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THE USE OF JACARANDA LEAVES TO DETERMINE THE DISTRIBUTION OF TRACE ELEMENTS IN PRETORIA.

by

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ABSTRACT

The spatial distribution of trace elements in Pretoria is investigated by reