type class.

The only contrary result is with Cu which in Glasgow is undoubtedly an L-type whereas in Liege it is an S-type. Since both mass-median diameter lie within the reported range then this again may simply reflect different industrial activity.

3.7.4.4 Enrichment Factors

The enrichment factors calculated to Fe for each stage are given in Table 3.43.

The following points can be made from these results.

i) All the enrichment factors found lie within the range reported in Section 3.6.

TABLE 3.42 ELEMENTS* CLASSED AS A SIZE FUNCTION

Element	Type of Function	Rahn (et al)
Al	L	L
Cu	L	S
Cr	LS	-
Fe	LS	L
Zn	M	M
Cd	S	M
Ni	S	-
Pb	MS	-
Mn	F	F

TABLE 3.43 ENRICHMENT FACTORS OF ELEMENTS* ON EACH STAGE

	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Stage 2	3	1358	9	74	1	1	22	1426	759
Stage 3	2	754	8	76	1	1	28	2132	380
Stage 4	2	8390	7	71	1	1	372	7604	8980
Stage 5	1	2511	16	41	1	1	136	4904	363

* ATMOSPHERIC PARTICULATES - GLASGOW UNIVERSITY.

ii) Al, Cr, Cu, Fe and Mn vary very little from stage to stage. The enrichment factors of 41 for Cu and 16 for Cr in stage 5 are probably not signficant.

iii) Cd, Ni and Pb are more enriched in the smaller particle range.

iv) Zn tends to be more enriched in the small-medium size range.

These results are in partial agreement with those of Colovos <u>et</u> <u>al</u> (260) who found -

i) enrichment factors for Pb and Cd were inversely proportional to particle size. This was found here for Pb but only for Cd in the very broadest sense.

ii) enrichment factors for Zn and Cu were independent of particle size. This was found for Cu but not for Zn which had a large fraction in stage 4.

iii) Fe, Mn, Ca, and Mg in all size ranges had essentially identical ratios as average crustal material. This as can be seen from Table 3.43 was also found here.

The uniformity of Al, Mn, Fe and Cr, and the closeness to soil ratios provides further evidence of a common source for these elements.

Ni is close to the soil ratio down to 0.45 μm after which it increases dramatically. This is in agreement with this element having additional industrial sources. These high temperature processes favour the formation of small particles.

Cd, Pb and Zn are also more enriched in the small particle range suggesting industrial sources. The enhanced enrichment factor for Pb in the smaller particle range is also consistent with the emission size of the element from automobile exhausts.

3.7.5 Conclusions

The size distribution of elements in Glasgow's atmosphere in terms of the mass-median diameter and size functions are in good agreement with those reported from elsewhere with the exception of Al and Cd.

The most toxic elements (Cd, Ni, Pb) have extremely high proportions in the smallest respirable particle range which can easily enter into the alveoli. The other elements have 29 - 83% in the same size range, i.e. less than 1 μm. The remaining fraction of these elements can easily pass the nasal passage and enter the upper sections of the lungs where adsorbed species can act more focally.

Enrichment factors for the elements suggest probable different sources and lie within the range of the whole sample analysis. (Section 3.6.3.2).

A note of caution must be made on conclusions drawn from the results as they are based on the analysis of one sample admittedly of 15 days duration and can only be considered to be of a tentative nature.

3.8 ASSESSMENT OF PROJECT AND POSSIBLE FUTURE WORK

This project has gone a long way to achieving the aims as set out in Chapter I.

The elemental levels of 21 elements have been measured over an extended period. From one site sampling the effect of weather has been studied and found to influence the levels and by studying various areas the city as a whole has been monitored. Possible sources of the elements have been suggested from their enrichment factors calculated to soil or rock ratios. The distribution of elements in the various size ranges has been investigated and the implications of the results discussed.

Future work would include as already mentioned further manipulation of the existing results to gain more precise information on the effect of weather conditions on elemental levels. The range of elements could be extended to include such elements as Be which has given cause for concern in recent years (1, 2, 261). Finally one study which was not carried out was the diurnal variation of the elements. This has been done in other cities finding peak values for certain elements during peak rush hours, e.g. (120). An attempt was made to do this but was abandoned because of insurmountable sampling problems. Because of the small pore size of the millipore filter paper large volumes of air could not be sampled in a short period. Conversely no pump was available which would sample enough air, drawn through for example a Whatman's filter paper to overcome the higher blank values of the latter filters.

CHAPTER IV WATER POLLUTION

4.1 INTRODUCTION

As stated previously the three main areas of human contamination by elements are through breathing air, eating food, and drinking water. The first of these has been extensively studied in Chapter III and the second was not considered here as it is monitored by the Department of the Regional Chemist which is now also involved in a survey of domestic drinking water for Pb, Fe and Cu. However, at the time this project was initiated this was not being done and to gain some information about this a survey of drinking water in the Glasgow area was initiated.

This survey is particularly important in the case of Glasgow because of the soft water supply and the use of lead piping. The problem is that soft water does not give pipes a natural coating of calcium carbonate and soft water itself tends to dissolve metals more readily than alkaline waters. Moreover many metals exhibit higher toxicities in soft water than in hard water. This is said to be partly caused by competition with the calcium present in hard water which can block the toxic action of metals by occupying enzymic sites.

There have been several studies carried out in the Glasgow area where attempts have been made to correlate mental retardation problems and the occurrence of cardiovascular disease with the presence of lead in drinking water (262-265). In a study of 71 houses in the Highlands a combination of soft water and lead lined tanks was found to give cold tap water values of the order of 18 times the upper acceptable level of that element (266). Bones of people in soft water areas have been found to have higher lead content than those in hard water areas (267). There have been other studies of this type in Britain (268,269) and also in other countries (270-273).

However, several people feel that the relationship between soft water, lead content, mental retardation and cardiovascular disease have been over emphasised with the handling of the statistics a main weakness (274) and Elwood <u>et al</u> in particular has in at least three studies found:-

i) No significant difference between the mean lead content of homes of mentally subnormal children and those of control normal children (275).

ii) The returns for deaths for 1969-1973 in N.W. Wales failed to support an association between water lead values and mortality from cancer or cardiovascular disease (276).

iii) That water lead was an unimportant source of blood lead levels in N.W. Wales an area of high lead content in the water (277).

Whatever the medical opinion, however, it is a wise precaution to know the metal levels in any soft water area for future reference.

4.2 METALS STUDIED

The obvious metals to study are those which are common in plumbing materials - Pb, Zn, Fe, Cu, Cr and Ni. Cd was also added to this list as it has been identified in drinking water in Sheffield and on that occasion was found to be above the W.H.O. maximum of 0.01 ppm (1).

4.3 SAMPLING

4.3.1 Contamination

Because of the ever present possibility of contaminating the sample or causing loss of analyte element, all stages of sample handling were executed with due care. The metals to be determined in these samples are present at trace levels and consequently even small amounts of contamination will drastically alter the concentration. Similarly, loss of even a few micrograms of element by absorption or precipitation will have a very serious effect. Consequently all plastic storage bottles were new and cleaned by standing overnight containing $^{N}/10$ HCl and then thoroughly rinsed with de-ionised water. All glassware used was new and also cleaned with $^{N}/10$ HCl and de-ionised water. Pipette tips for presenting the sample to the spectrophotometer which are an additional source of contamination especially Fe, were rinsed in $^{N}/10$ HCl and de-ionised water immediately before use and only used once.

4.3.2 Collection

Bottles were distributed to members of the Chemistry department as this was found to give a reasonably good coverage of the whole city and surrounding area and amounted to some 120 samples. In 12 cases two samples were taken, one of the water standing in the pipes overnight and the second after running the water for 5 minutes. In the remainder only the second type of sample was taken (running water).

Participants were asked to complete the questionnaire illustrated in Figure 4.1

4.3.3 Storage

Samples were acidified with glacial acetic acid (1 ml per 100 ml water) to stabilise the metals and prevent absorption on to container walls. Such samples are stable for up to one month and except for Pb can be stable for up to 4 months (278).

4.3.4 Preparation

Metals in water may be divided into four classes - dissolved, suspended, total and extractable, the terms being self-explanatory. Of these four only dissolved metals were studied here since this represents the "normal" background level, as suspended and total are subject to fluctuation with erosion of the piping. Extractable in terms of human ingestion is meaningless and is more important in river and loch systems.

Samples were therefore filtered through a 0.45 μm membrane filter and the filtrate then acidified with acid for storage. (The filter size although somewhat arbitrary is in common use).

4.4 ANALYSIS

Samples were analysed by atomic absorption spectroscopy using a Perkin Elmer 306 double beam instrument equipped with a heated graphite atomiser (H.G.A. - 74 model) and deuterium background corrector.

FIGURE 4.1 QUESTIONNAIRE FOR DOMESTIC WATER SURVEY

Directions:-

Run the cold water tap in the kitchen for approximately 5 minutes before taking the sample to clear the pipes of water lying in them, and fill the bottle provided.

The following questionaire is to allow a comparison of all the factors to be made.

(1) Name:-

(2) Address (street name and district only required):-

(3) Bottle Number:-

(4) Approximate age of house:-

(5) *Material of plumbing (lead, copper etc.):-

(6) *Does the cold water come from a tank in the house or street mains?

(7) *If a tank - material of tank:-

(8) Any other relevant information (water going brown etc.)

It has been found that with power plant effluents analysed by H.G.A. aqueous standards give good agreement with the standard additions method, hence samples could therefore be compared directly against the aqueous standards (278). Also as these water samples analysed here are characterised by low salinity and low dissolved solids content (even more so with soft water) the metals can therefore be determined directly against aqueous standards as calibration. Acetic acid was added to standards to give the same acid matrix.

A de-ionised water blank was processed in the same manner as the samples.

4.4.1 Accuracy

Since there is virtually no sample preparation the main sources of error in this analysis are:-

i) Measurement and pipetting of the sample into the furnace.
ii) Measurement of peak heights.
iii) Straight line fit of standards.

From duplicate analysis of samples using difference standard solutions the accuracy of these results has been estimated to be ± 10%.

4.4.2 Reliability

To determine the weight which can be placed on reporting the results of one set of analysis, samples were taken each morning for 7 days after running for five minutes from two chosen sites. Samples of overnight water were also taken on 3 days. The results are given in Table 4.1 and indicate that there is a fairly uniform level from day to day both in standing and running water.

4.5 RESULTS

The results of the survey are given in Table 4.2 together with the W.H.O. limits (279) and the comparison of standing and running water is given in Table 4.3. The Pb level is the maximum permitted by the World Health Organisation. Cu, Fe and Zn levels are the highest "desirable" levels which the W.H.O. would like. However, at present the maximum levels of these elements are 1500 μg/l, 1000 μg/l and 15,000 μg/l respectively. The W.H.O. report recommends periodic checks for Cr levels but gives no limits and Ni is not mentioned at all.

Pb in Glasgow's domestic water is higher than the W.H.O. limit.

Cu is close to the maximum "desired" level but well below the present limit. Zn and Fe are well below the "desirable" levels as are presumably Ni and Cr since no limits are given.

The classification of Table 4.2 into plumbing materials was found to be the most convenient way of presenting the results as there were no relationships found between the age of house and the metal levels or area and levels. This was probably because in recent years due to government grants, both in private and corporation houses, the plumbing (together with electrical wiring) has been renewed in the older properties.

Statistically there is no difference between the metal levels found in the different classes, in fact the ranges tend to overlap.

TABLE 4.1 VARIATION OF METAL LEVELS IN DRINKING WATER DURING ONE WEEK (μg/l)

Site 1
Copper Pipes

	Pb	Cu	Zn	Ni	Cr	Fe	Cd
Monday Running	29	80	10	3	ND	30	0.21
Tuesday "	32	78	10	3	ND	22	0.19
Wednesday "	29	70	20	3	ND	32	0.13
Thursday "	32	82	10	3	ND	34	0.20
Friday "	28	82	10	2	ND	28	0.32
Saturday "	29	80	20	2	ND	30	0.20
Sunday "	28	76	20	2	ND	46	0.21
Monday Standing	48	640	120	5	ND	20	0.18
Wednesday "	45	290	150	7	ND	22	0.20
Saturday "	48	600	150	7	ND	20	0.19

Site 2
Lead Pipes

	Pb	Cu	Zn	Ni	Cr	Fe	Cd
Monday Running	116	16	20	3	ND	64	0.25
Tuesday "	96	14	20	3	ND	60	0.21
Wednesday "	98	16	20	5	ND	50	0.16
Thursday "	92	14	10	8	ND	94	0.22
Friday "	90	14	20	2	ND	92	0.19
Saturday "	94	14	10	3	ND	92	0.22
Sunday "	109	16	10	3	ND	36	0.22
Monday Standing	205	660	230	4	ND	188	0.23
Wednesday "	124	712	220	4	ND	164	0.20
Saturday "	143	144	200	3	ND	136	0.18

ND = Not Detected

TABLE 4.2 AVERAGE LEVELS OF METALS IN RUNNING TAP WATER (μg/l) IN GLASGOW.

Plumbing Material	Pb	Cu	Ni	Cr	Zn	Fe
Lead	264	51	10	ND	103	59
Copper	137	68	44	ND	109	58
Lead/Copper	402	50	25	ND	150	67
W.H.O. Limit	100	50	-	-	5,000	100

ND = Not Detected

TABLE 4.3 COMPARISON OF METAL LEVELS IN STANDING AND RUNNING WATER (μg/l)

IN GLASGOW.

Material	Pb		Cu	
	Standing	Running	Standing	Running
Lead	350	30	390	20
	420	280	250	20
	1230	320	40	30
	1300	600	50	50
	500	50	20	20
Copper	30	30	490	130
	20	30	110	120
	240	110	190	40
	40	20	680	50
	70	130	970	180
	60	90	60	10
	0	0	60	20

A reason for this is quite probably that participants were unaware of the true nature of the plumbing. In many cases the plumbing consists of copper to the sink but lead under the floorboards leading from the street mains. Evidence for this can be seen where copper piping has a very high Pb content (Table 4.3).

However, there are some trends. On average it can be said that in the case of lead plumbing Pb levels tend to be higher than in copper plumbing. Conversely in copper plumbing Cu tends to be higher. Ni is higher in copper plumbing perhaps due to it being incorporated at manufacture to form an alloy rather than true copper. Zn and Fe are relatively constant and this is probably a general background level either by being intrinsically in the water itself or coming from street mains. Cd was only determined in 40 samples chosen to give a representative spread across the city and showed little variation throughout, having an average level of 0.24 µg/l.

From Table 4.3 it can be seen that in some cases both Cu and Pb are high and as said above is evidence for the point made about the plumbing. In fact in these cases with copper piping the Pb level rose in the running water and could be due to water lying in the lead pipe section overnight. A further sample taken after running for a longer period would probably show reduced levels. In general, however, there is a marked decrease in the metal levels of running compared with standing water - as would be expected.

4.6 LEACHING FROM PIPES

The previous exercise has shown at least in terms of average values that the plumbing material will be leached into the drinking water. To study leaching in a more controlled environment the following experiment was carried out.

Five pipes, made of material commonly used in plumbing, were cut into 1 foot lengths. These were - lead, copper, stainless steel, plastic and lead/copper made from 6 inch lengths of each material and soldered at the joint with a tin based solder in common use.

For practical reasons pipes could not be obtained of exactly the same cross-section. In an attempt to compensate for this a volume of de-ionised water equal to half the internal volume of the pipe was added to each pipe. The pipes were placed on an end over end shaker overnight (16 hours). In the morning the water was filtered through a 0.45 μm membrane filter. Glacial acetic acid was added to correspond to 1 ml per 100 ml water and the samples stored in clean plastic bottles.

This was repeated on three consecutive nights with the same pipes.

The samples were analysed by atomic absorption spectroscopy in the same manner as the domestic water.

The average results are given in Table 4.4 and the findings are more or less self evident. The lead pipe is high in Pb, the copper pipe in Cu and the lead/copper pipe in both. The latter two pipes are also higher than the lead pipe in Ni but not enough to confirm what was said previously about Ni perhaps being present in copper pipes as an alloy. All three are high in Zn and about the same in Fe.

TABLE 4.4 METAL LEVELS IN LEACHING WATER (µg/l) FROM VARIOUS PLUMBING MATERIALS

Pipe	Pb	Cu	Zn	Cr	Ni	Fe
Lead	33,000	20	580	1	3	54
Lead/Copper	22,700	1640	220	2	7	54
Copper	100	2280	580	1	6	34
Stainless Steel	61	35	1300	140	120	116
Plastic (P.V.C)	113	10	1500	4	10	104

Stainless steel has higher Zn and Fe values than the other three pipes examined and also is much higher in Cr and Ni. The latter two of course are the main constituents of stainless steel. Stainless steel pipes are usually given an internal zinc coating and this is reflected in the high level of that element in the water. Fe again is probably a contaminant from the manufacture of the pipes.

The interesting figures for the plastic pipes are the relatively high levels of Pb, Zn and Fe. Lead acetate is used as a filler in the manufacture of plastic pipes, zinc stearate as a stabilizer and Fe is again probably present as a contaminant at the time of manufacture.

4.7. CONCLUSIONS

The amount of element leached from domestic water pipes can be set into classes according to the plumbing material, with limited success.

Of the 7 elements studied in the survey only Pb gives cause for concern as judged by W.H.O. standards. In later years Cu could become more of a problem as the limit is reduced to the "desirable" level.

Water lying in pipes overnight has higher metal levels and should be run off before the water is used.

Plumbing material is leached out into the domestic water, but simply replacing lead piping with copper, stainless steel or plastic will only change the nature of the problem but will not necessarily rectify it.

4.8 ASSESSMENT OF PROJECT AND POSSIBLE FUTURE WORK

In terms of the aims as set out in Chapter I the project has been successful - as far as it goes. The levels of 7 trace elements in the domestic water supply have been measured and compared to W.H.O. standards, thereby emphasising the ones which do or might cause concern.

There would be little point in extending the range of elements studied, as the project has covered the main elements found in plumbing materials. More information would be obtained by extending the survey to include more houses covering a wider area.

CHAPTER V INDUSTRIAL WASTE

5.1 INTRODUCTION

The historical reasons for the comparatively large number of industrial waste tips in Central Scotland has been well documented elsewhere (280). The main type is of course colliery waste. In recent years these coal bings, as they are called, have attracted the attention of environmentalists presenting many interesting problems from the point of view of growing plants. This aspect has been studied extensively in recent years (280).

One of the biggest problems is associated with the oxidation of the mineral pyrite which produces large amounts of acid. This causes large amounts of Fe, Al and Mn to be brought into solution at levels toxic to plants when the pH falls below 4.5-5.0. Al is said to come from the breakdown of illite clay at low pH. Other trace metals present may also be brought into solution at toxic levels as the pH falls and in the case of extensive leaching could result in the removal of these metals from the root zone causing deficiencies and they could possibly ultimately pass out of the bing altogether.

When the situation is reached that the bing effluent is sufficiently acid, large amounts of soluble Fe will be leached away usually into neighbouring streams where the ensuing higher pH causes precipitation, thus coating the stream bed with iron oxides. This of course will not be limited to Fe, and other metals present will be leached in a similar manner. In the absence of obvious run-off there is also the possibility of seepage of metals into surrounding soil which could lead in severe cases to levels either high enough to stunt crop growth or cause problems to grazing animals.

It was therefore decided in this study to concentrate on two chemical aspects:-

i) Assessment of the metal content of the bings in terms of both total levels and also that which is immediately available to plants.

ii) Assessment of the effect of the bings on the immediate countryside in terms of seepage, blow-off and run-off.

5.2 TRACE METAL LEVELS IN SCOTTISH COAL MINE WASTE

5.2.1 Sample Collection and Preparation

Samples were collected from five sites in Central Scotland the map references of which are given in Table 5.1. They were air dried and sieved through a 2mm sieve. The 2 mm fraction was retained and analysed as this is standard soil procedure.

5.2.1.1 Acetic Acid Extractable

0.5M acetic acid was used as an extracting medium as this again is accepted soil practice when assessing the availability of nutrients to plants and therefore will allow comparison to be made with soil data.

10g of sample were shaken on a reciprocating shaker for 18 hours with 100 ml, 0.5M acetic acid and the suspension filtered and stored in pre-acid cleaned plastic bottles.

5.2.1.2 Total

A method similar to that of Hartstein <u>et al</u> (281) was used to dissolve the sample. A representative 100 mg of sample was placed in a pre-acid washed teflon dissolution bomb with a screw top. 5 ml "Aristar" H_2SO_4 and 4 ml "Aristar" HNO_3 were added and heated at 200°C for 2.5 hours on a sand bath. The bomb was thoroughly cooled and 5 ml "Aristar" HF added to the clear solution and heating continued for a further 1 hour. The bomb was again thoroughly cooled and the contents transferred to a 100 ml standard flask containing 3g boric acid and made up to the mark with deionised water.

The H_2SO_4/HNO_3 mixture was used for the reasons given in Section 3.6, i.e. split peaks.

TABLE 5.1 MAP REFERENCES OF SAMPLE SITES

(COLLIERY WASTE.)

Site	Reference
Lumloch	NS 640 702
North Lodge	NS 753 553
Stane	NS 884 587
Stoneyburn	NS 978 634
Dykehead	NS 867 608
Meadowhall	NS 770 518
Larkhall	NS 762 525
Meikle Earnock	NS 712 531

The boric acid is present to suppress Si interference during analysis as it will be present rather than removed as SiF_6 as would be the case if, e.g. a sodium fusion dissolution technique was adopted.

The best way of getting the boric acid into solution was found to be to add the boric acid to about 50 ml de-ionised water in the standard flask and with frequent shaking most of the boric acid was dissolved before the sample was added.

A blank solution containing all reagents was made and analysed together with the samples.

5.2.2 Analyses

The samples were analysed by atomic absorption spectroscopy, using a Perkin Elmer 306 double beam instrument with deuterium arc background corrector and H.G.A. 74 flameless atomiser.

5.2.2.1 Total

Fe, Ni, Mn, Cu and Zn were determined using an air/acetylene flame, Al using a nitrous-oxide/acetylene flame and Cr and Pb using a heated graphite atomiser.

100 mg of sample per 100 ml solution is a relatively weak solution in terms of metal content and the main interferences will arise from the matrix effects of the acids and salinity from salts of Na, K, Ca and Mg. These 4 elements were determined using the appropriate flame and ionisation suppressor, and were found to have average values of 100 ppm sample solution for Na and Mg, 20 ppm for K; and 30 ppm for Ca. These concentrations were added to the standards together with the acid mixture with the background corrector compensating for the discrepancies in salt concentration from sample to sample.

To test the reliability of this method of dissolution and matrix matching a crushed rock standard (282) was dissolved and analysed by this procedure. The results of duplicate analysis together with those of the average values of inter-laboratory studies are given in Table 5.2. The Al and Fe are expressed as a percentage and the remainder as ppm. The Pb concentration in the standard rock was only 7.8 ppm which after dissolution will not be detected. No Pb was detected in the samples at least indicating that levels greater than the true value in the samples will not be obtained.

To test the accuracy of the method one sample was analysed 5 times using five separate 100 mg batches. From these results the standard error for the analysis was calculated to be:-

Ni, Cu, Al, Fe : 2%
Cr : 3%
Mn, Zn : 6%
Pb : 12%

This error is not purely analytical but also includes a sampling error and as such is a very good indicator that a uniform well mixed sample is being analysed.

5.2.2.2 Acetic Acid Extractable

The "available" levels were analysed in the Department by I.D. Pufford who from a similar exercise has calculated the standard errors to be:-

Cr, Al : 2%
Mn, Zn, Pb : 5%
Ni : 7%
Cu, Fe : 10%

TABLE 5.2 RESULTS FOR STANDARD ROCK (U.S.G.S.W.1.)
(BY ATOMIC ABSORPTION.)

	Interlaboratory Value	Sample 1	Sample 2
Al	7.9%	7.0%	7.2%
Fe	7.8%	8.3%	8.1%
Cu	110 ppm	107 ppm	109 ppm
Zn	86 ppm	93 ppm	90 ppm
Ni	76 ppm	78 ppm	80 ppm
Mn	1278 ppm	1241 ppm	1276 ppm
Cr	114 ppm	108 ppm	112 ppm
Pb	7.8 ppm	ND	ND

ND = Not Detected

5.2.3 Results

As said earlier the biggest problem in coal bings is the oxidation of pyrite. Duncan et al (283) have found that this takes the form of a cycle in terms of pH and sulphate content in unburnt material. Based on this cycle, bing material may conveniently be sub-divided into pre-acid, acid and post-acid. Burnt material forms a fourth class.

The samples were divided into these four classes and the range and average values for the 8 metals are given in Table 5.3. The results are not statistically different as can be seen from the range of values. This is in retrospect probably due to variation of material with different sites and a detailed study of one site would have produced better statistical differences. However general trends can be projected from the average values although at this stage these must be treated with caution.

5.3.2.1 Total

The total levels found in bing material, with the exception of Cu which is higher, lie within the normal soil ranges (284). There is a general increase in the metal concentrations as the oxidation of pyrite progresses except for Pb which decreases. This increase in post-acid over pre-acid is probably due to re-precipitation in the fine fraction, of the elements which were released from the coarse fraction as the acid was leached from the bing leaving this fine fraction more enriched in trace metals.

Combustion within the bing also causes an increase in the total metal content of the material, again with the exception of

TABLE 5.3 METAL LEVELS OF SCOTTISH COLLIERY WASTE (ppm)

		Fe		Al		Mn		Cu	
		Total %	Ext	Total %	Ext	Total	Ext	Total	Ext
Pre-Acid Unburnt material	Range	1.30 - 5.31	ND- 108	6.1 - 12.2	20- 700	294- 1822	14-89	39- 205	ND- 10
	Mean	3.35	56	8.4	188	716	40	107	3.1
Acid Unburnt material	Range	4.14- 8.38	140- 825	7.4- 17.2	15- 100	10- 3330	9- 284	29- 319	2.1- 9.0
	Mean	6.20	307	11.2	46	1376	69	101	4.0
Post-Acid Unburnt material	Range	1.77- 7.29	ND- 40	6.2- 19.8	ND- 155	1122- 8109	23- 190	40- 491	ND- 5.8
	Mean	4.38	15	12.1	67	3047	84	199	2.3
Burnt material	Range	2.89- 12.59	ND-233	7.9- 13.8	140- 1070	99- 6263	1.2- 165	20- 535	2.0- 19.0
	Mean	7.08	51	11.2	543	1937	39.5	337	9.1

ND = Not Detected

TABLE 5.3 (CONTD.)

		Zn		Ni		Pb		Cr	
		Total	Ext	Total	Ext	Total	Ext	Total	Ext
Pre-Acid Unburnt material	Range	58 - 478	6.2 - 17	98 - 201	ND- 3.6	1.1- 108.5	0.2- 1.0	151- 303	0.13- 0.28
	Mean	247	10.4	137	2.2	37.2	0.5	224	0.21
Acid Unburnt material	Range	38- 1226	3.8- 13	89- 369	0.8 -8.0	1.3 -128	0.1- 0.5	150- 531	0.05 -0.54
	Mean	276	7.0	182	2.6	31.5	0.2	277	0.19
Post-Acid Unburnt material	Range	121- 2658	6.9- 177	121- 470	1.7- 10.5	2.5 -47	0.5- 4.7	169- 440	0.01- 0.32
	Mean	916	45.9	223	5.7	12.4	1.6	268	0.12
Burnt material	Range	197- 1794	60- 160	138- 515	ND- 12.9	1.2 - 14.0	0.1- 0.8	233- 559	0.11- 0.95
	Mean	680	36	291	3.1	6.4	0.4	342	0.41

ND = Not Detected

Pb. This concentrating effect is due to the loss of organic material which can constitute up to 80% of the unburnt material. The temperature within the bing must be greater than 450°C to burn off the organic material and convert the black to red material. At this temperature Pb could be lost due to volatilization and this could explain the decrease in Pb concentration in the red material.

5.2.3.2 Acetic Acid Extractable

These levels again lie within the usual soil range with the exception of Cu which is higher.

The trends for acetic extractable levels are not as definitive as those for the totals. Fe increases dramatically from pre-acid to acid showing the influence of the oxidation of pyrite.

Al and Cr show a decrease in the post-acid material compared with pre-acid. Mn, Zn, Ni and Pb are all present in higher concentrations in the post-acid stage and Cu is surprisingly constant throughout.

As with the total levels, burning influences considerably the extractable metal levels. The level of extractable Al is substantially increased, due to the lattice breakdown of illite mentioned earlier. Fe and Mn levels are of the same order as those found in pre-acid material, probably due to the formation of higher oxides. Pb levels are comparable with pre-acid. Cu, Zn, Ni and Cr levels are all increased. It would appear therefore that certain trace elements have been made more extractable by combustion and this has obvious implications on the suitability of burnt material as a plant growth medium.

5.3 EFFECT ON THE SURROUNDING COUNTRYSIDE

The bing situated at Stoneyburn (NS 978634) was chosen to study the effect of coal waste tips on the environment for the following reasons -

i) It is situated in the countryside surrounded by agricultural land and well removed from the nearest main road.

ii) The surrounding land is generally level, therefore there will be no obvious bias towards seepage in a particular direction.

iii) The surrounding land was all under grass giving similar conditions in all directions at the time of sampling.

iv) Two streams run past the bing one on either side allowing a study to be made of the seepage from the bing.

v) One stream ran along the north side. Therefore the prevailing south-west winds would be expected to carry material over the stream thus eliminating any possible confusion with seepage material.

vi) The bing had been shown to contain both pre-acid and acid material as well as red material.

A map of the bing and surrounding area is given in Figure 5.1. This represents the completed project which was not the case at the time of sampling. The ditch along the west side and the new ditch along the south side were not present.

5.3.1 Effect on Streams

There was evidence of actual bing material being carried into the stream on the north side caused simply by downward movement presumably by water. This stream was therefore not studied. The stream on the south side was more uniform with no obvious signs of plant life and there was evidence of iron oxide precipitation on

FIGURE 5.1 CHART OF STONEYBURN BING AND SURROUNDING LAND

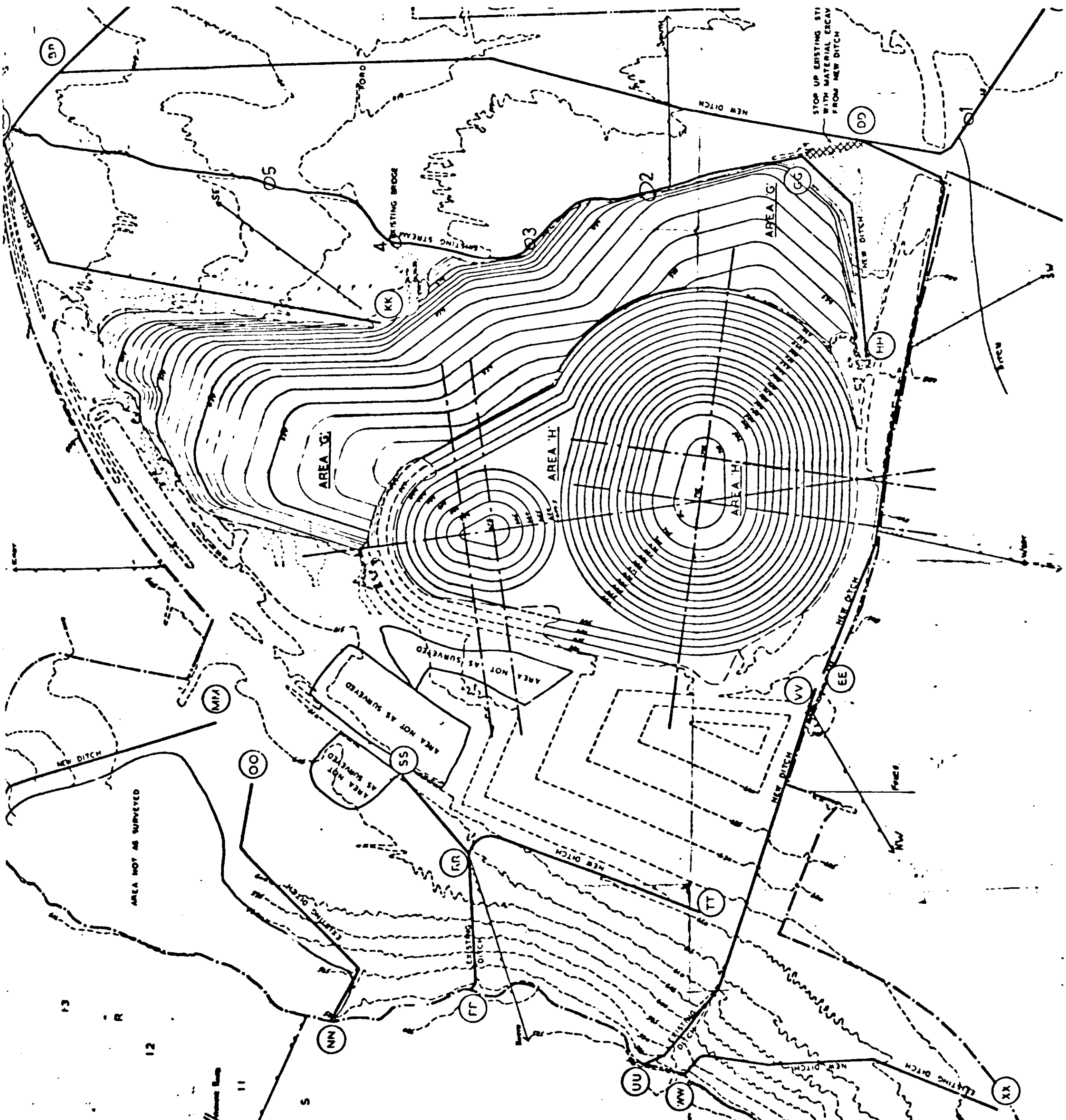
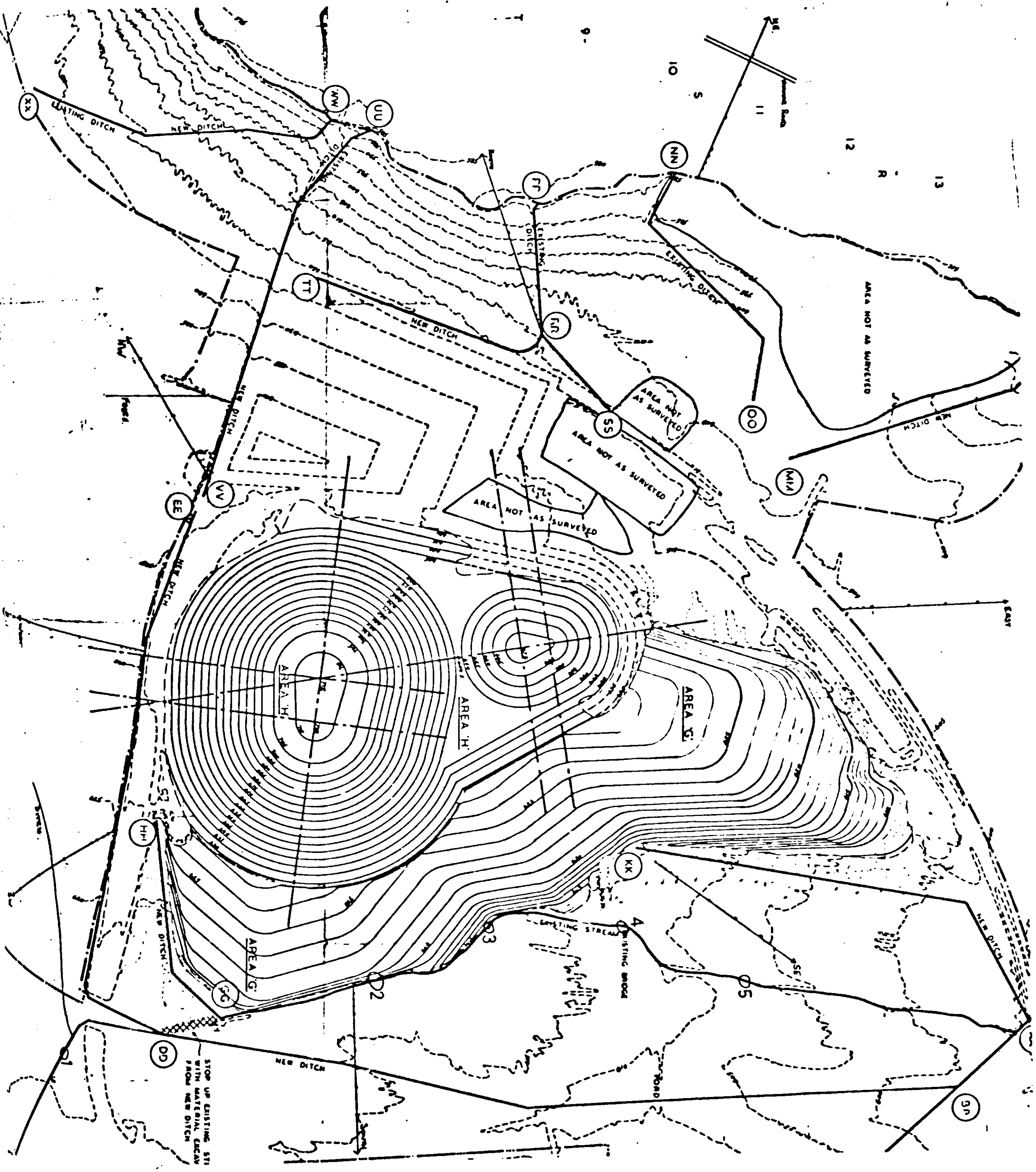


FIGURE 5.1 (CONTD.)



the bed but no obvious signs of actual bing material could be recognised.

Samples of sediment and water were taken at 100 yard intervals along the stream as indicated in Figure 5.1. The stream is flowing from sampling point 1 to sampling point 5. The water was analysed by atomic absorption spectroscopy using the method of standard additions after being filtered through a 0.45 μm membrane filter. The sediment was analysed by the method used previously for the determinations of total metals in the bing material.

The results are given in Table 5.4. Of the stream sediments Al, Zn, Pb and Cr are lower before and after contact with the bing. Fe and Cu are lower before the bing but remain high after contact indicating that these elements are carried further before precipitation occurs. The trends for Mn and Ni are confused by high values before the bing, but higher values were noted for both, adjacent to the bing.

The water samples all show an increase in metal levels as the water passes over the sediment. The most dramatic increases were noted for Al, Mn, Zn and Ni. Fe does not exhibit this big increase presumably due to the insoluble nature of the iron oxide precipitate.

5.3.2 Effect on Land

Soil samples were taken in January to minimise possible conflictions due to plant uptake, covering the eight compass points at distances of 0, 5, 10, 15, 20, 50, 75 and 100 yard intervals out from the bing. The samples were taken to a depth of 12 inches and well mixed.

TABLE 5.4 METAL LEVELS IN SEDIMENT AND WATER OF STONEYBURN STREAM

	Fe		Al		Mn		Cu	
Sample No.	Sediment	Water	Sediment	Water	Sediment	Water	Sediment	Water
	%	ppm	%	ppm	ppm	ppm	ppm	ppm
1	2.2	0.018	3.7	0.085	985	1.7	4.9	0.02
2	4.1	0.026	8.0	0.70	731	6.5	20.9	0.05
3	33.3	0.026	4.2	1.89	1870	10.9	17.8	0.05
4	24.8	0.041	3.8	3.60	614	16.6	40.9	0.07
5	32.2	0.025	1.9	1.32	685	15.3	19.6	0.07

	Zn		Ni		Pb		Cr	
Sample No.	Sediment	Water	Sediment	Water	Sediment	Water	Sediment	Water
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	125	0.06	118	0.05	118	0.018	24.7	ND
2	595	0.28	219	0.12	4590	0.026	65.1	0.002
3	597	0.42	45	0.25	219	0.026	23.4	0.006
4	194	0.99	82	0.30	184	0.041	35.9	0.001
5	127	0.84	29	0.30	160	0.025	19.8	0.001

ND = Not Detected

The samples were sieved through a 2 mm sieve and air dried within 2 days of sampling. After statistical sampling the total and acetic extractable levels were determined in the same manner as for the bing material.

A problem of split peaks was encountered with the acetic extractable Pb determinations on the heated graphite atomiser. This was possibly due to the presence of mixed anions (see Section 3.6.2.3). Adding excess phosphate resulted in the formation of a single peak. However when the phosphate solution was added directly to the carbon rod reproducible results were not obtained. The best results were obtained by adding 1 ml of sample solution to a 1 ml solution containing 1000 ppm P as phosphoric acid in a test tube. After shaking and leaving for 5 minutes, aliquots were then injected on to the rod. Cr was also analysed by the heated graphite atomiser but the problem of split peaks did not arise.

5.3.2.1 Results

A brief description of the land in each direction is included below to help in the interpretation of the results. The results are illustrated graphically in Figure 5.2. With only a few exceptions the levels lie within the normal soil range. The exception is acetic extractable Cu which like the bing material itself is higher than normal.

5.3.2.1.1 North (N):- The land in this direction runs downhill fairly steeply from 0-75 yards to the stream with the 100 yard sample taken just across the stream.

FIGURE 5.2 GRAPHIC REPRESENTATION OF METAL LEVELS IN SOIL AROUND BING

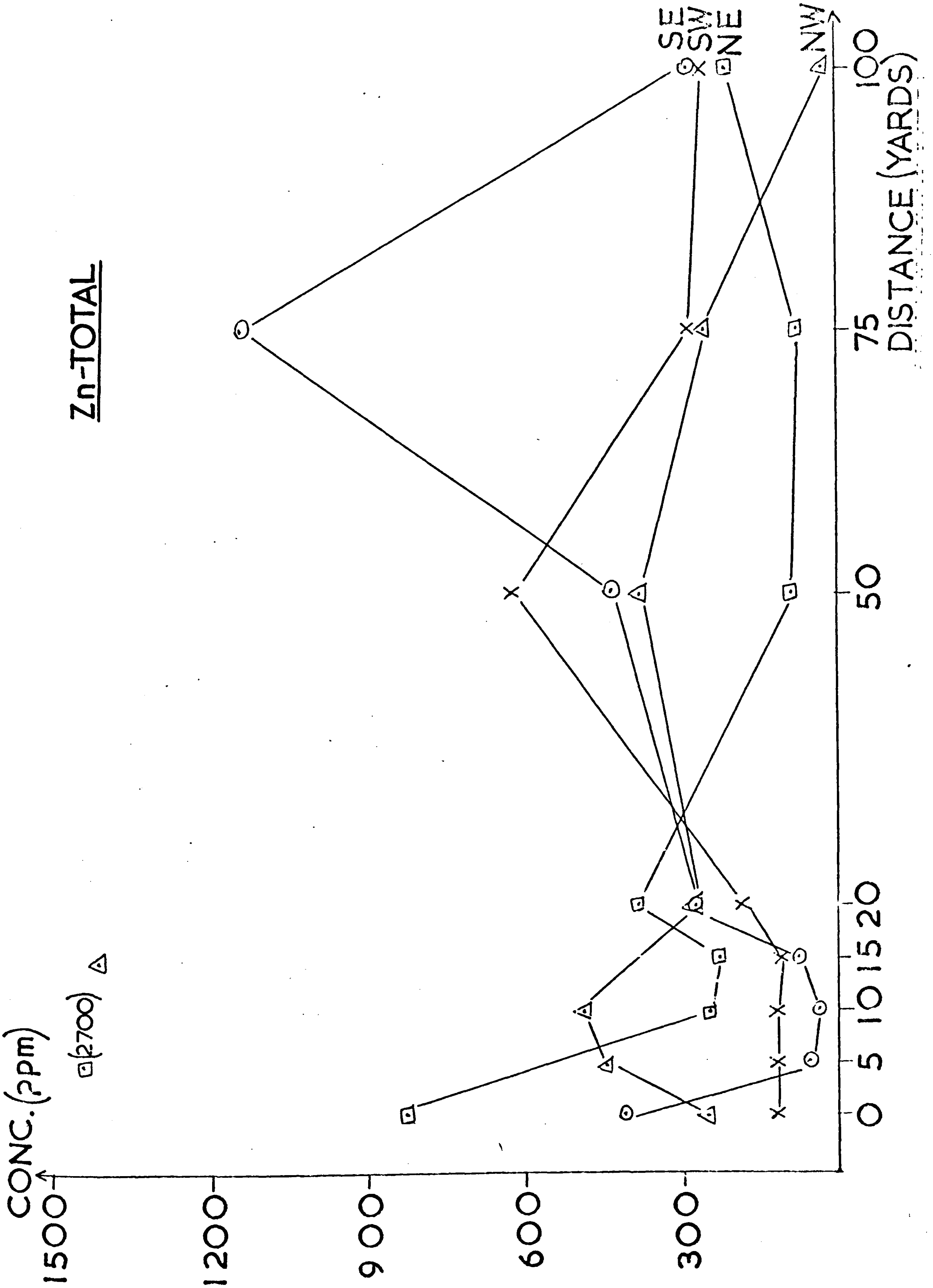


FIGURE 5.2 (CONTD.)

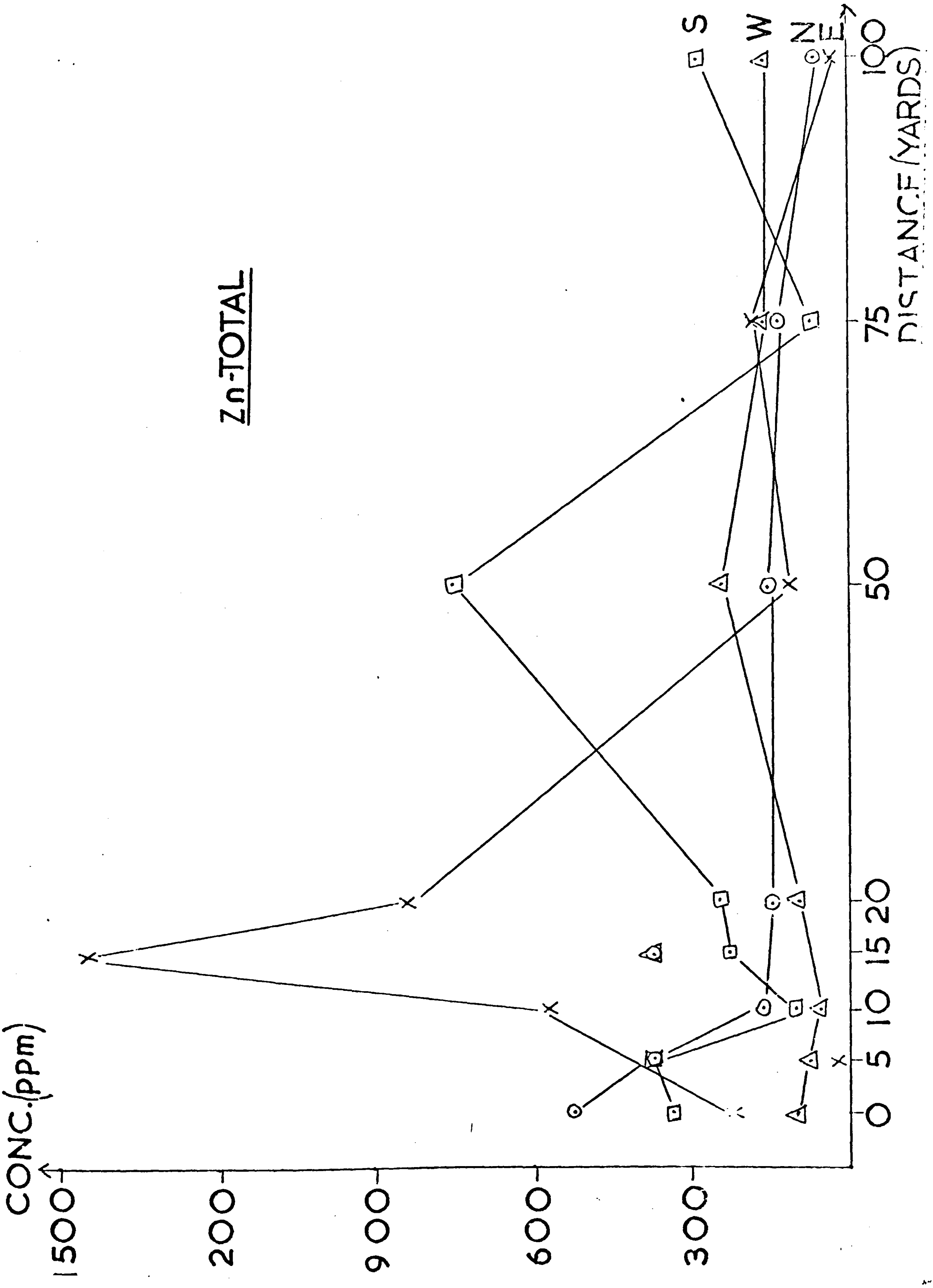


FIGURE 5.2 (CONTD.)

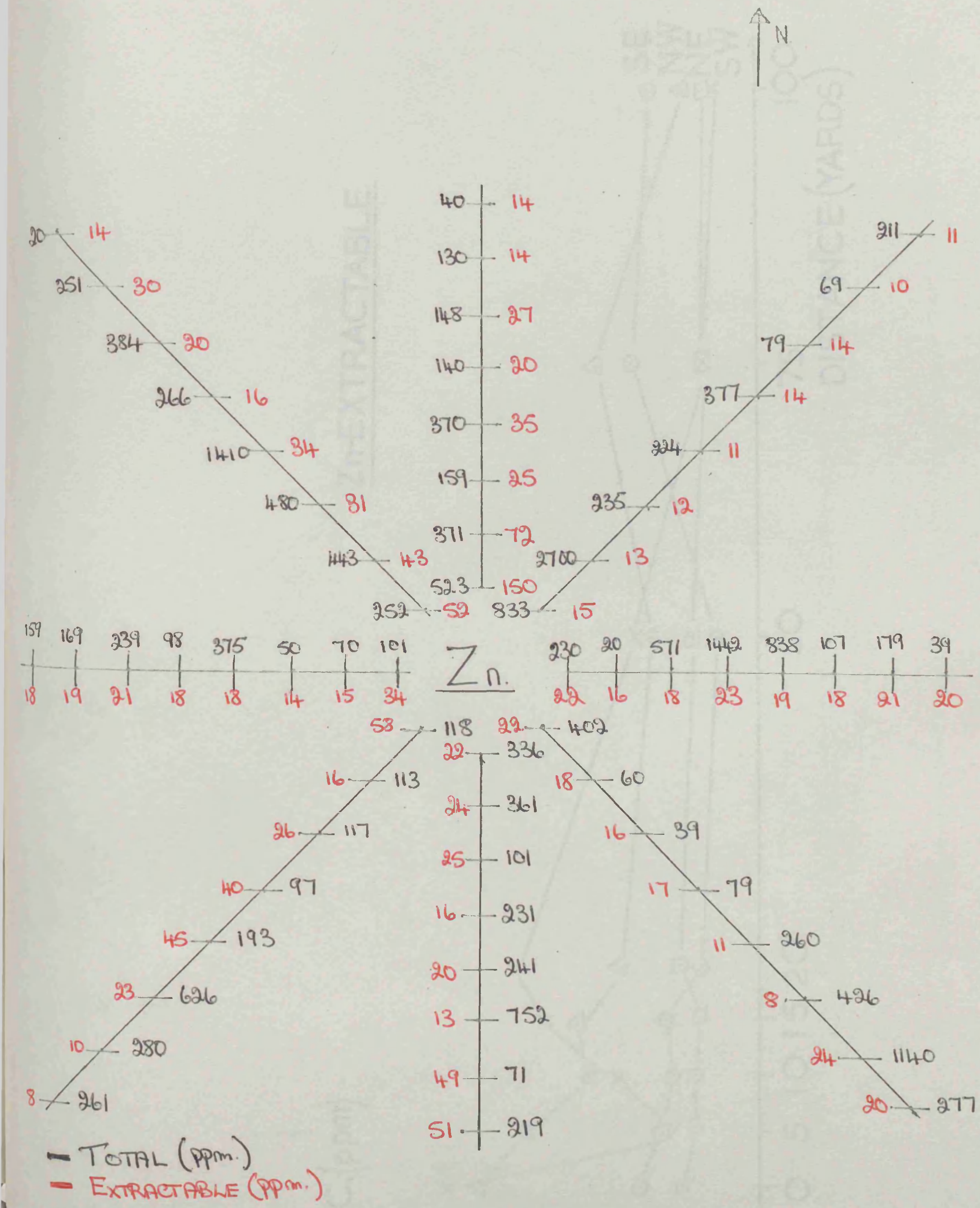


FIGURE 5.2 (CONTD.)

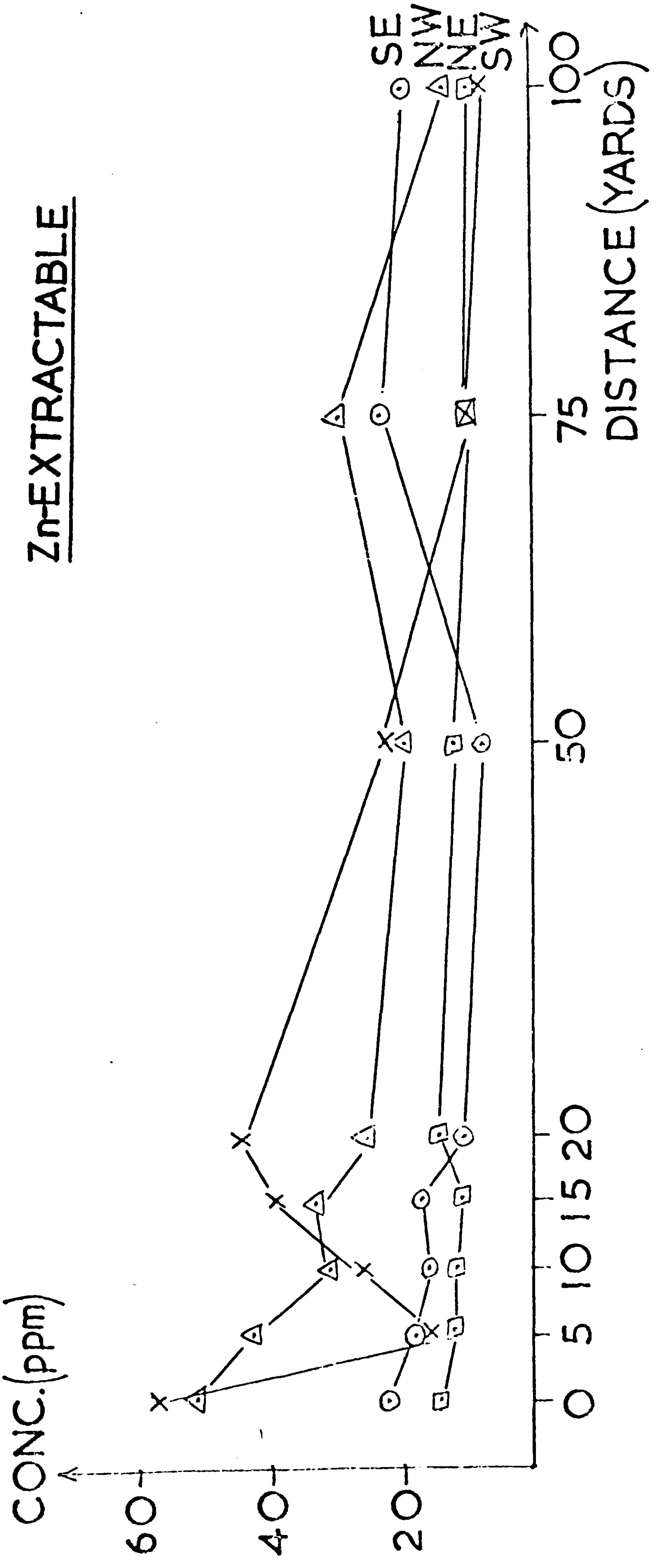


FIGURE 5.2 (CONTD.)

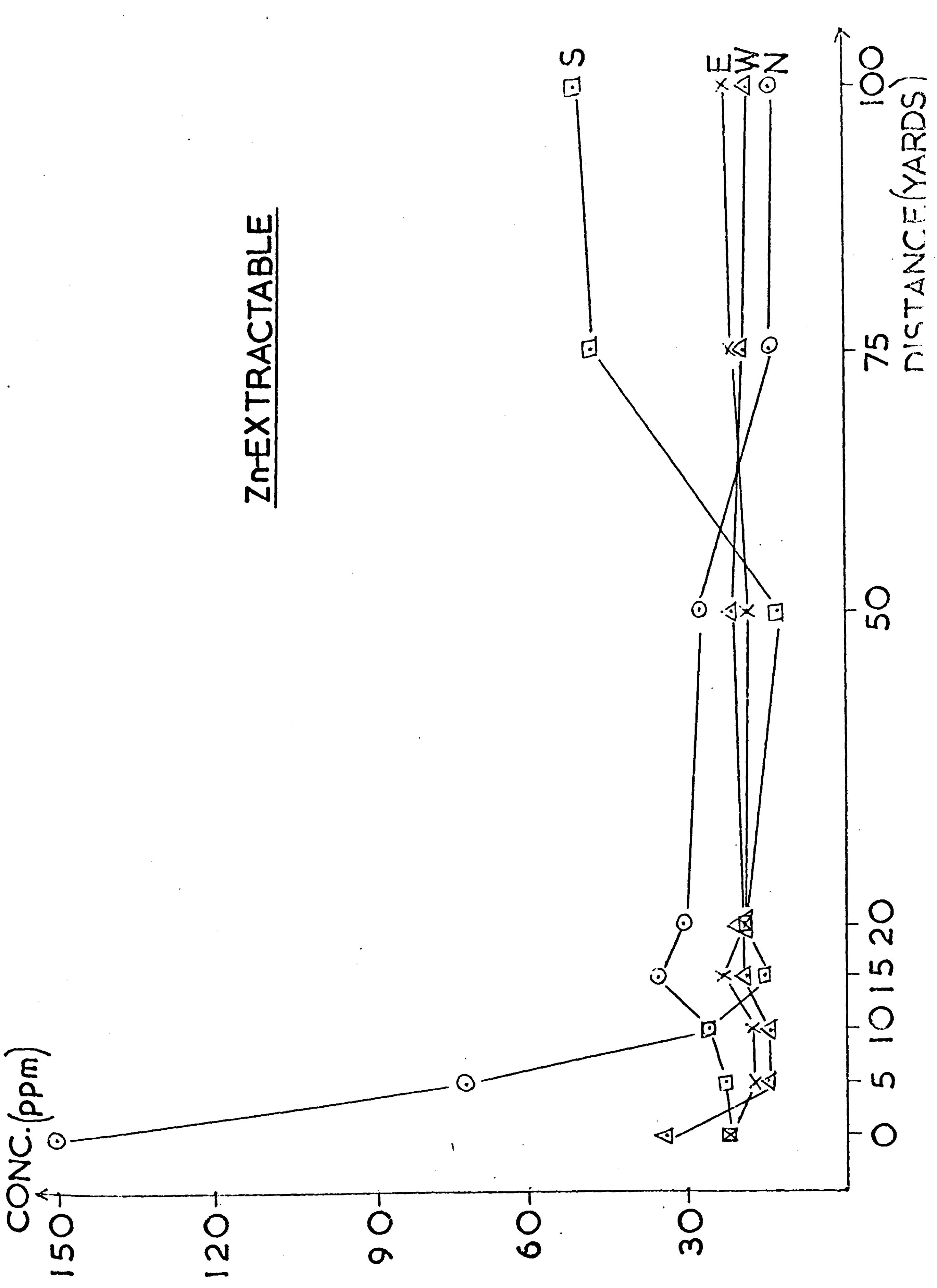


FIGURE 5.2 (CONTD.)

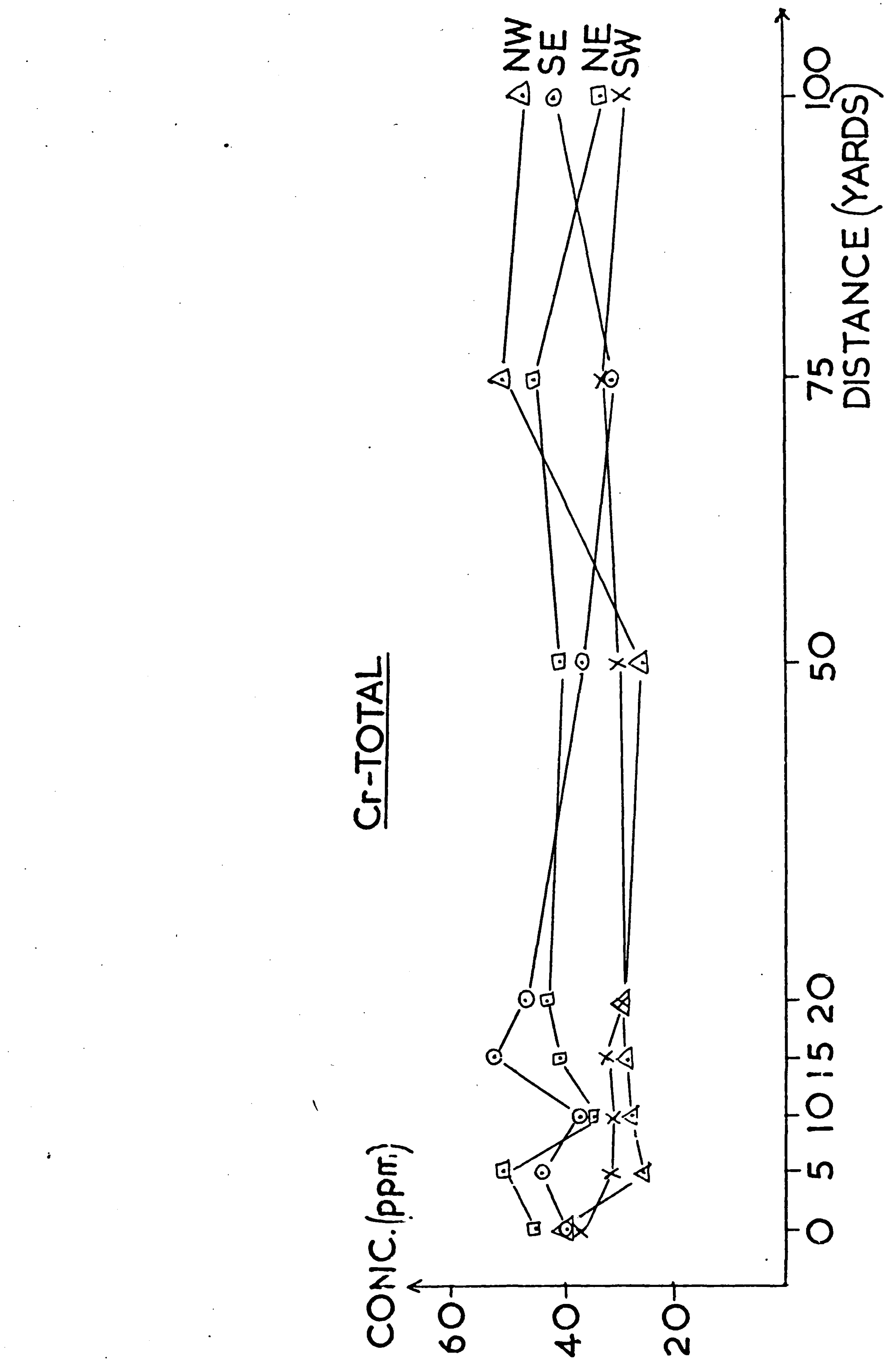
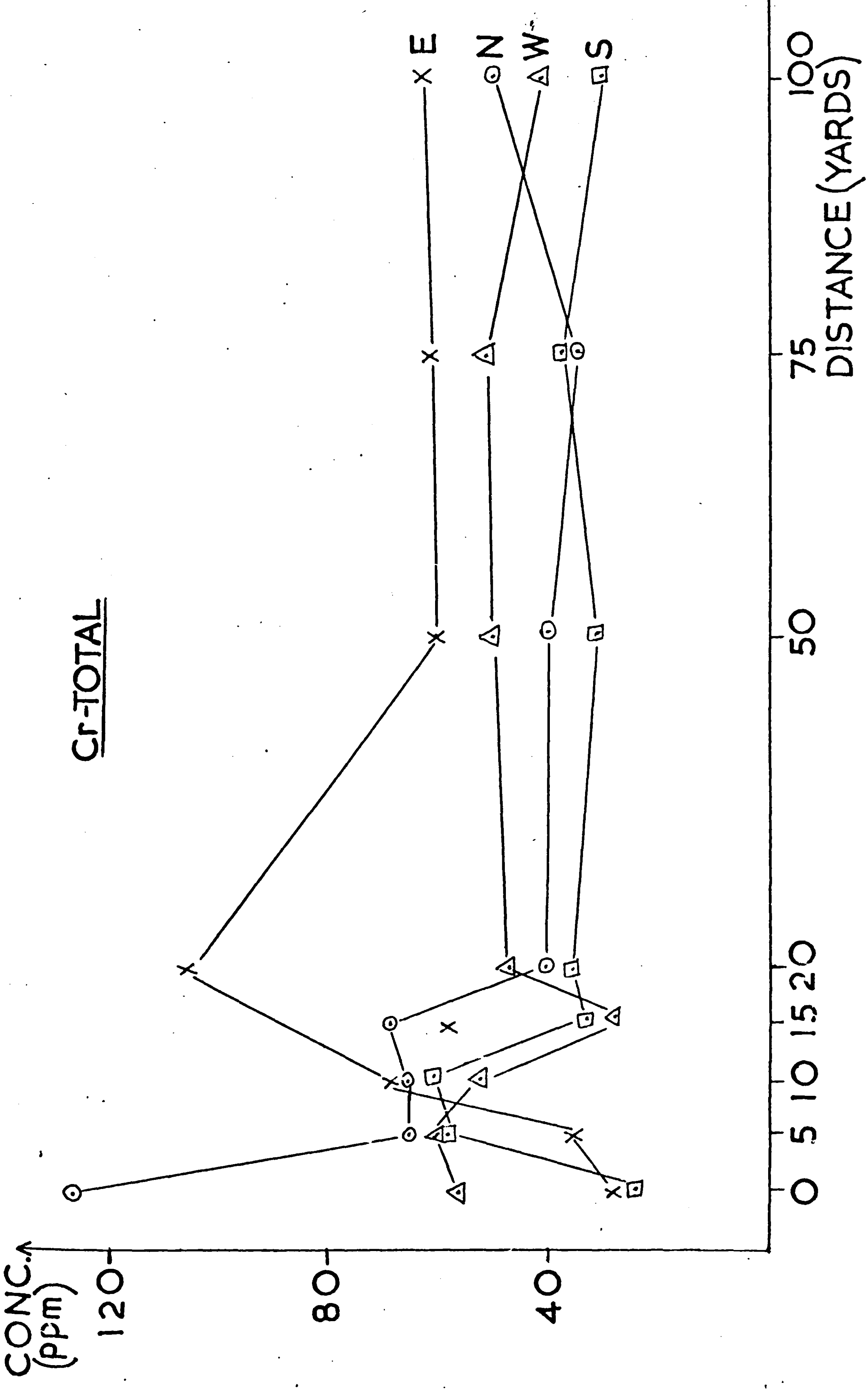


FIGURE 5.2 (CONTD.)



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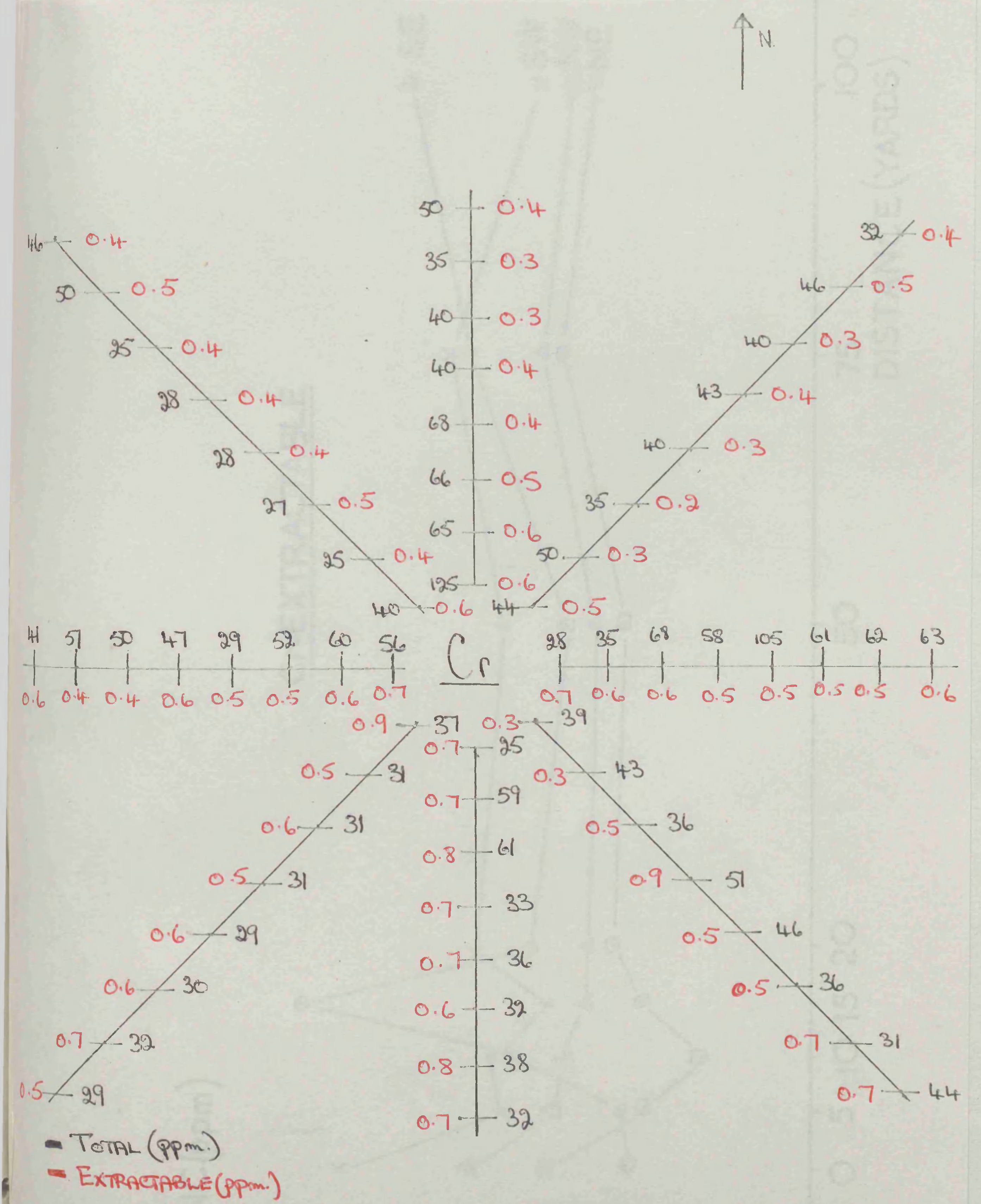

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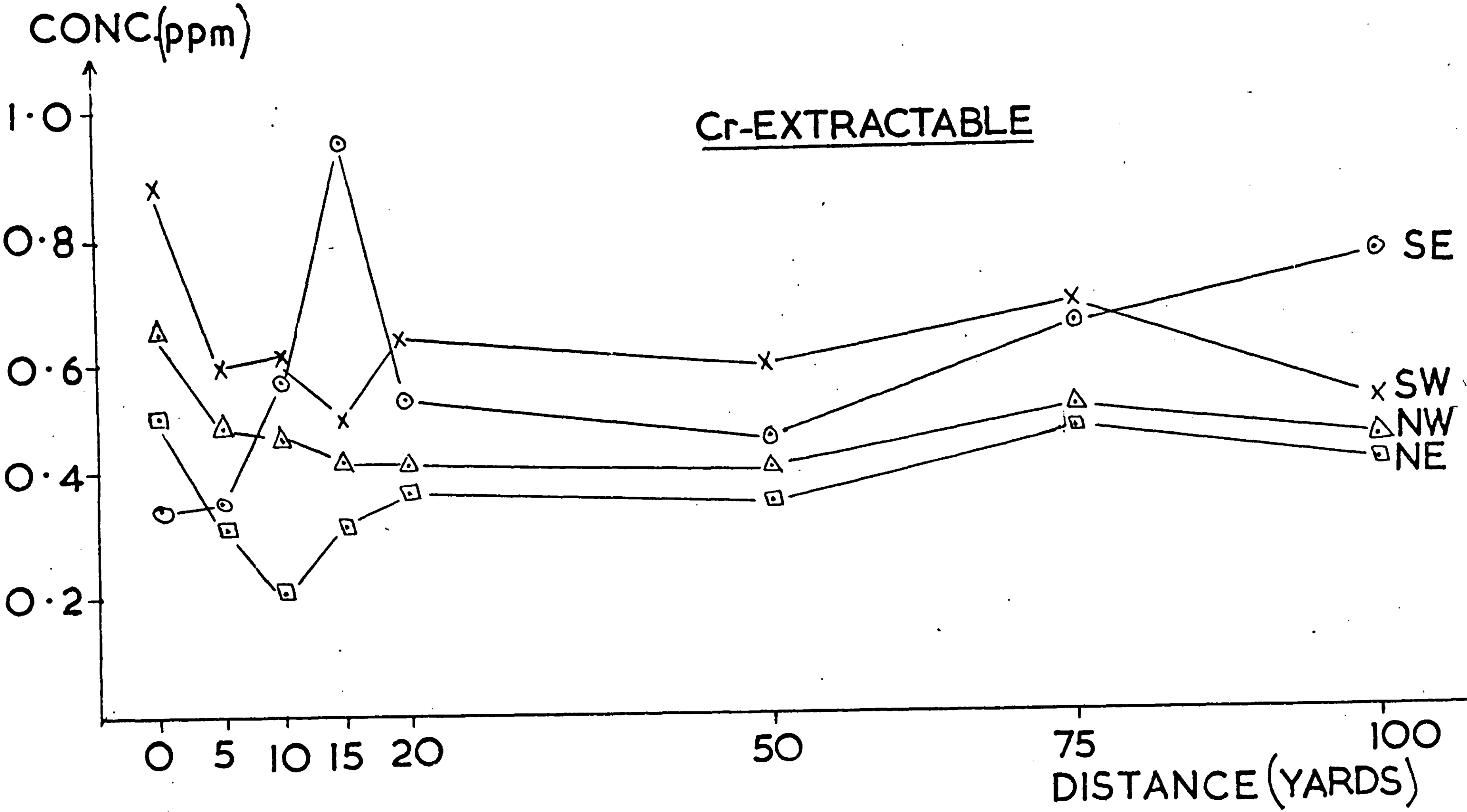

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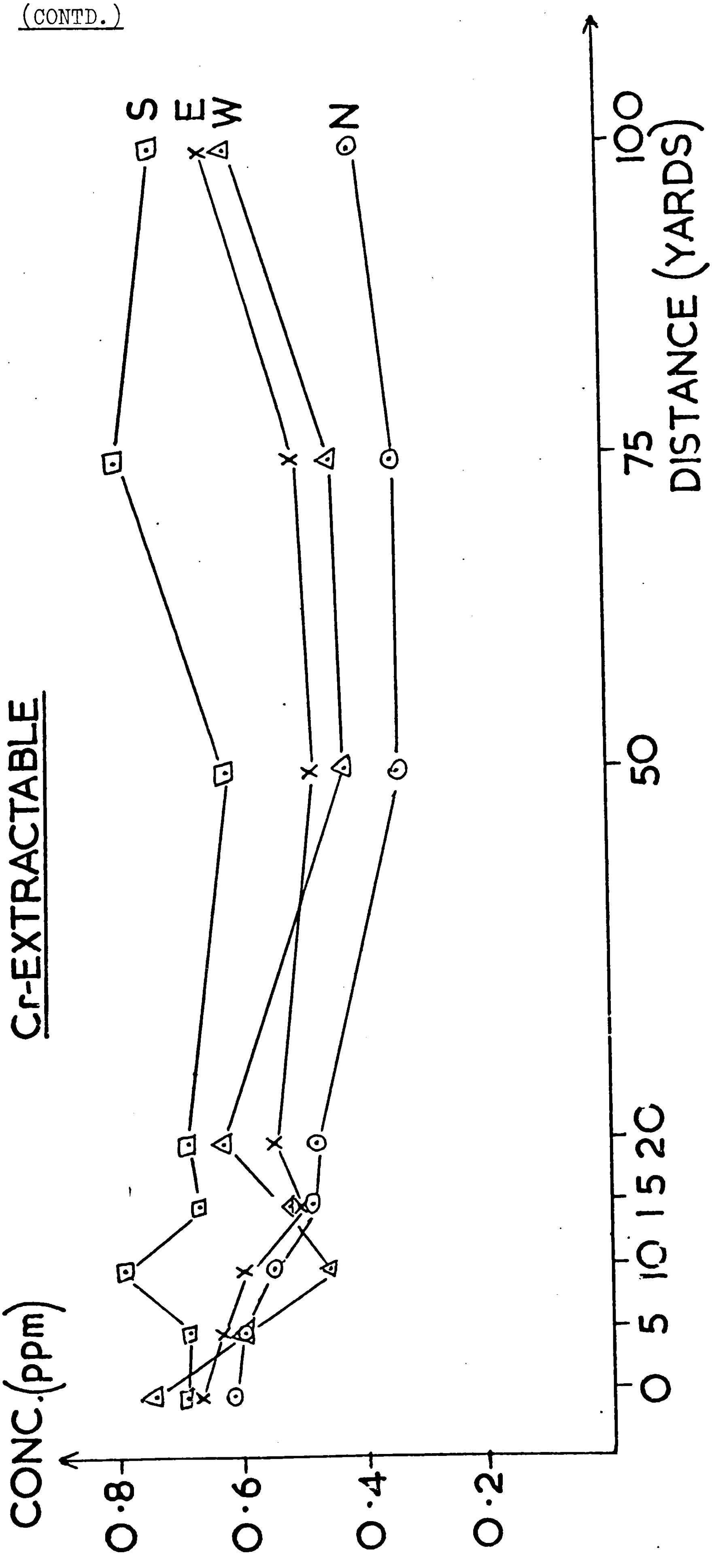

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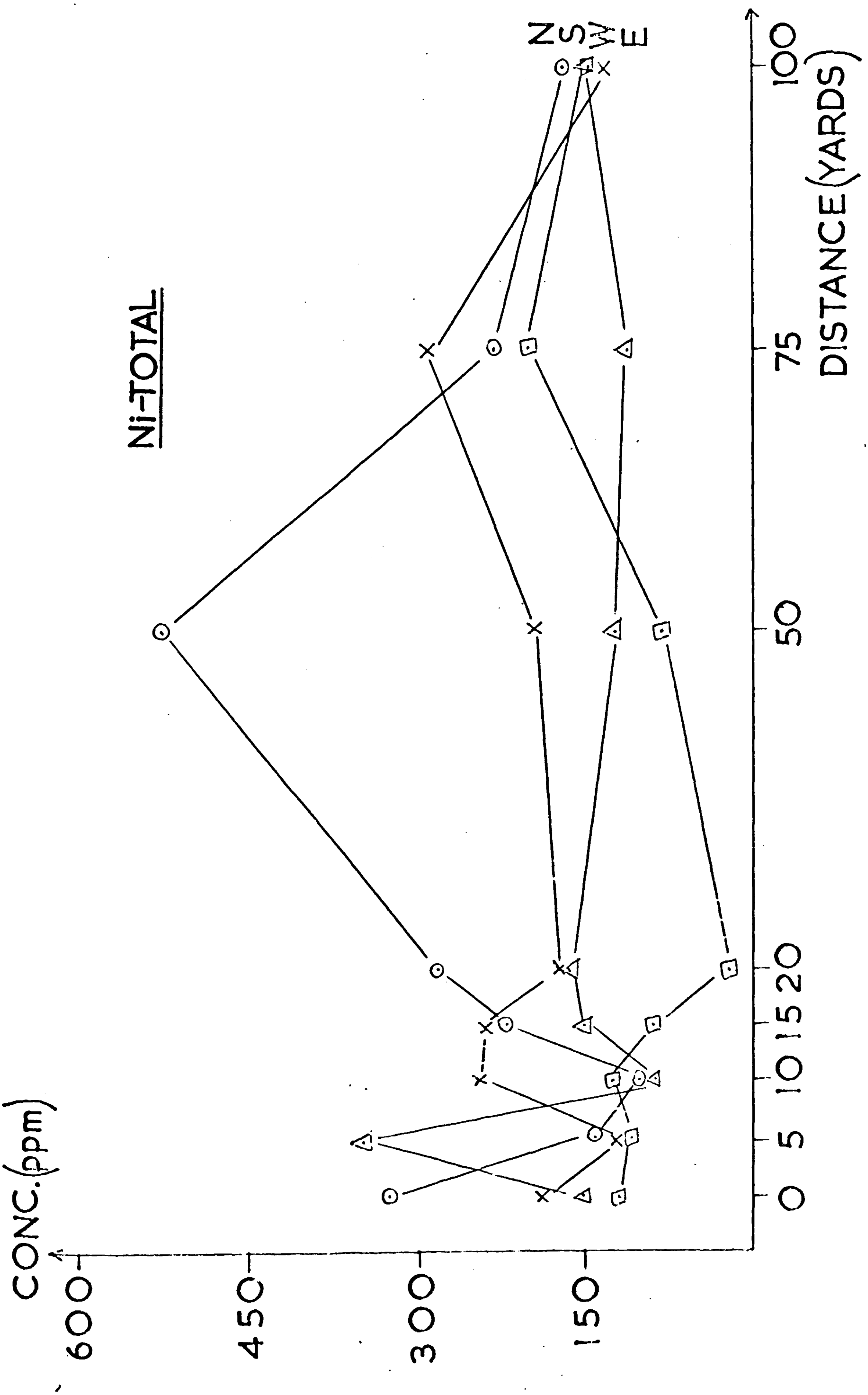

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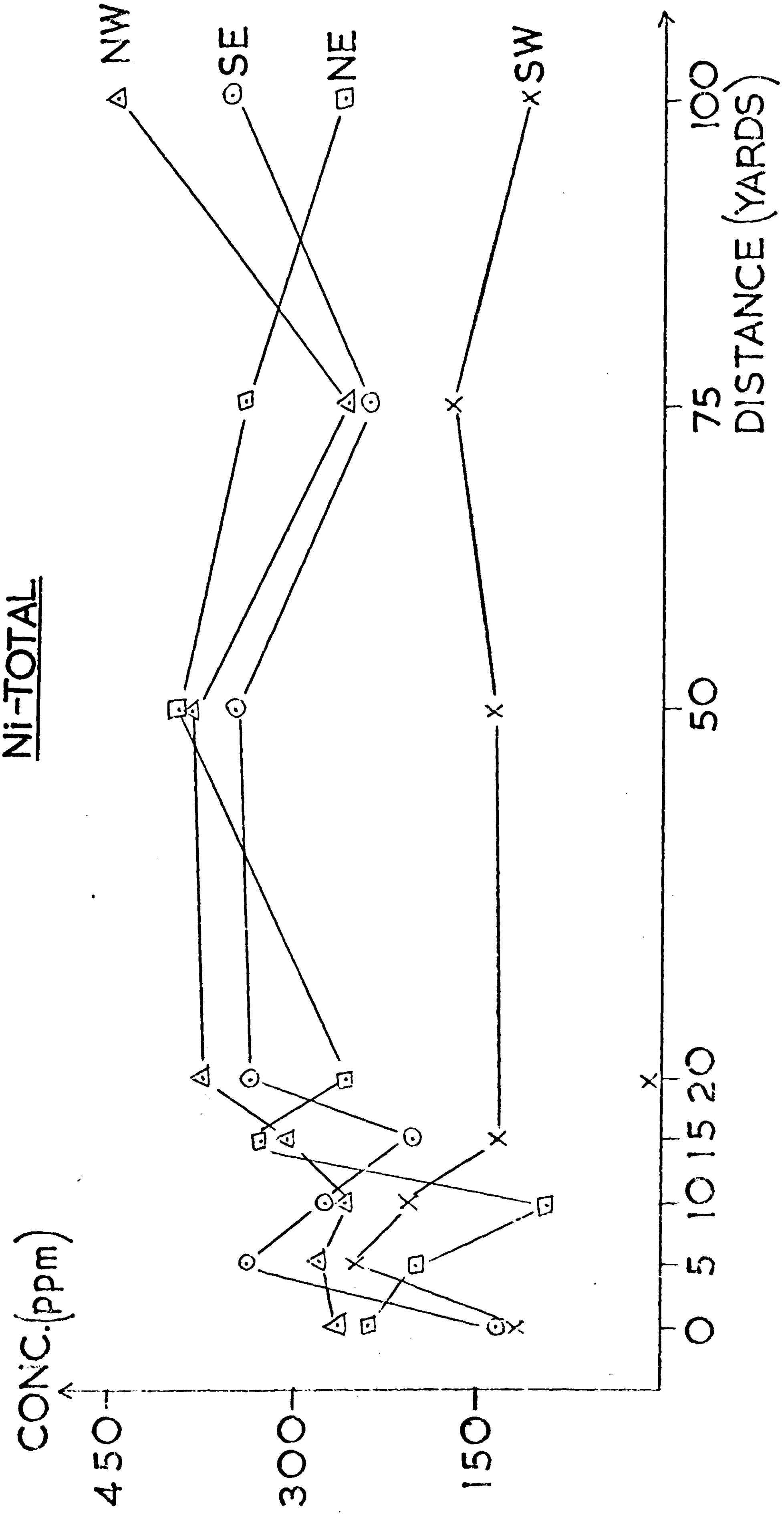

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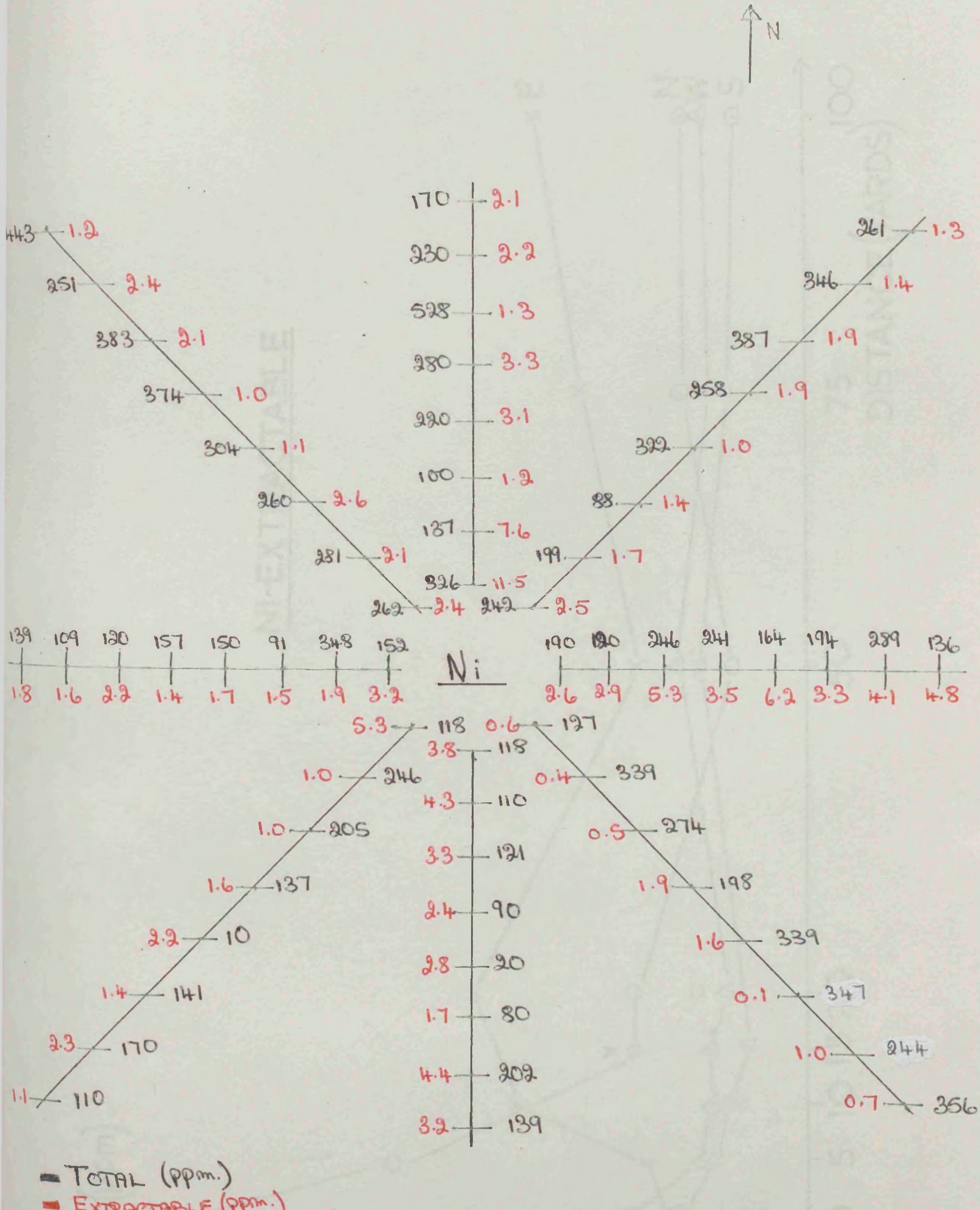

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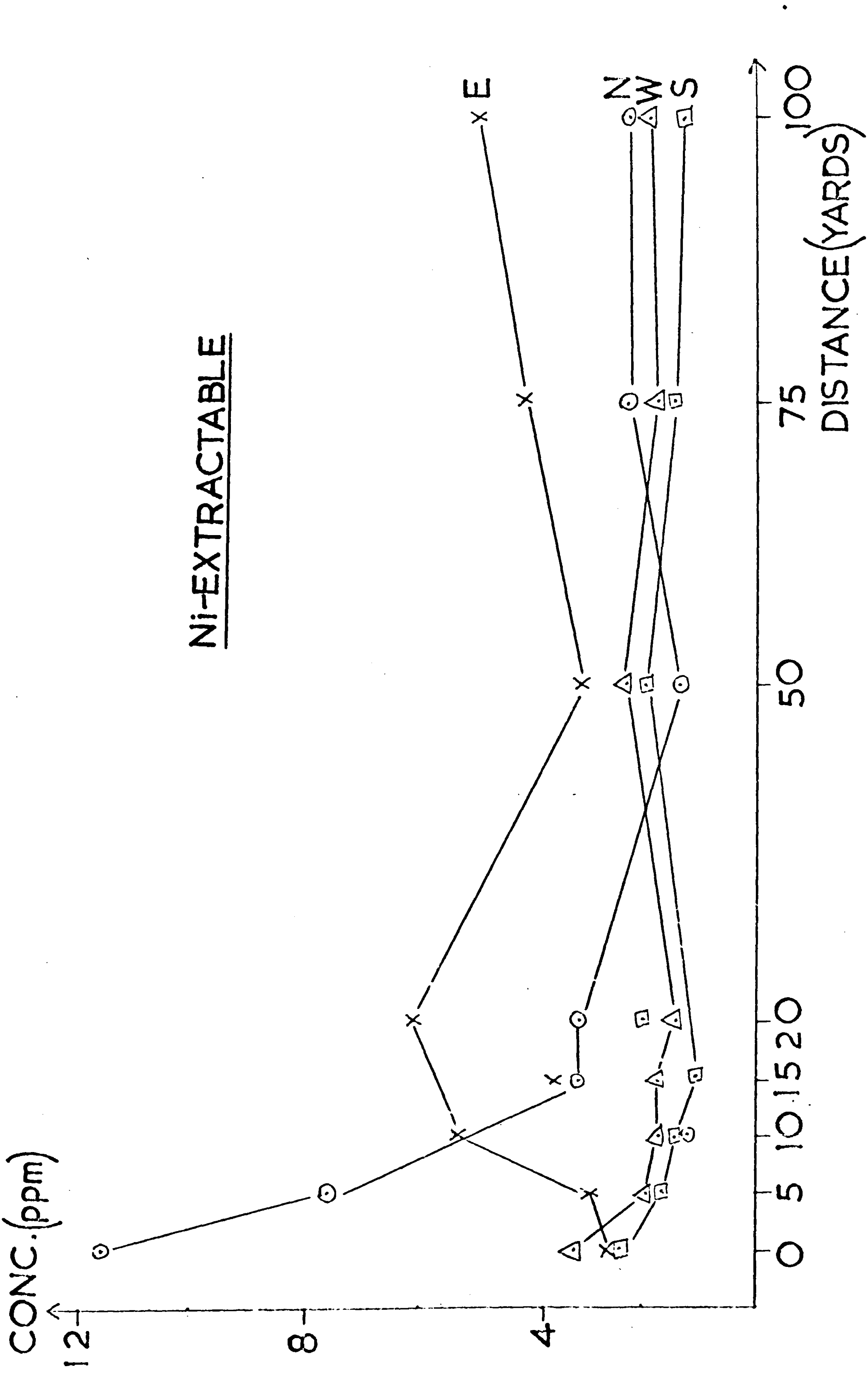

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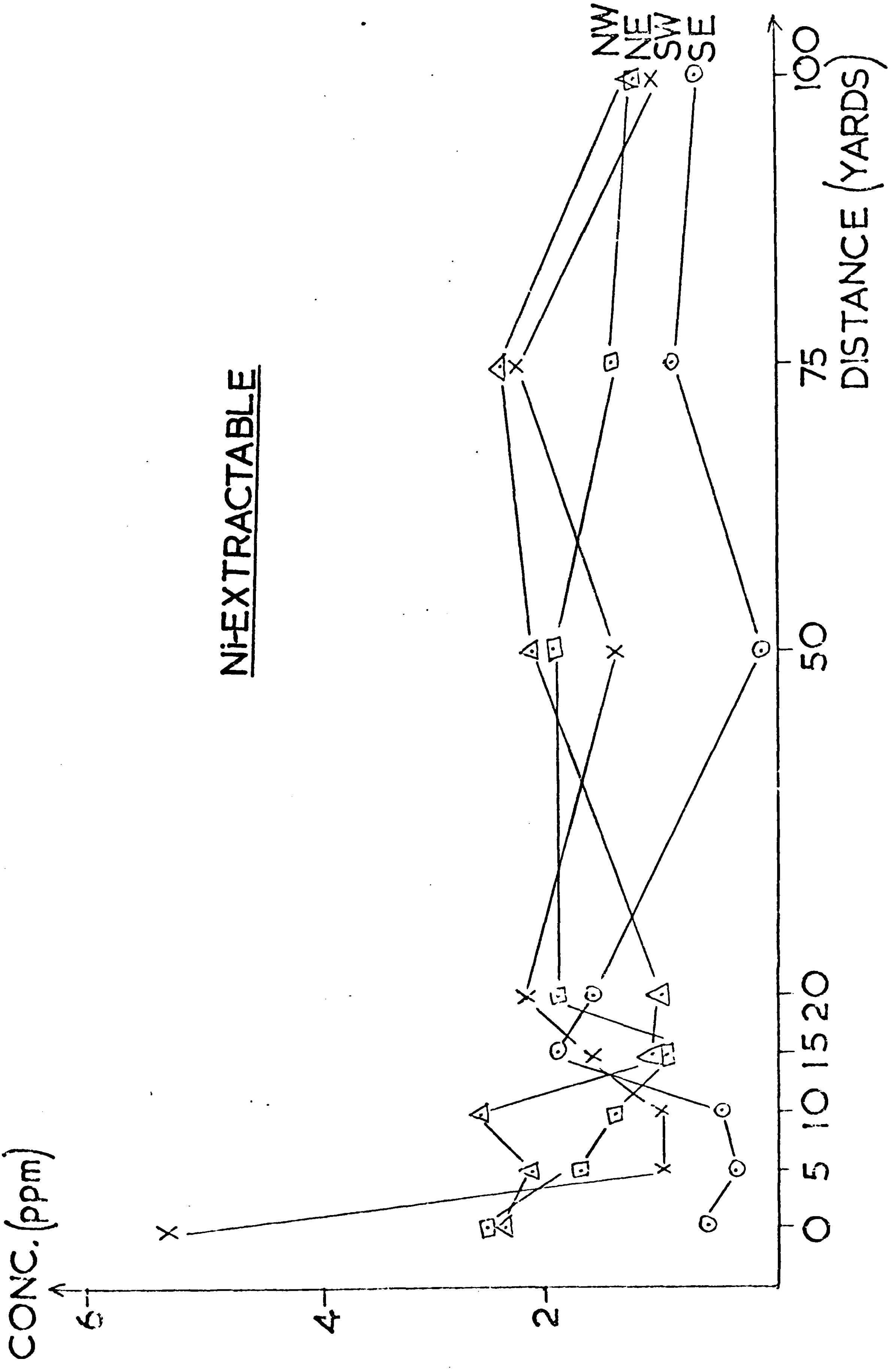

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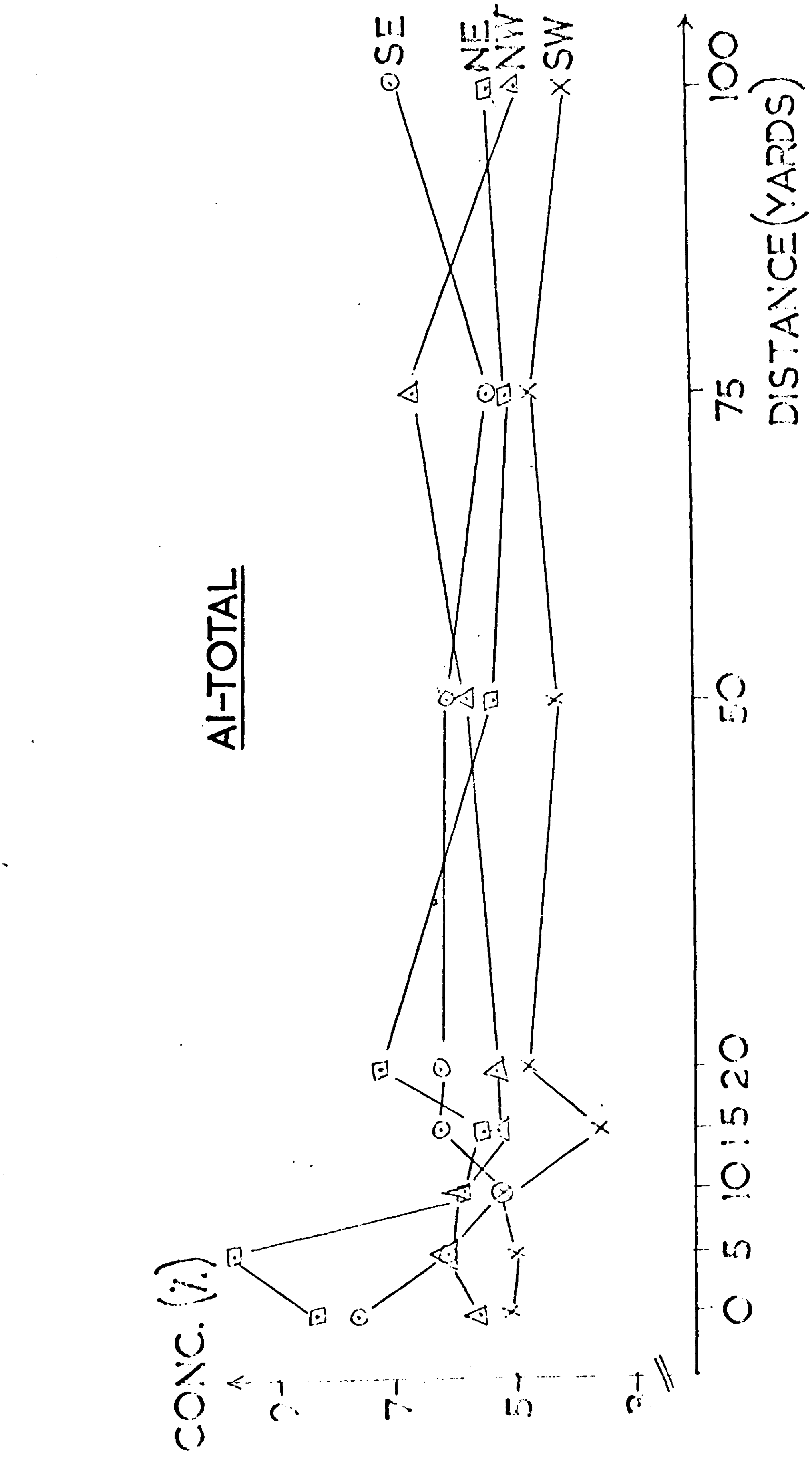

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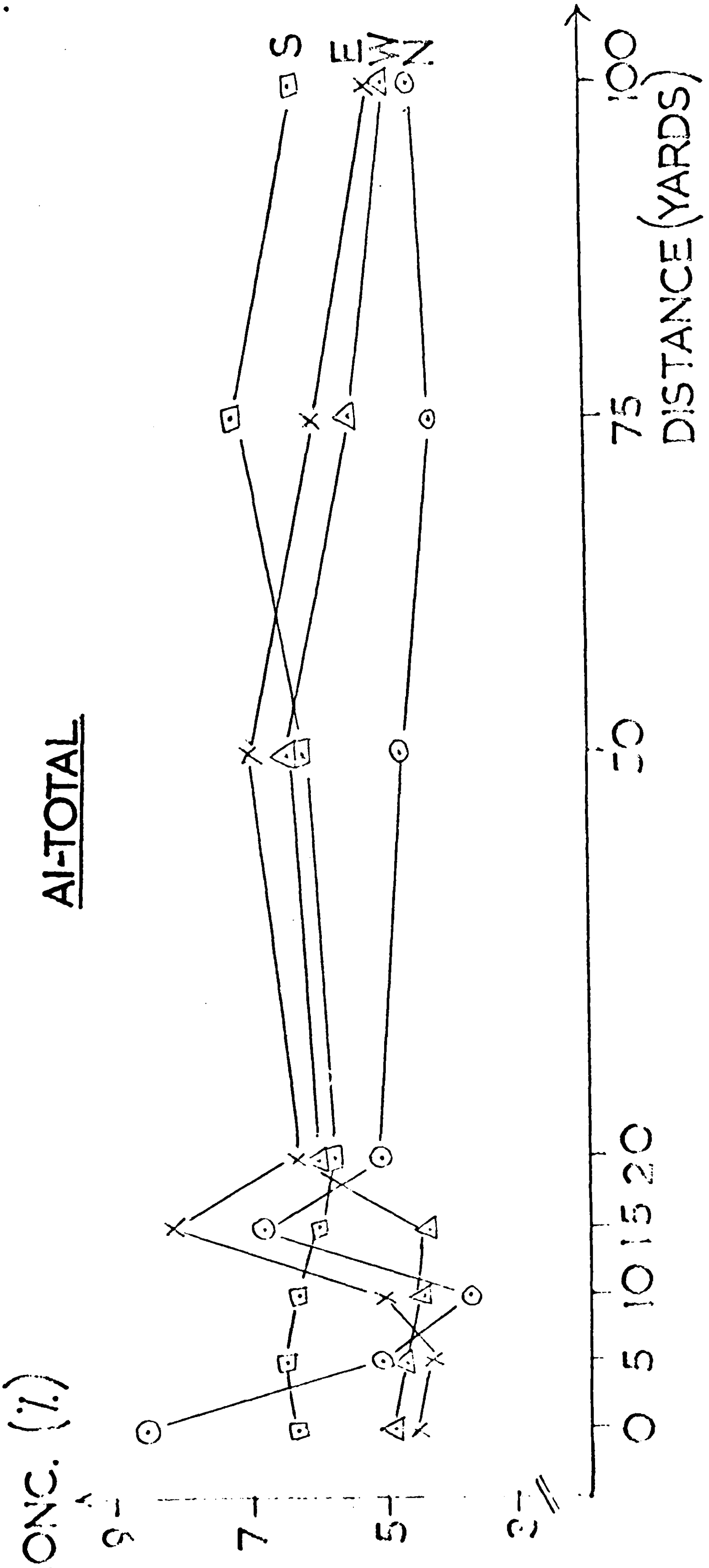
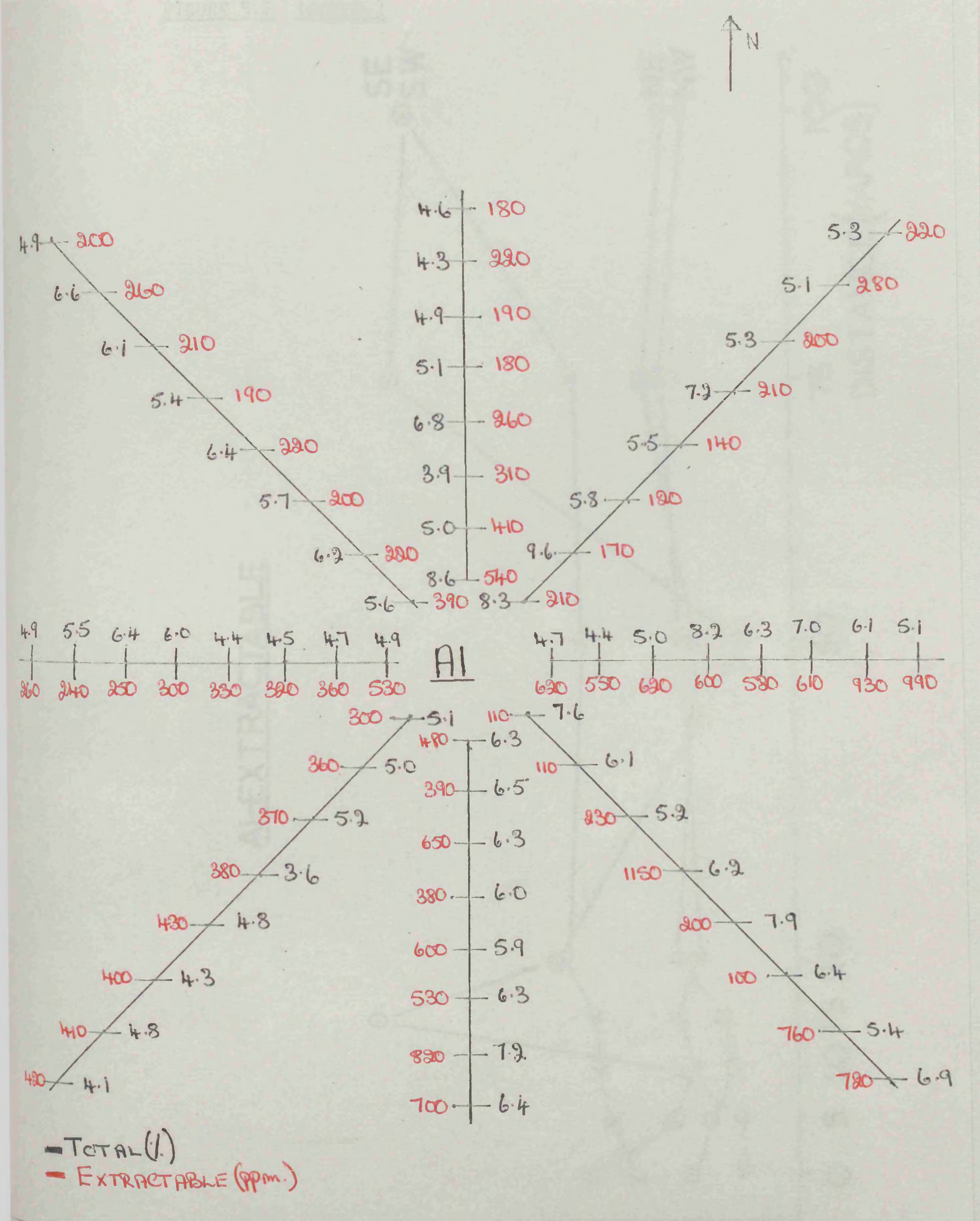



N.
4.6 180
4.3 220
4.9 190
5.1 180
6.8 260
3.9 310
5.0 410
8.6 540
4.9 200
6.6 260
6.1 210
5.4 190
6.4 220
5.7 200
6.2 220
5.6 390
5.3 220
5.1 280
5.3 200
7.9 210
5.5 140
5.8 120
9.6 170
8.3 210
4.9 5.5 6.4 6.0 4.4 4.5 4.7 4.9
260 240 250 300 330 320 360 530
A1
4.7 4.4 5.0 8.2 6.3 7.0 6.1 5.1
630 550 690 600 580 610 930 990
300 5.1
360 5.0
370 5.2
380 3.6
430 4.8
400 4.3
440 4.8
420 4.1
480 6.3
390 6.5
650 6.3
380 6.0
600 5.9
530 6.3
820 7.2
700 6.4
110 7.6
110 6.1
230 5.2
1150 6.2
200 7.9
100 6.4
760 5.4
720 6.9
— Total (%)
— Extractable (ppm.)

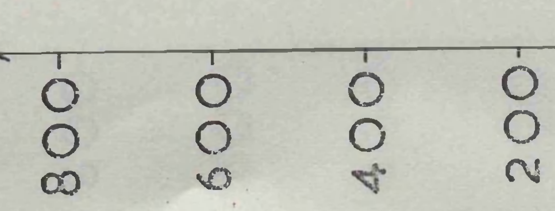
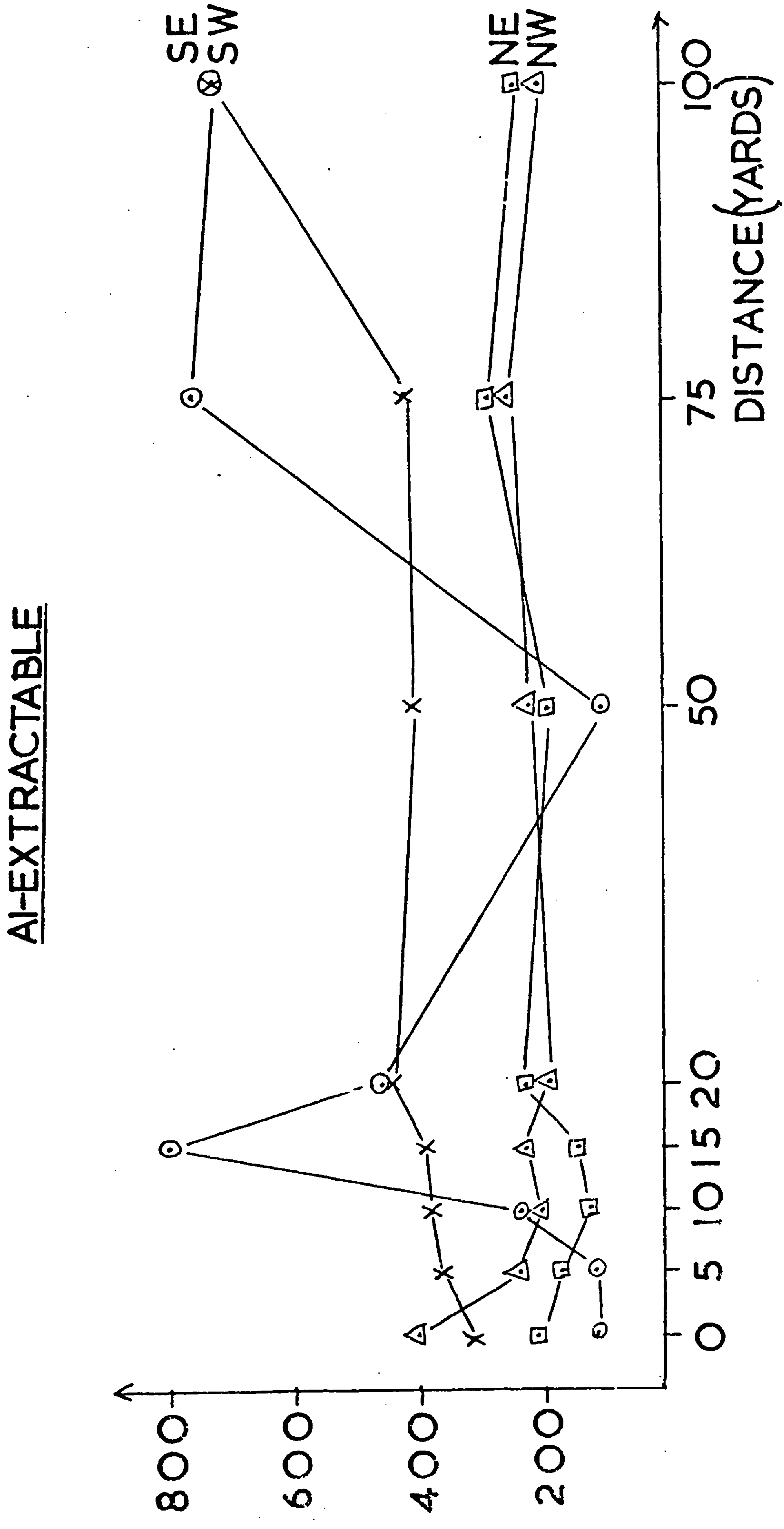

800
600
400
200

FIGURE 5.2 (CONTD.)



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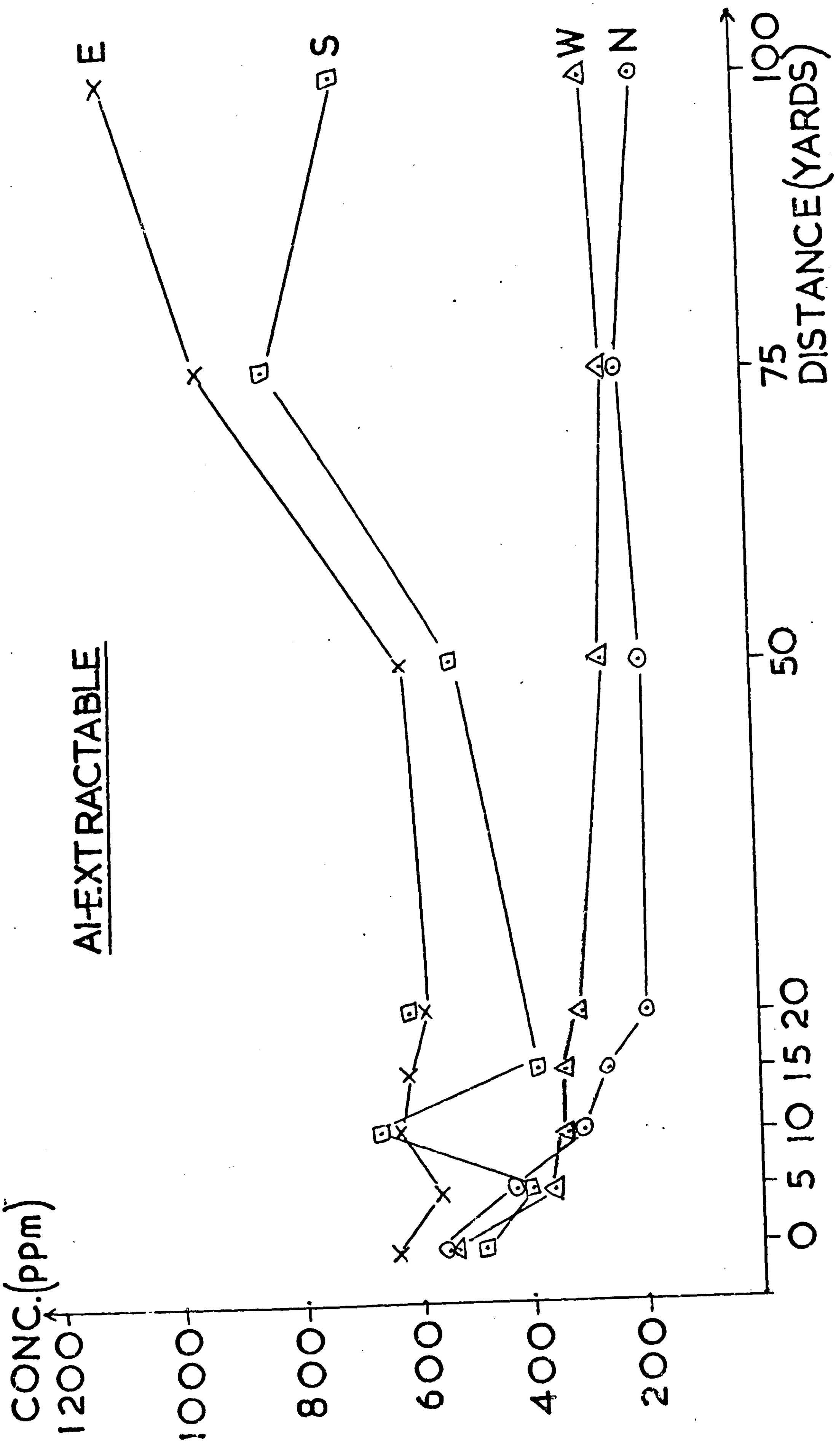

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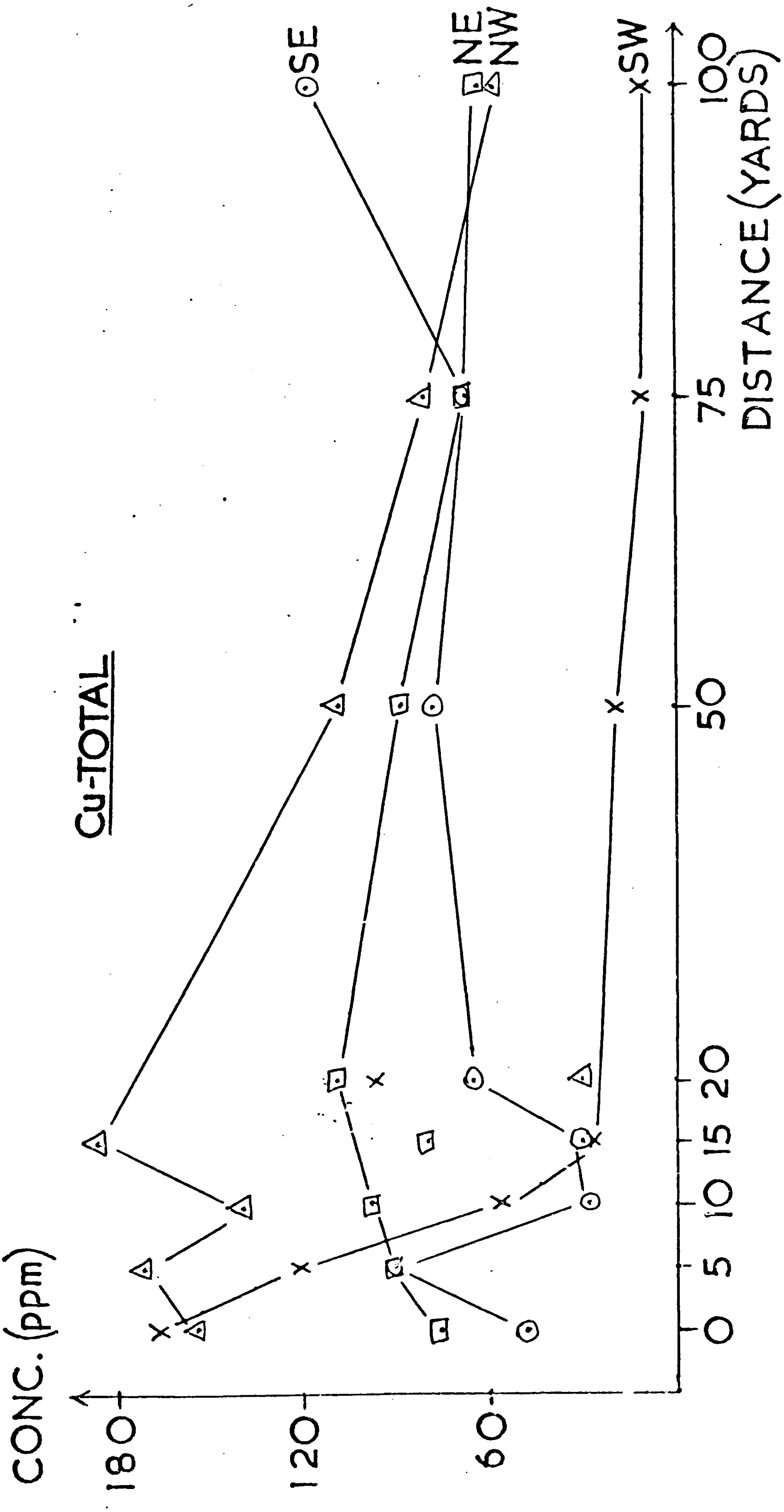
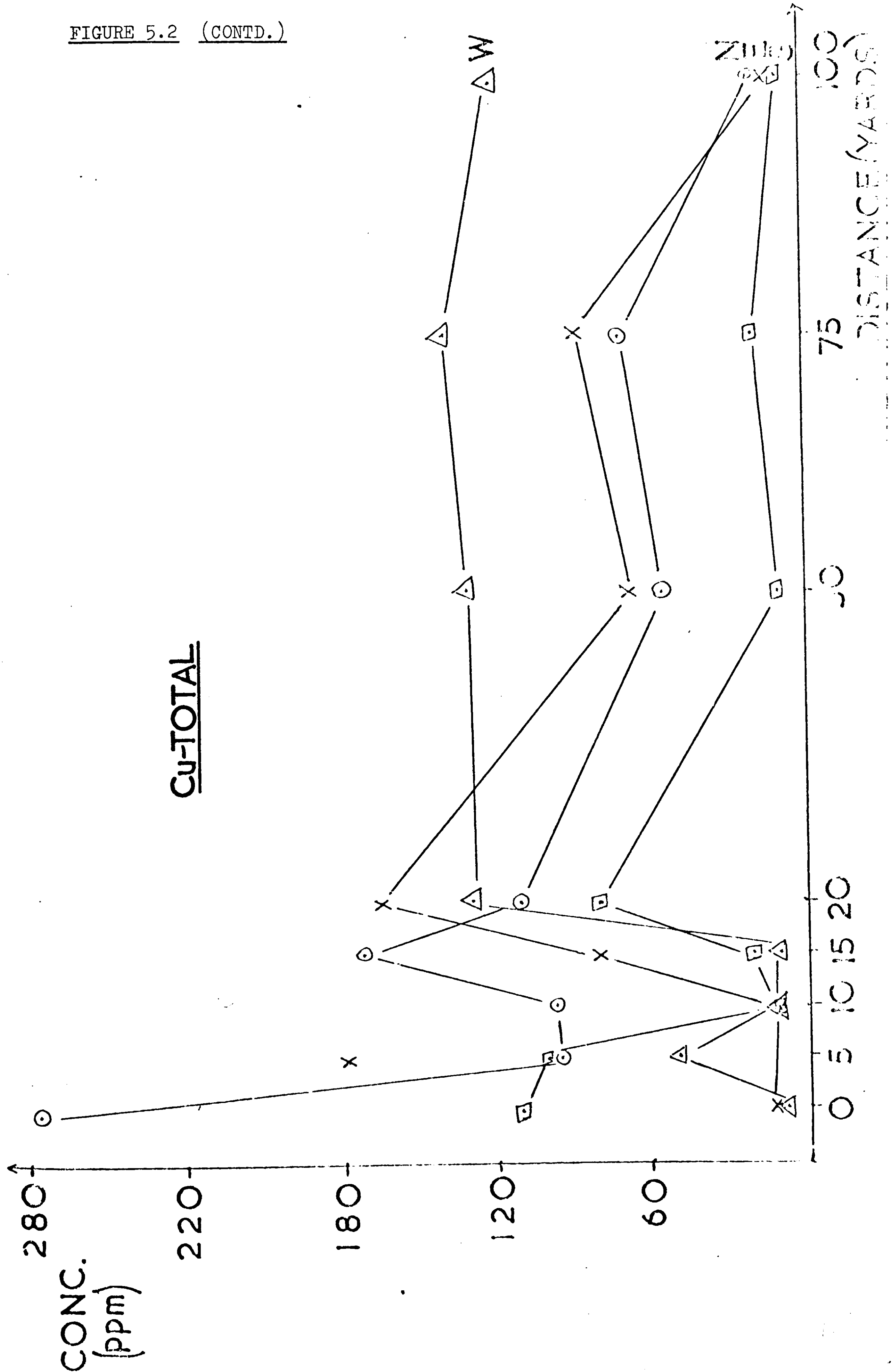


FIGURE 5.2 (CONTD.)



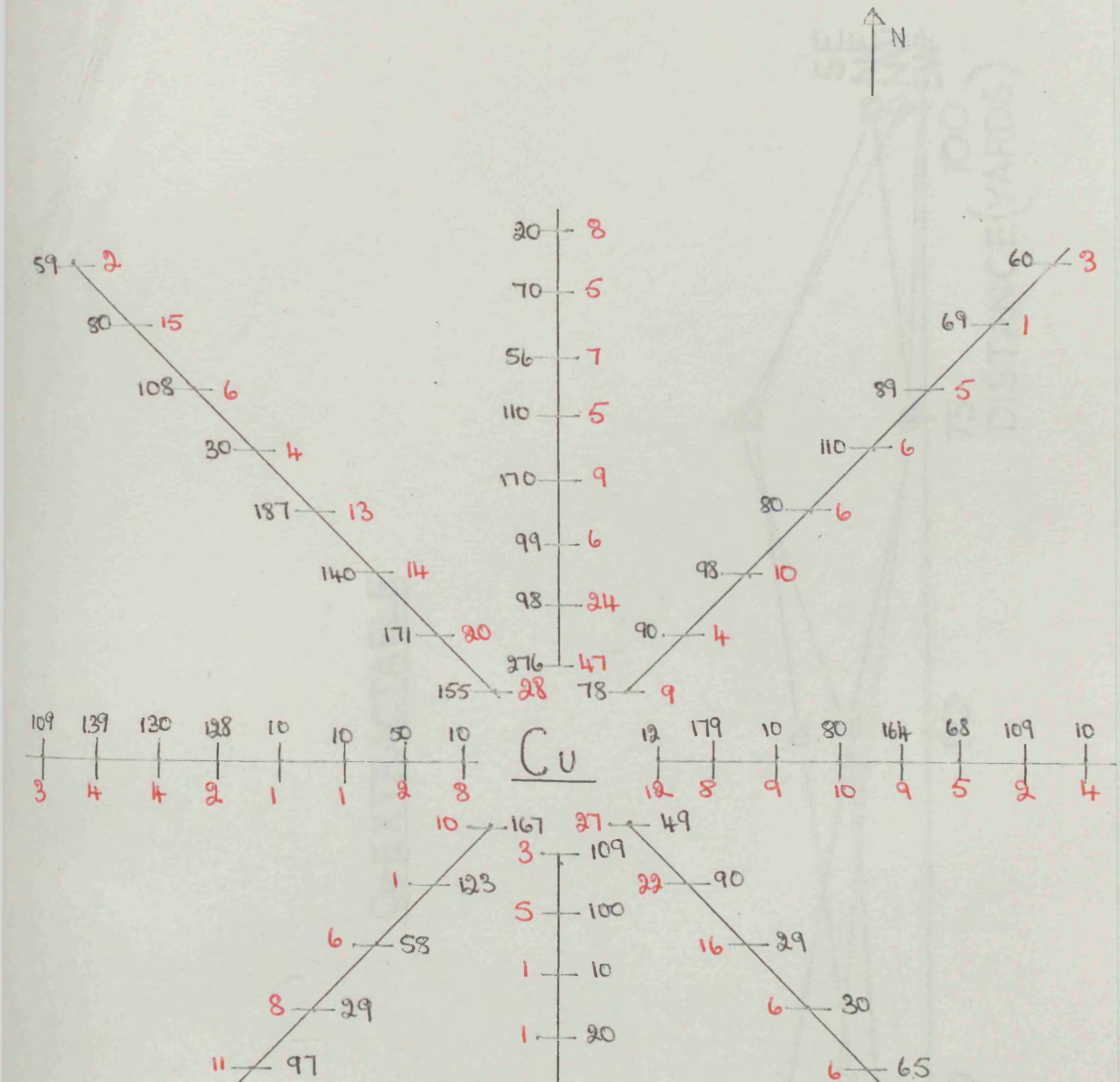
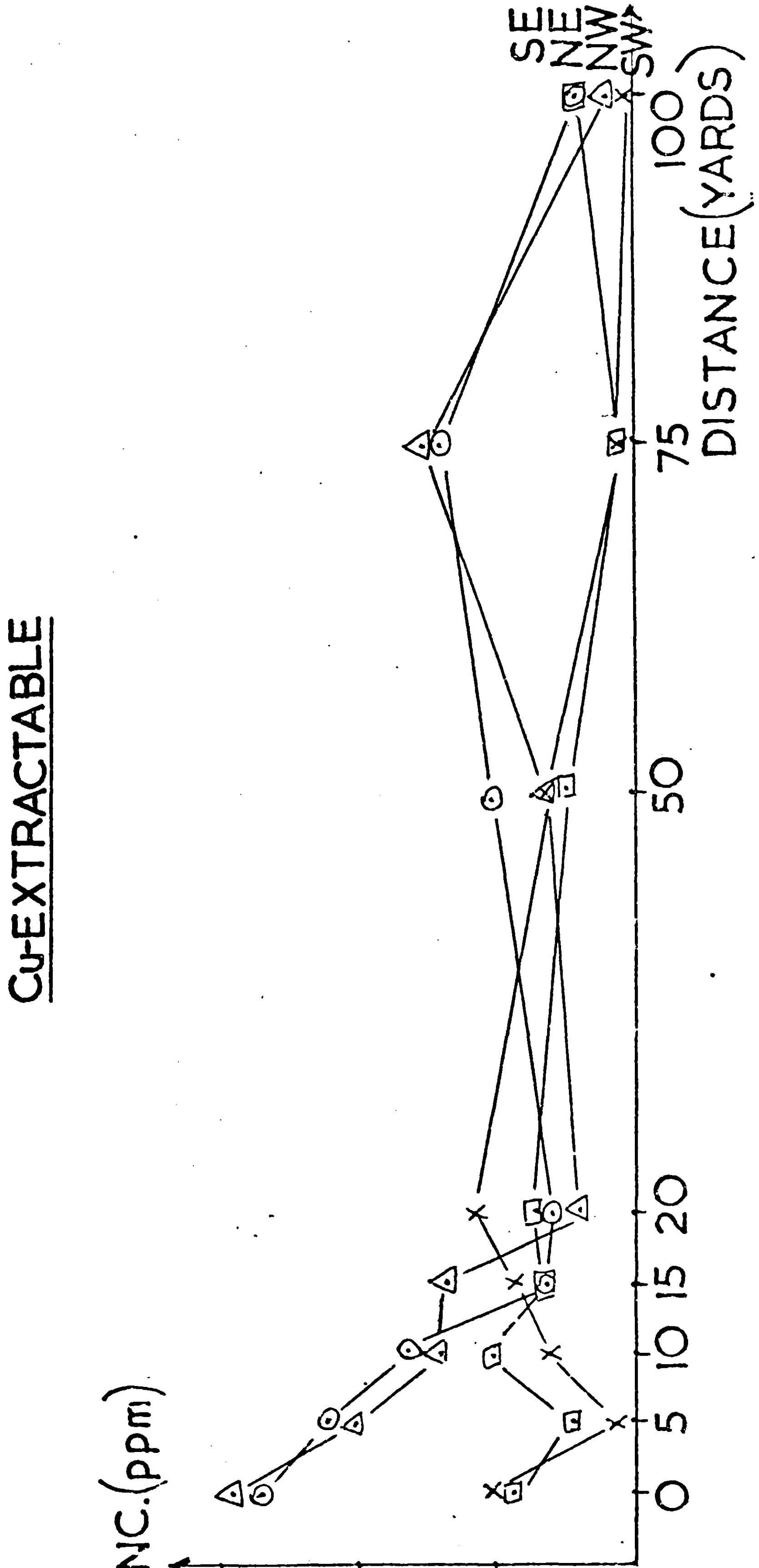

N
Cu
59 2
80 15
108 6
30 4
187 13
140 14
171 20
155 28
20 8
70 5
56 7
110 5
170 9
99 6
98 24
276 47
60 3
69 1
89 5
110 6
80 6
98 10
90 4
78 9
109 3
139 4
130 4
128 2
10 1
10 1
50 2
10 8
12 12
179 8
10 9
80 10
164 9
68 5
109 2
10 4
10 167
1 123
6 58
8 29
11 97
6 20
1 10
0.1 10
3 109
5 100
1 10
1 20
0.1 80
0.4 10
0.1 20
4 10
27 49
22 90
16 29
6 30
6 65
10 79
14 68
4 119
TOTAL (ppm.)
EXTRACTABLE (ppm.)

FIGURE 5.2 (CONTD.)



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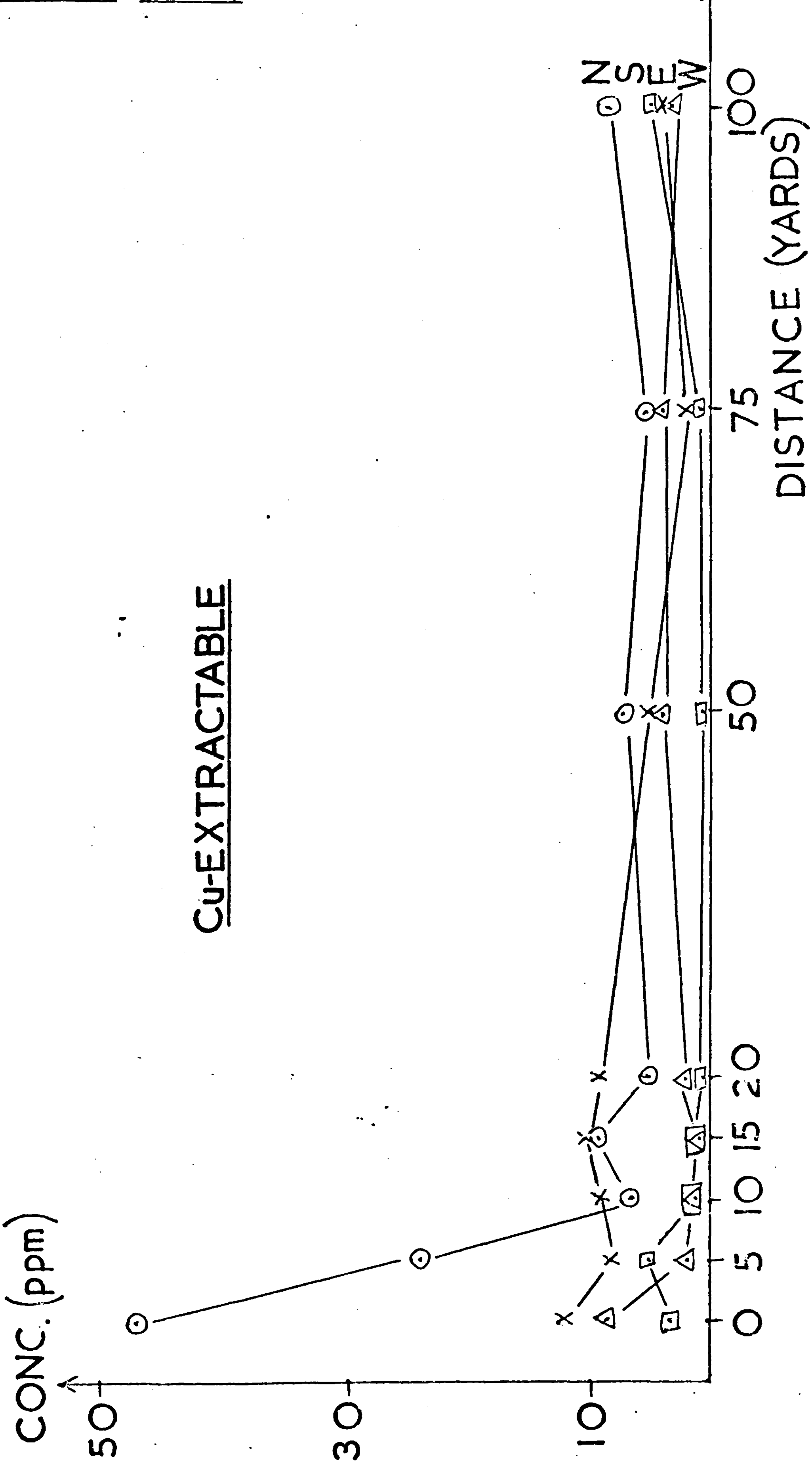


FIGURE 5.2 (CONTD.)

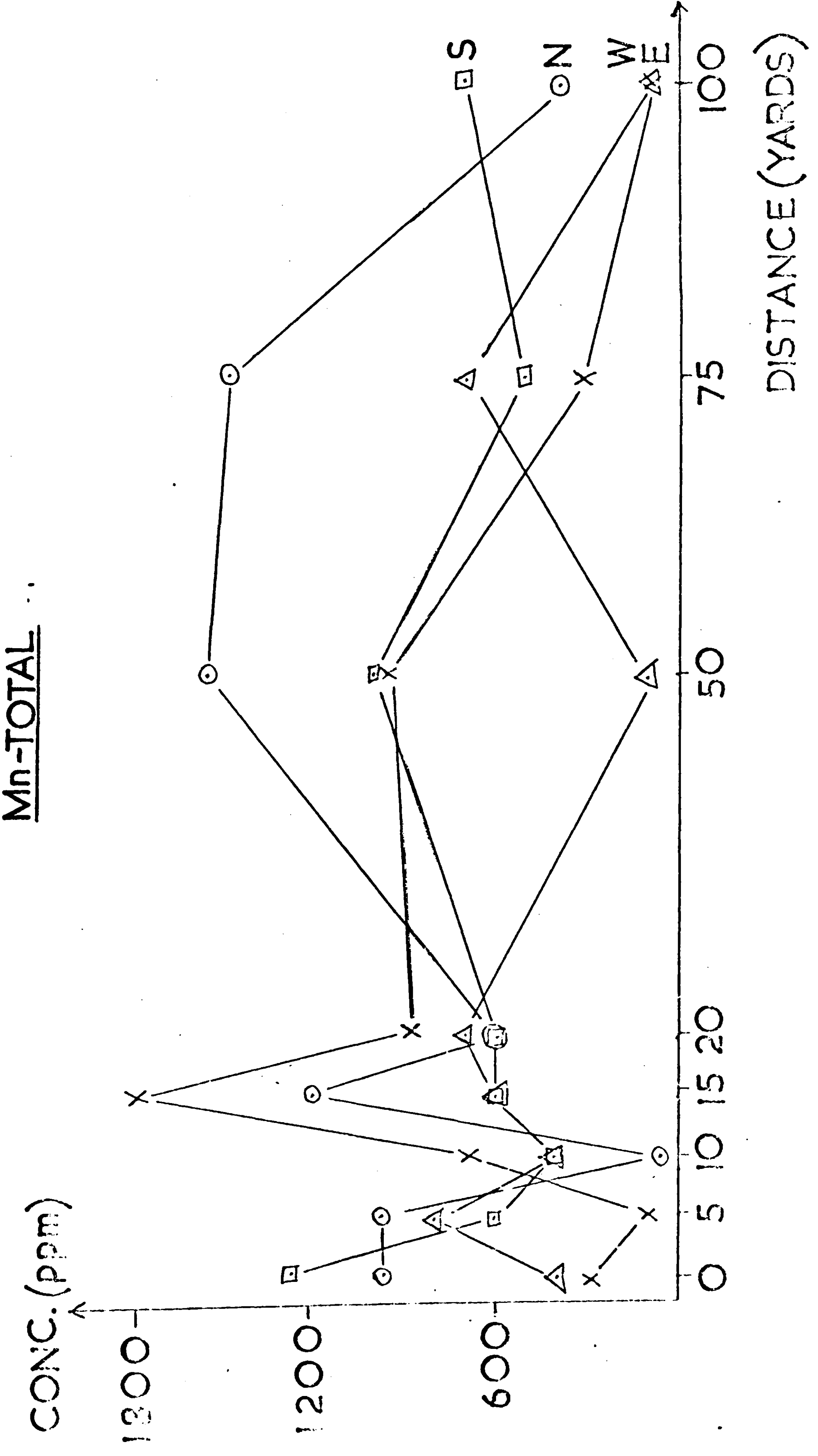
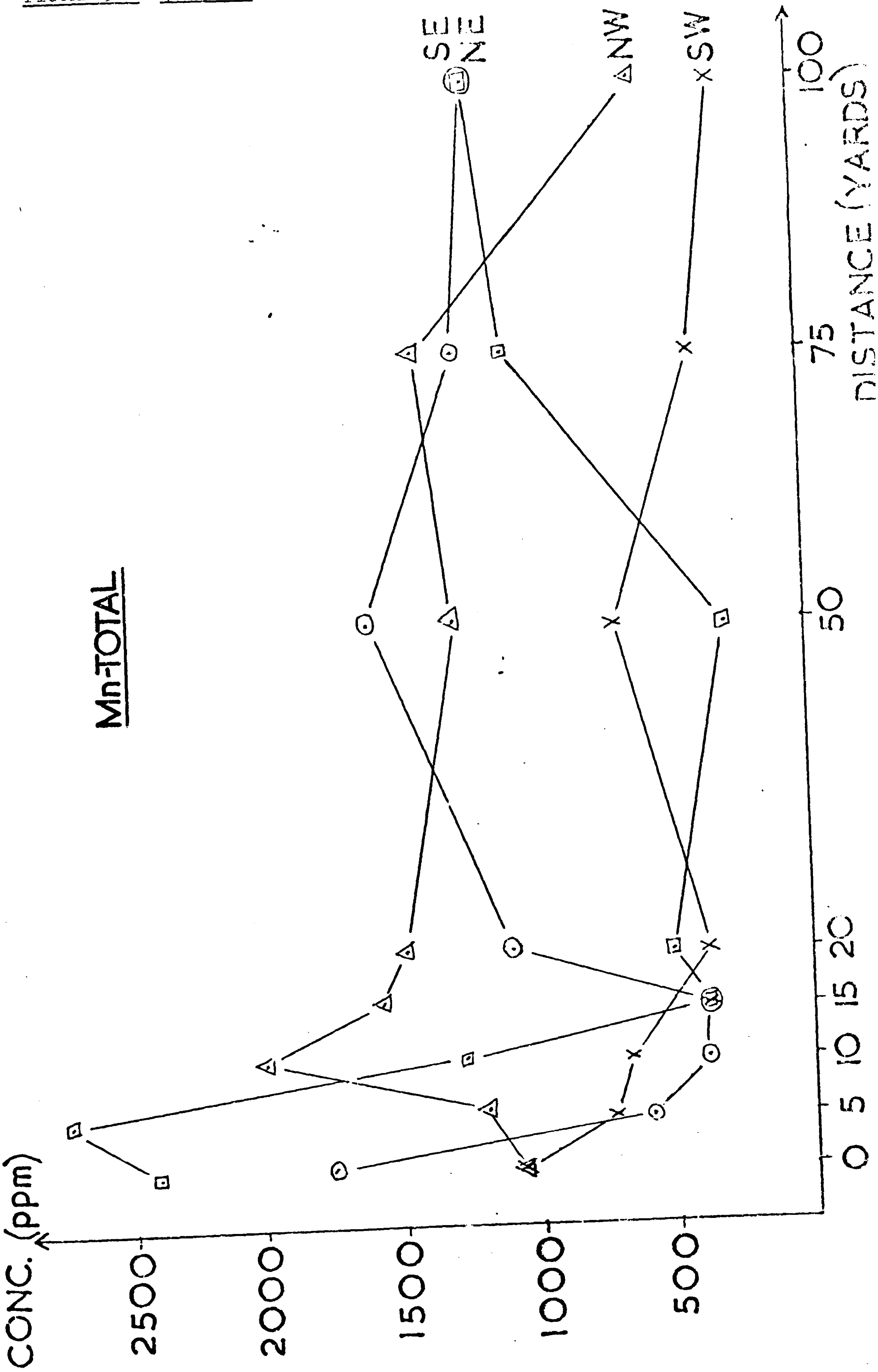


FIGURE 5.2 (CONTD.)



Mn-TOTAL

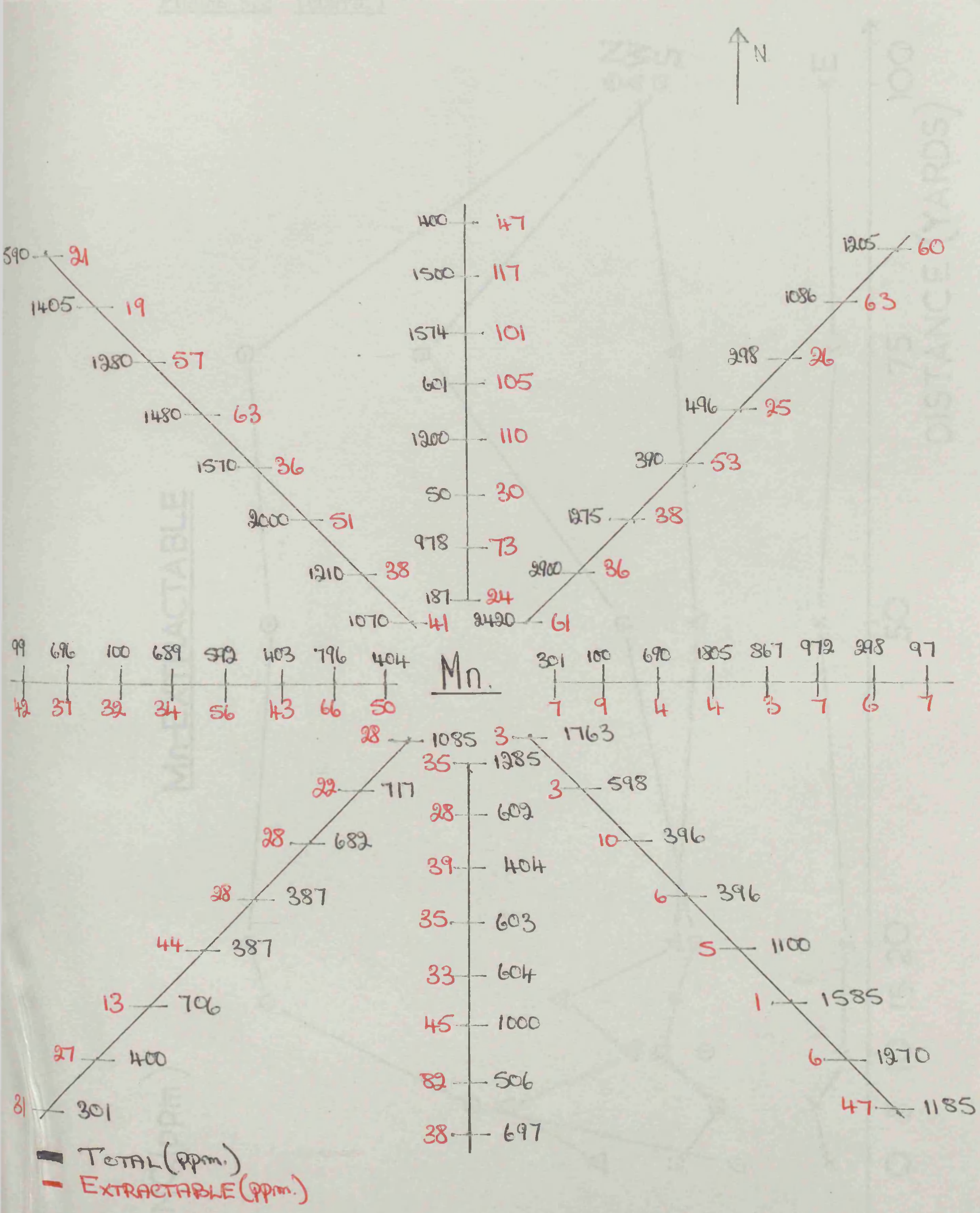

N
Mn.
1400 47
1500 117
1574 101
601 105
1200 110
50 30
978 73
187 24
590 21
1405 19
1280 57
1480 63
1570 36
2000 51
1210 38
1070 41
1205 60
1086 63
298 26
496 25
390 53
1275 38
2900 36
2420 61
99 42
696 37
100 32
689 34
592 56
403 43
796 66
404 50
301 7
100 9
690 4
1805 4
867 3
972 7
298 6
97 7
28 1085
22 717
28 682
28 387
44 387
13 706
27 400
81 301
35 1285
28 602
39 404
35 603
33 604
45 1000
82 506
38 697
3 1763
3 598
10 396
6 396
5 1100
1 1585
6 1270
47 1185
TOTAL (ppm.)
EXTRACTABLE (ppm.)

FIGURE 5.2 (CONTD.)

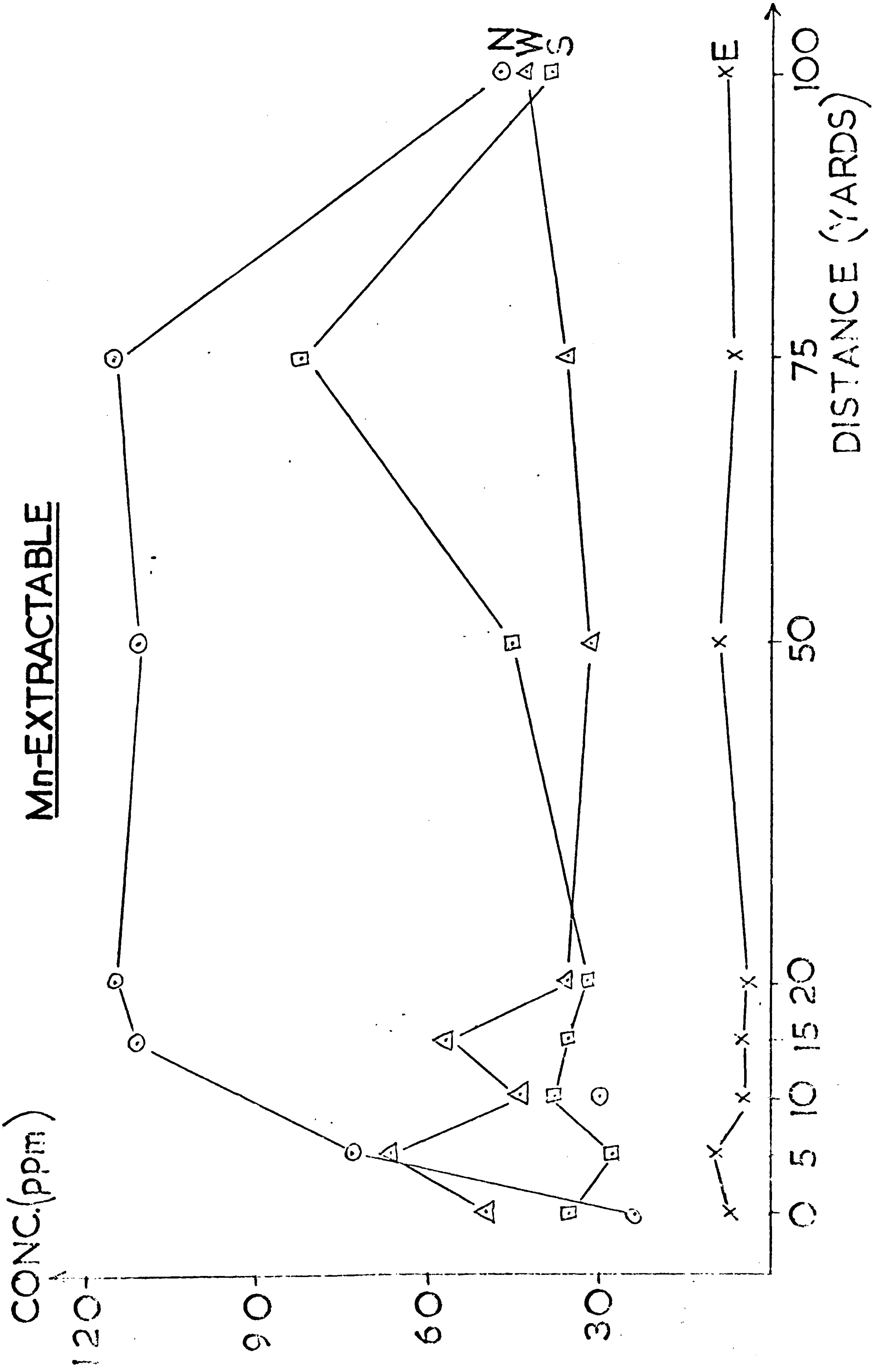


FIGURE 5.2 (CONTD.)

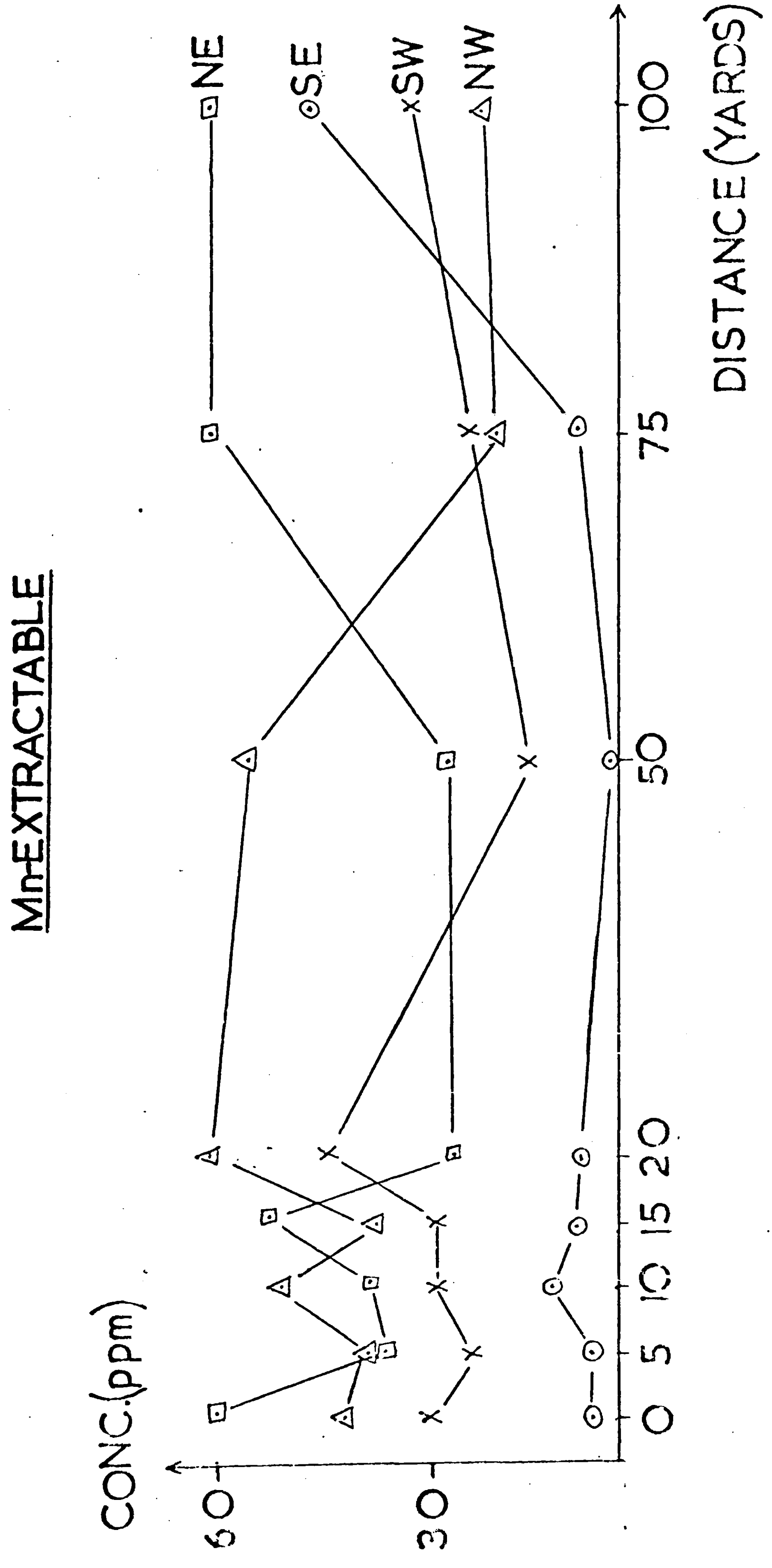


FIGURE 5.2 (CONTD.)

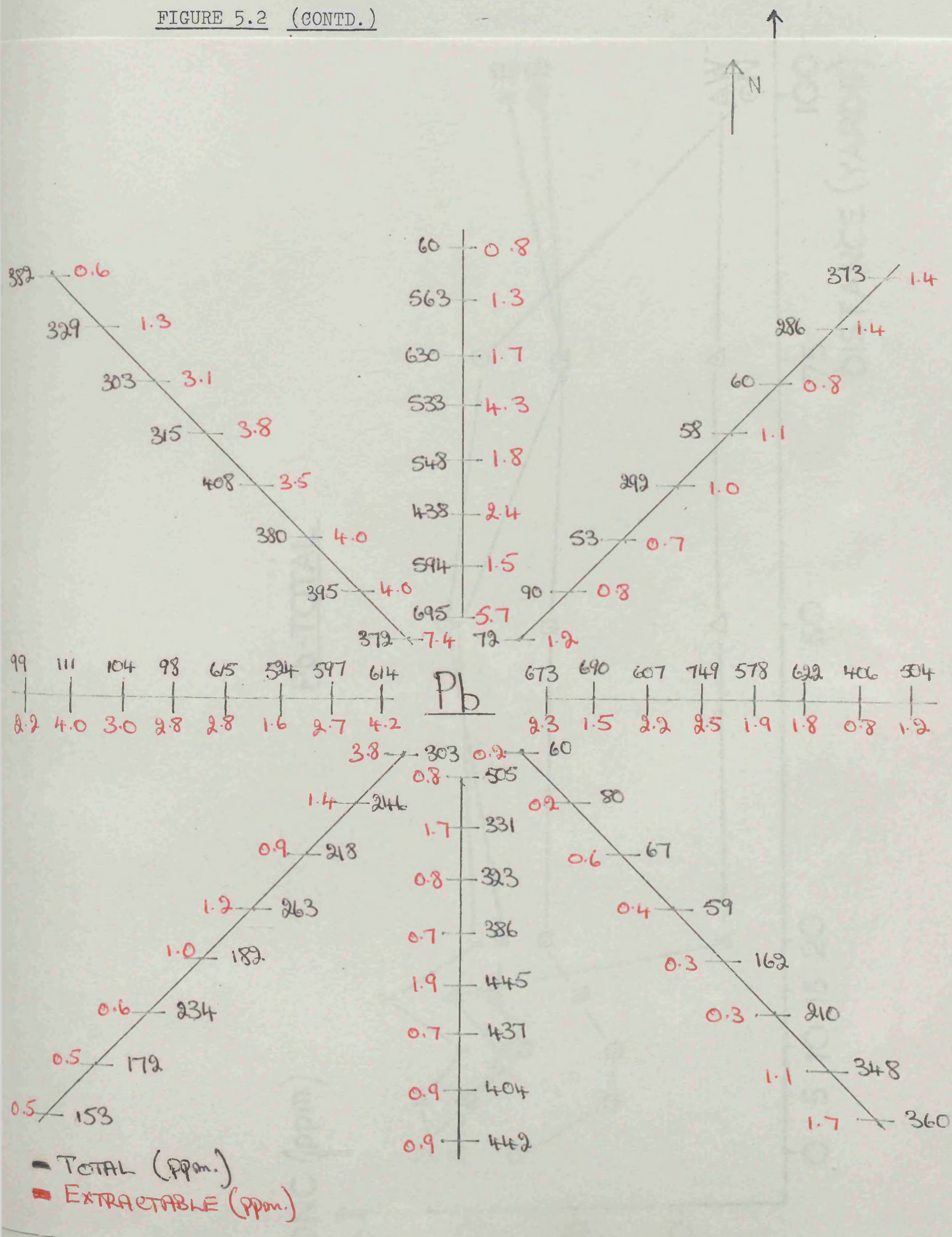


FIGURE 5.2 (CONTD.)

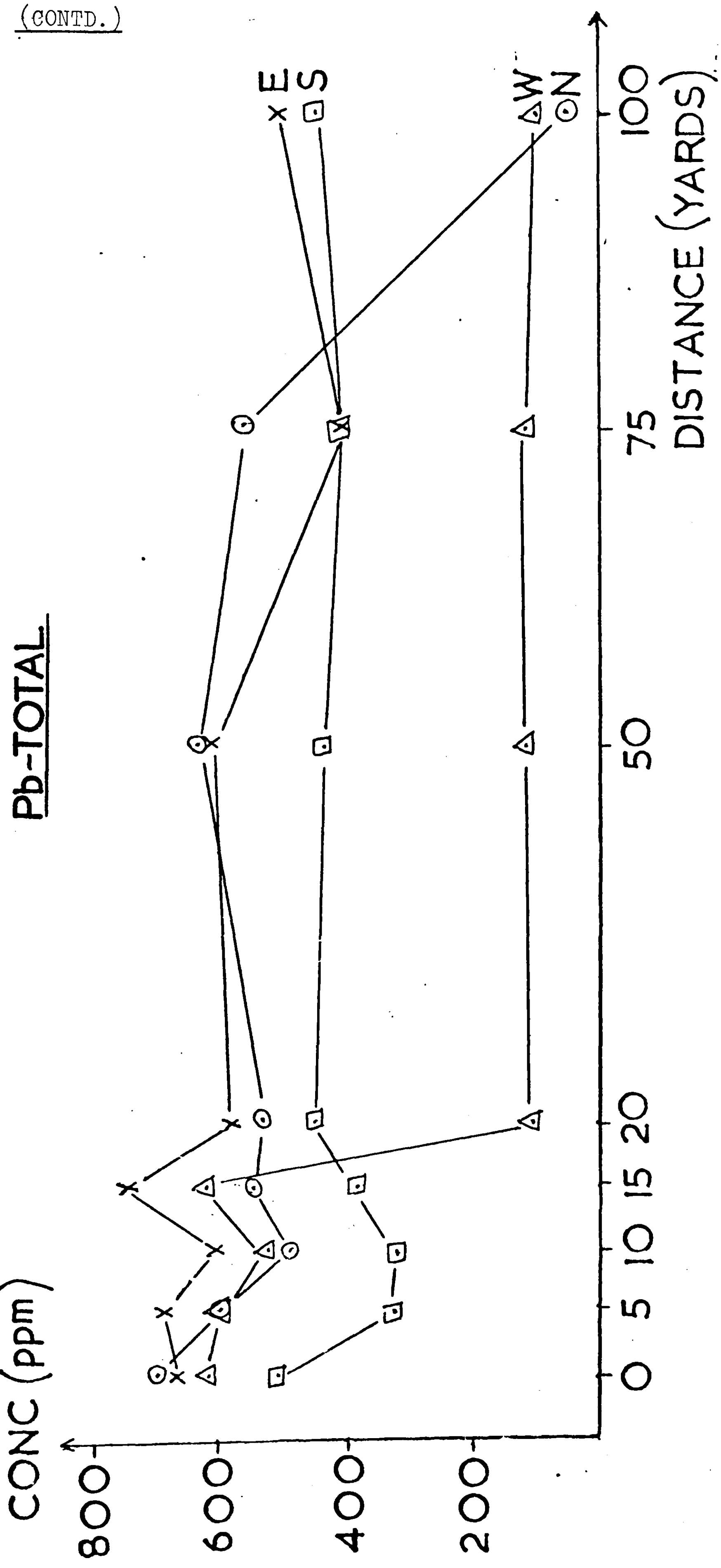


FIGURE 5.2 (CONTD.)

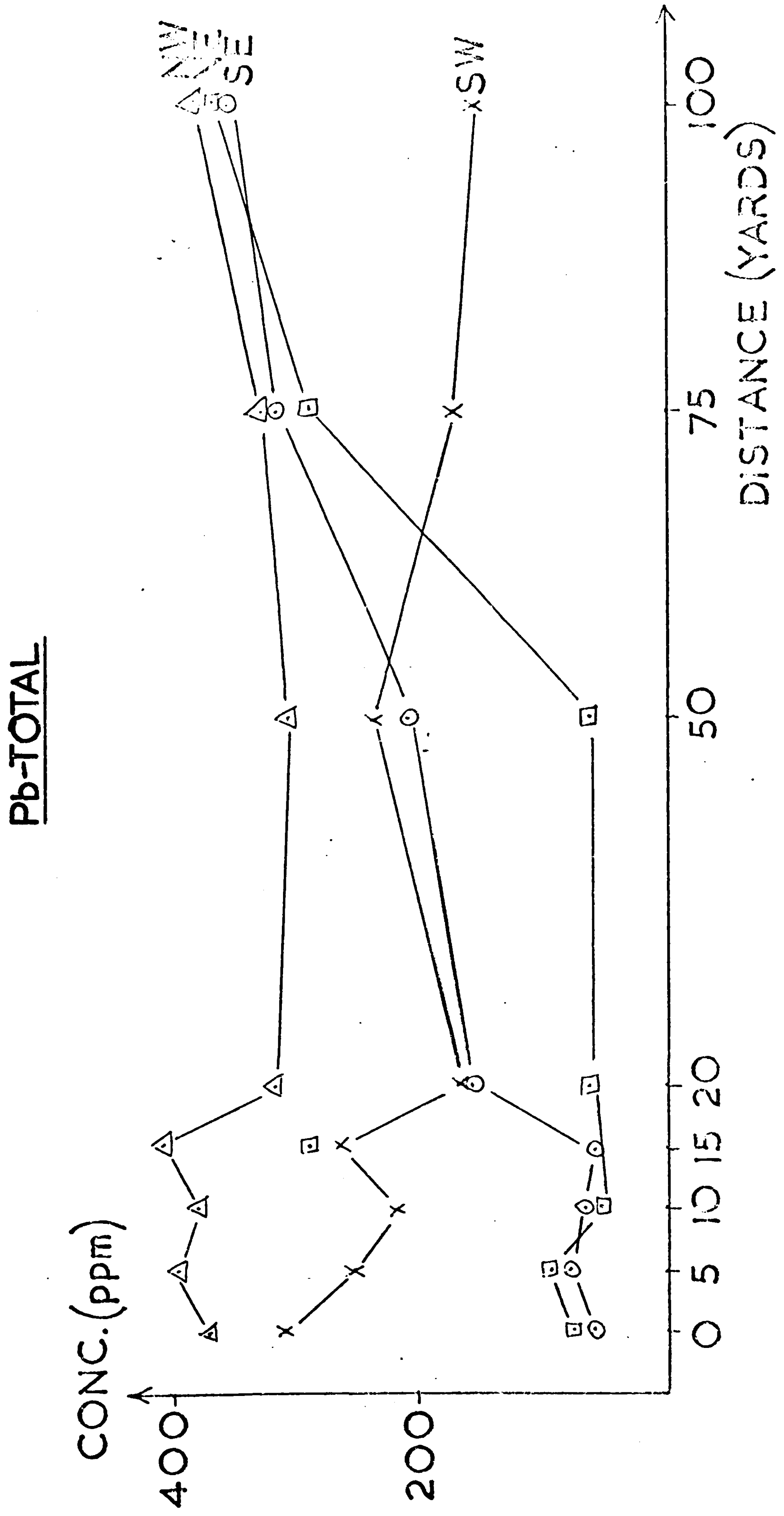


FIGURE 5.2 (CONTD.)

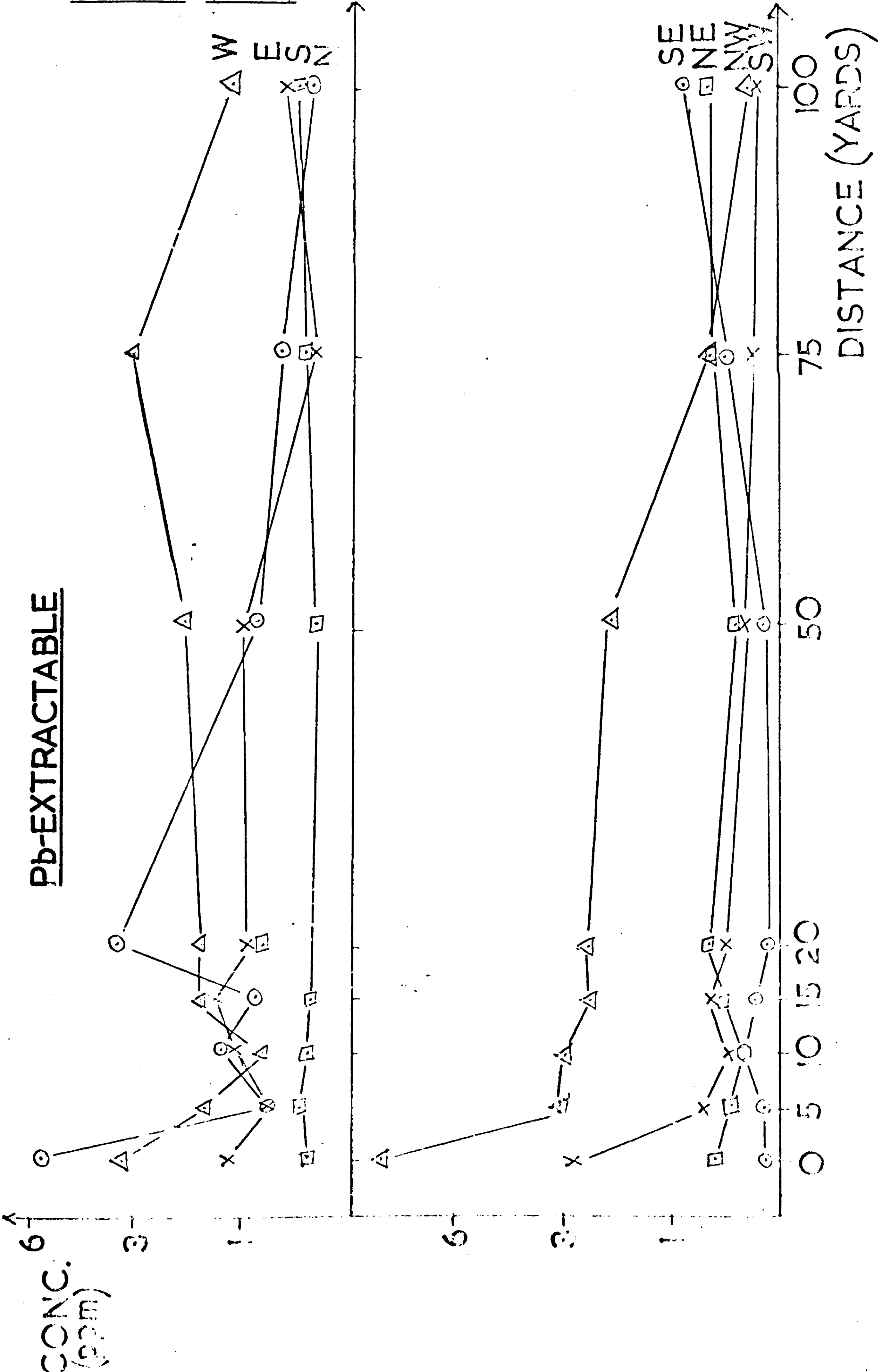


FIGURE 5.2 (CONTD.)

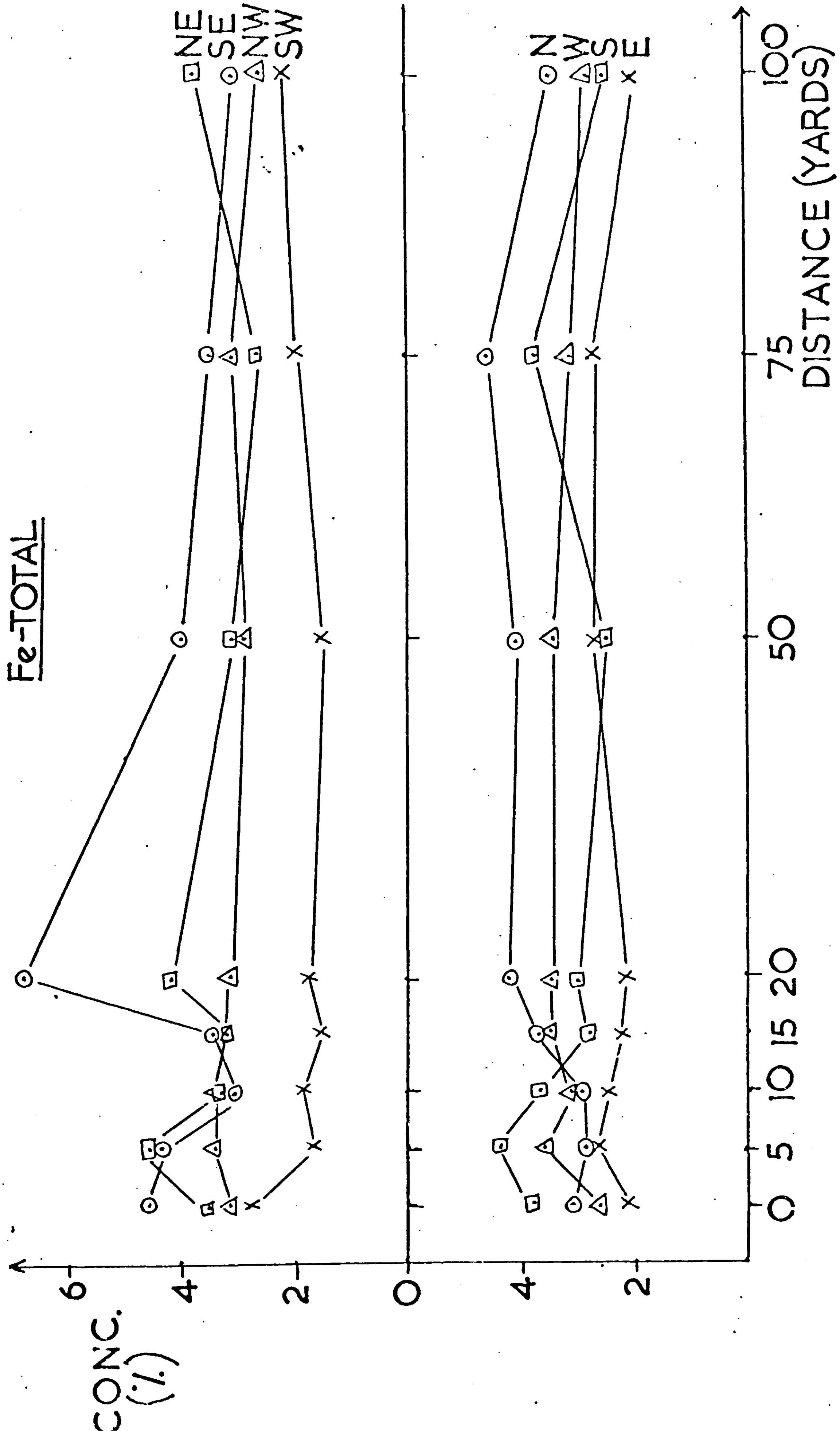


FIGURE 5.2 (CONTD.)

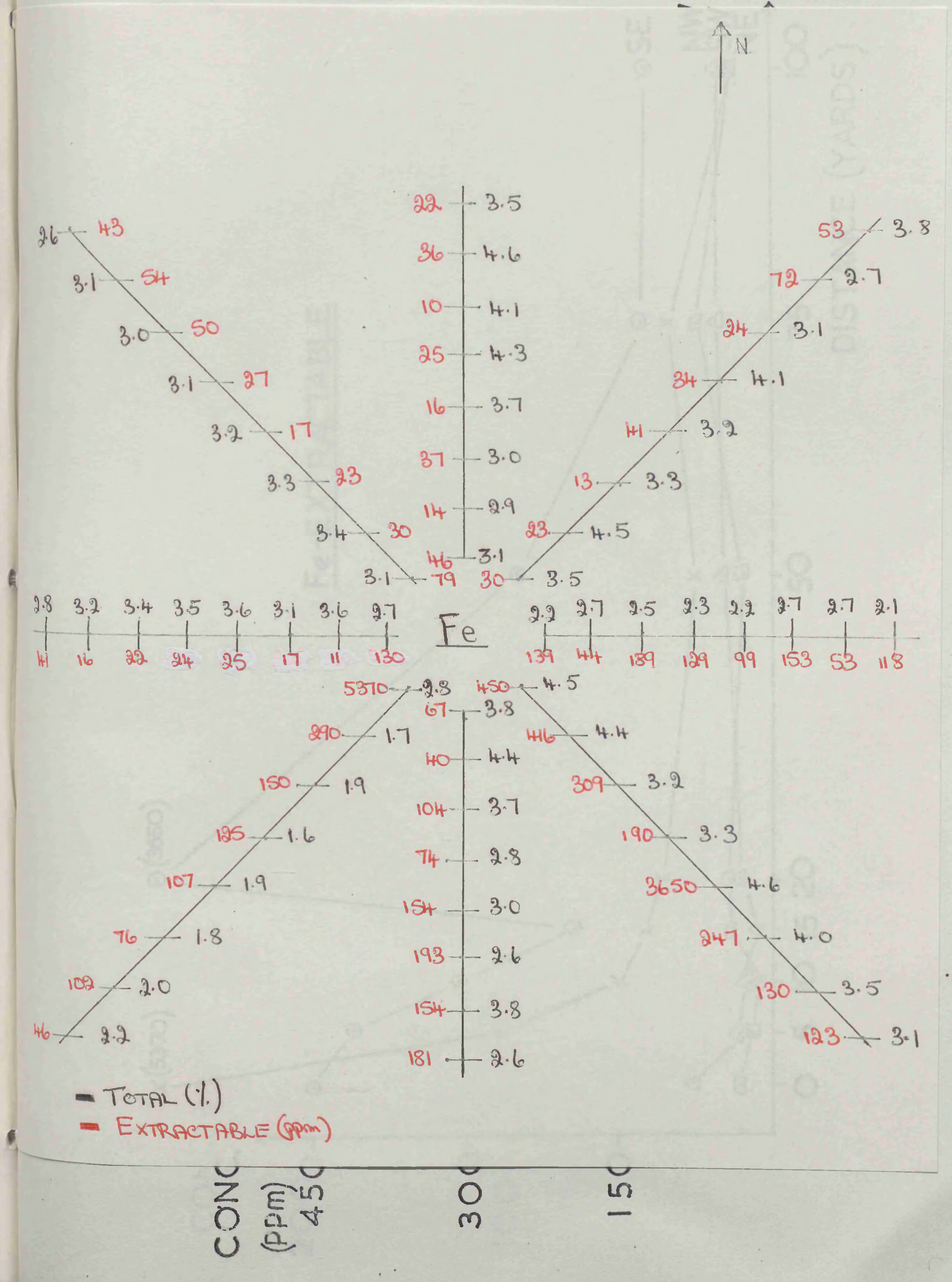


FIGURE 5.2 (CONTD.)

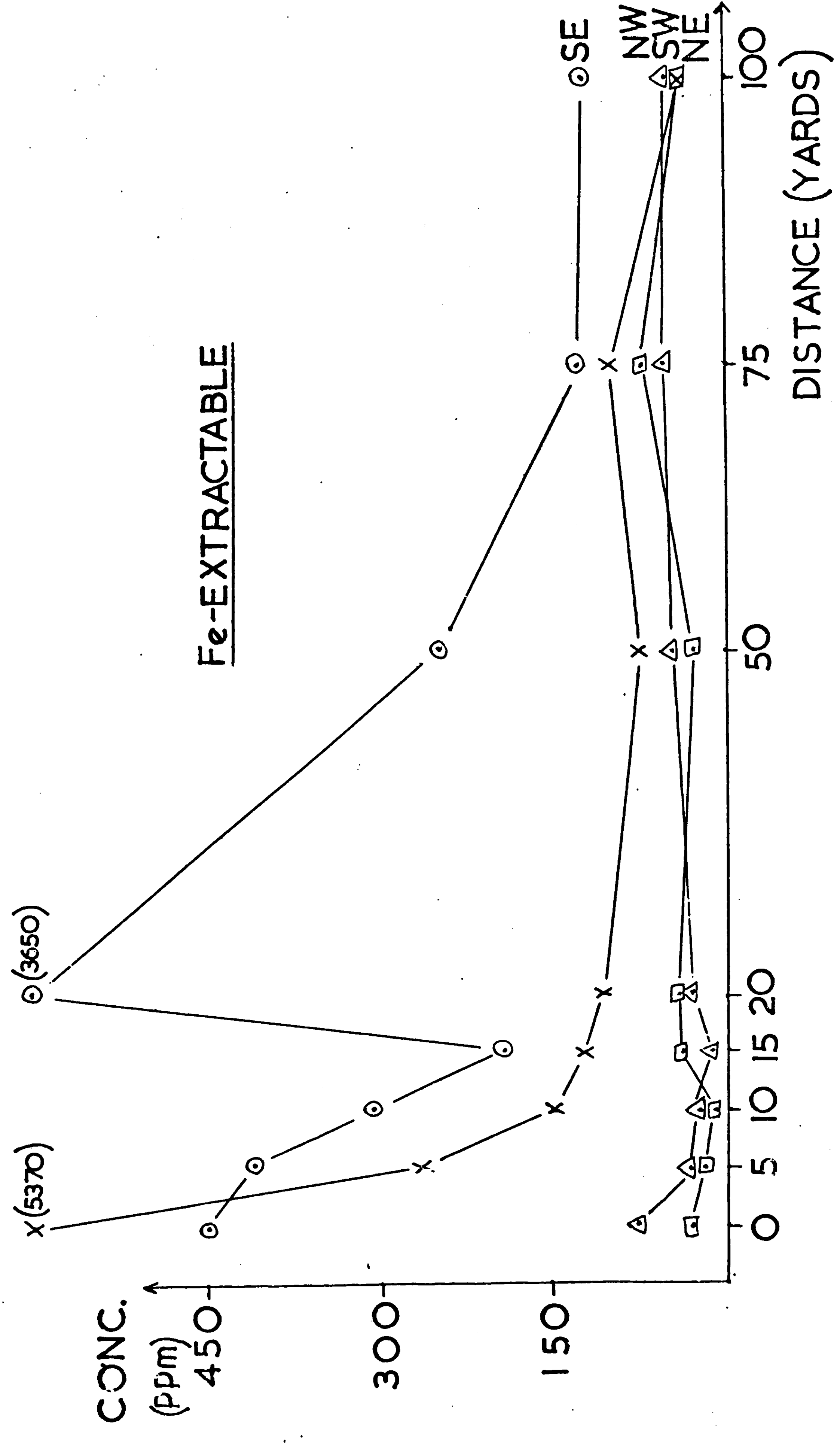
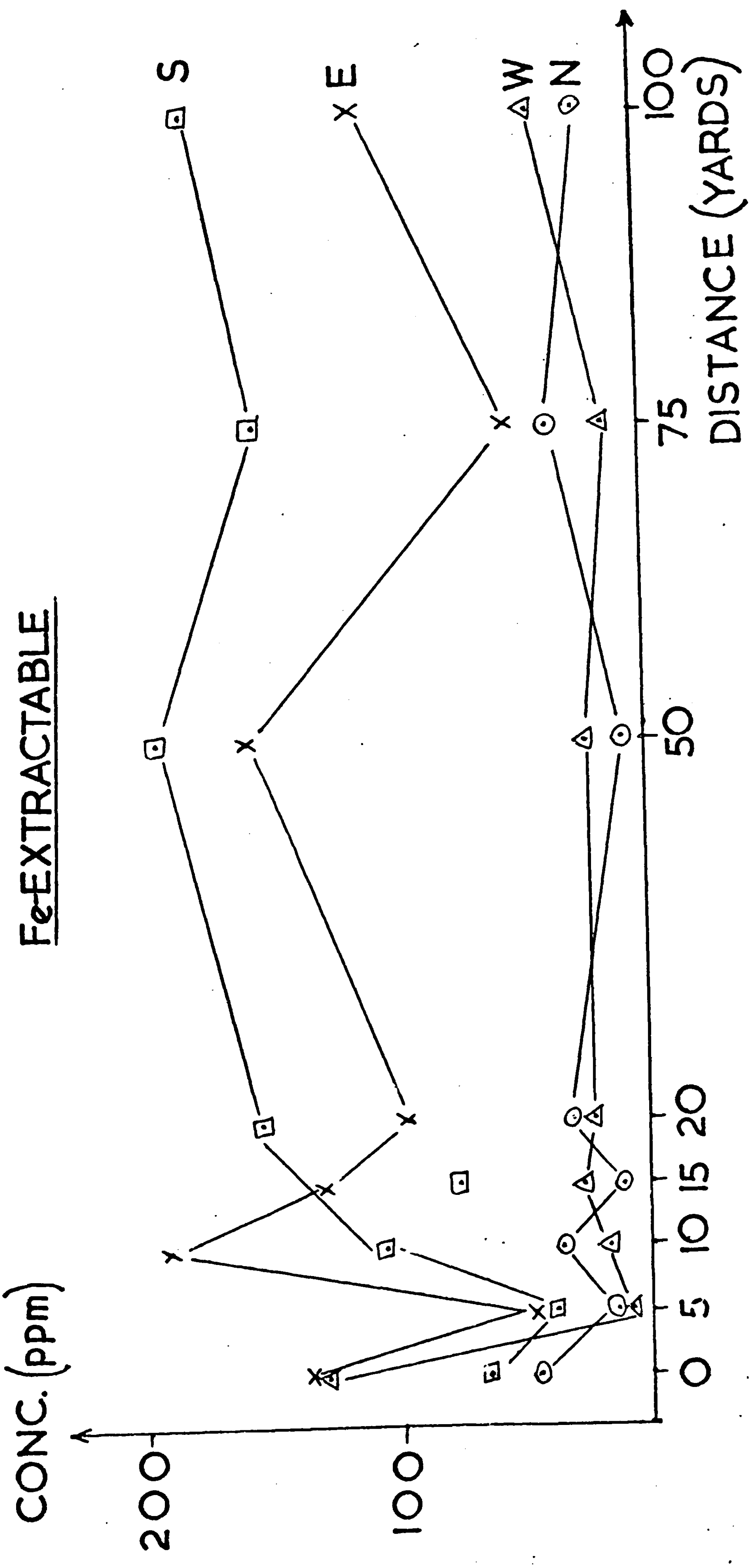


FIGURE 5.2 (CONTD.)



Total Levels

Al and Pb have V-shapes from 0-15 or 20 yards after which the Al falls to 75 yards while Pb fluctuates randomly. Cu and Ni have U-shapes over the ranges 0-15 and 0-50 yards respectively. Ni then shows a big drop to 100 yards while the fall of Cu is not so dramatic. Cr and Zn generally fall to 75 or 100 yards while Fe rises to 75 yards. Mn tends to fluctuate randomly.

Acetic and Extractable

The general trend is a decrease with increasing distance from the bing. Al, Cr, Zn fall to 75 yards with the decrease of Zn being steep initially. Ni falls only to 50 yards. Cu falls to 10 yards and levels out. Fe only falls to 5 yards before levelling out. Pb has a U-shape from 0-20 yards before falling to 75 yards and Mn has a broad ∩-shape covering the whole 0-100 yards range.

There is no evidence from the results for the stream preventing the movement of metals across to land on the other side although in general there is a drop on crossing the stream. Only in the case of Mn (total and acetic extractable) Pb (total) and Cu (total) is there a dramatic drop on crossing the stream.

2.5.1.2 North East (NE) The land in this direction is separated from the bing by a stream. Zero point was taken across the stream. The land slopes upwards to the 75 yards sampling point with the 100 yards point across a tarmac road. This is the direction which will be subject to the prevailing winds.

Total Levels

Al, Fe, Mn, Ni, Zn fluctuate randomly along the sampling line while Cr remains fairly constant. Pb remains approximately constant to 50 yards before rising to 100 yards. Cu has a U-shape from 0-20 yards, thereafter falling to 100 yards.

Acetic Extractable Levels

Zn, Pb, Cu and Al all remain very much the same throughout. Fe is more variable but by and large remains constant. Cr falls to 10 yards and rises to 100 yards. Ni falls to 5 yards, rises to 20 yards and again falls to 100 yards. Mn fluctuates randomly.

2.5.2.1.3 East (E):- A rough track cut out of the bing separates the bing and land in this direction; the land remaining fairly level.

Total Levels

Al, Cr, Mn, and Zn show a rise to 15 yards (20 yards for Cr) and a fall to 100 yards: Mn and Zn being more dramatic. Ni, Fe, Pb and Cu show no trends but fluctuate randomly, Fe less so than others.

Acetic Extractable Levels

All elements except Ni and Fe are in general the same throughout. Ni increases to 20 yards, falls to 50 yards before increasing again to 100 yards: Al also starts to rise after 50 yards. Fe fluctuates randomly.

2.5.2.1.4 South East (SE):- As can be seen from the map this direction has been modified to carry drainage water which will tend to obscure any trends.

Total Levels

Cr is generally the same throughout with slight fluctuations. Pb is the same to 15 yards before increasing to 100 yards. Cu also increases over the range 15-100 yards but is random up to 15 yards. Zn and Fe have U-shaped trends from 0-20 yards after which Fe falls sharply to 100 yards, while Zn peaks at 75 yards. Ni and Al levels fluctuate randomly. Changes in Mn levels are most dramatic with a fall to 15 yards, a rise to 50 yards and a further fall to 100 yards.

Acetic Extractable Levels

Zn is generally the same throughout as are Mn and Pb up to 75 yards and 50 yards respectively before rising to 100 yards. Ni is generally the same except for a peak at 15-20 yards and a trough at 75 yards. Cr peaks at 15 yards with a gradual increase to 100 yards. Cu falls gradually to 20 yards, rising slightly to 75 yards. Al levels are random, peaking at 15 and 75 yards. Fe shows the most dramatic changes with a V-shape covering 0-20 yards following by a dramatic fall to 100 yards.

2.5.2.1.5 South (S):- The land in this direction lies across the stream studied earlier for metal burdens with the zero point taken across the stream from the bing.

Total Levels

Al, Fe, Mi, show a general fall to 20 yards (50 yards for Fe) rising to 75 yards and falling again to 100 yards. Zn, Pb and Cu show a U-shape over 0-20 yards after which Zn fluctuates, Pb remains the same and Cu has a drop to 50 yards before generally levelling out. Cr demonstrates the reverse over the 0-75 yards range, ie. ∩-shaped and thereafter remains the same. Mn fluctuates randomly.

Acetic Extractable Levels

Cu and Pb are generally the same throughout. Cr and Zn are generally the same up to 50 yards, but rise to 75 or 100 yards. Mn and Fe show a general rise to 50 or 75 yards and fall again to 75 or 100 yards. Ni shows a general fall to 50 yards, rising to 100 yards with a peak at 75 yards. Al fluctuates randomly.

2.5.2.1.6 South West (SW):- The land in this direction is level well beyond the 100 yards point.

Total Levels

Fe and Cr are generally the same throughout. Al, Pb and Cu generally fall to 100 yards. The reduction for Cu is dramatic to 15 yards and more gradual to 100 yards. Ni has a ∩-shape covering the range 0-15 yards remaining the same to 100 yards. Zn is generally the same to 15 yards, while Mn falls to 20 yards after which they both fluctuate, rising to 50 yards and then falling to 100 yards.

Acetic Extractable Levels

Al shows a general rise to 100 yards, while Fe shows a dramatic fall to 100 yards. Pb falls to 10 yards with a more gradual fall to 100 yards. Zn, Cu, Cr and Ni have U-shapes over a 0-20 yards range before falling to 100 yards. Mn has a general rise to 20 yards falling to 50 yards and rising again to 100 yards.

2.5.2.1.7 West (W);) Like SW the land is this direction is level well beyond the 100 yards point.

Total Levels

Fe shows a slight fall from 15-100 yards but generally remains the same as does Zn. Pb shows a dramatic fall to 20 yards and remains at that level to 100 yards. Al shows a V-shape from 0-20 yards followed by a steady fall to 100 yards. Cu is generally the same to 15 yards followed by a dramatic rise to 20 yards where it remains constant to 100 yards. Cr shows a gradual fall to 15 yards and after a slight rise to 20 yards remains constant to 100 yards. Ni and Mn fluctuate to 15-20 yards after which the Ni level falls to 75 yards while the Mn level remains the same.

Acetic Extractable Levels

Al shows a gradual fall to 100 yards. Cu, Zn, and Fe show an initial fall to 5 yards, and generally remain at that level to 100 yards. Ni shows a gradual fall to 20 yards, while Mn fluctuates, after which both generally remain the same to 100 yards. Pb fluctuates falling to 15 yards then gradually rising to 75 yards with a further fall to 100 yards. Cr shows a V-shape from 0-20 yards with a much broader U-shape from 20-100 yards.

2.5.2.1.8 North West (NW):- The ground in this direction is level to 50 yards with the 75 to 100 yards points slightly higher in the neighbouring field.

Total Levels

Ni shows a general rise to 100 yards with a deep trough at 75 yards. Fe is generally the same throughout but has a gradual fall to 100 yards. Mn and Zn have a general ∩-shape. That for Mn covers the whole range while Zn exhibits two humps. One of the humps is over 0-20 yards followed by a broader one over 20-100 yards with an overall drop with distance from the bing to 100 yards. Cu fluctuates to 20 yards followed by a steady steep fall to 100 yards. Pb is generally the same to 15 yards falling to 20 yards after which it remains at this level to 50 yards before rising slightly to 100 yards. Cr after a slight fall is generally the same from 5-50 yards rising to 100 yards. Al fluctuates to 20 yards rising to 75 yards and falling again to 100 yards.

Acetic Extractable Levels

The general trend is for the levels to decrease with increasing distance from the bing. Zn and Pb both fall over the range 0-100 yards except for a slight peak of Zn at 75 yards. Cu, Ni, Fe and Al all decrease from 0-15 or 20 yards after which Al remains constant while Fe has a slight rise to 100 yards. Ni has a broad ∩-shape over the range 20-100 yards and Cu fluctuates, rising to 75 yards and falling again to 100 yards. Cr has a gradual fall to 50 yards and remains constant, rising slightly towards the 100 yard point. Mn fluctuates to 20 yards before falling to 100 yards.

From the foregoing descriptions of fluctuations in metal levels it is clear that no definite conclusions can be drawn and the absence of other similar work does not help. However certain overall trends do suggest themselves in terms of direction.

i) Directions Separated from the Bing

In two directions, NE which is separated from the bing by a stream and E which is separated from the bing by a dirt track road seepage will be restricted. In these directions the acetic extractable levels tend to remain more or less the same from 0-100 yards, while total levels are more variable. This might suggest blow-off of material particles rather than a seepage of solution.

ii) Directions in Contact with the Bing

These directions include N, NW, W and SW. SE is not included since as stated previously this direction shows obvious signs of being influenced by bing seepage. In the former four directions the overall trend, with some exceptions, is for acetic extractable levels to decrease with increasing distance from the bing. In N and SW directions this is also the case for the total levels but the fall is not so dramatic also in the W and NW there are no overall trends for total levels. The findings in these directions in contact with the bing might suggest that seepage is occurring since the variations are now being found in the acetic extractable rather than in the total levels.

The fluctuations in acetic extractable levels are not due to local fluctuations of pH value as can be seen from Table 5.5 which shows the pH values as calculated from a soil : water ratio of 1/2.5. As expected the SE direction has the lowest pH values due to bing drainage but in any one direction there is little variation in pH.

TABLE 5.5 pH VALUES OF SOIL AROUND STONEYBURN BING

Distance (yards)	0	5	10	15	20	50	75	100
North	4.8	5.0	5.4	5.2	5.5	5.8	5.5	6.2
North East	5.6	5.6	6.0	5.9	5.1	5.5	5.3	5.7
East	4.4	4.2	4.2	4.2	4.2	4.1	4.4	4.4
South East	3.1	3.1	3.3	3.9	3.0	3.3	4.5	4.5
South	4.4	4.8	4.7	5.9	5.5	5.2	4.9	4.8
South West	4.8	5.1	5.0	5.2	5.2	5.0	5.1	4.9
West	5.2	6.1	6.2	6.2	6.1	5.9	6.2	5.6
North West	5.4	6.0	6.0	6.1	6.3	6.3	5.8	6.3

5.4 CONCLUSIONS

As has been said repeatedly in this Chapter the statistics are not so good as they could be. This applies particularly to the splitting of the bing material into the four classes given on the basis of metal content. However even accepting that difficulties were experiencedin implementing the classification of bing material into pre-acid, acid, post-acid and burnt material, the metal levels themselves were accurate and represent the total and acetic acid extractable metal levels in bing material in Central Scotland. From the average values however trends suggest themselves and should be studied further. There is an increase in total levels in the 2 mm fraction as the pyrite oxidation cycle proceeds. Acetic acid extractable levels are more variable. Burnt material also shows higher values of total and acetic acid extractable levels due to loss of organic matter and mineral breakdown. Pb is the exception and decreases probably due to volatilisation.

The leaching of metals from the bing also presents a problem. This can be seen in terms of increased levels of metals in stream sediment and in the water passing over that sediment carrying the metals further down the aquatic system. Trends of metal levels in surrounding soil suggests that the bing is affecting the land in terms of seepage of acetic acid soluble forms and blow-off of total forms.

5.5 ASSESSMENT OF PROJECT AND POSSIBLE FUTURE WORK

This project has been partially successful. The levels of eight metals in coal-bing waste have been recorded and the analysis of soil and stream sediments and water have provided evidence for seepage and blow-off of metals from the bing.

Future work would include the analysis of more definitive samples carefully selected from sites to include pre-acid, acid and post-acid material to determine whether or not the theories put forward concerning the placing of the metals into these classes are statistically correct or not. A study of further sites is also required to determine the full effect of bings on the neighbouring land in any attempt to confirm or refute the tentative findings arrived at for this one site.

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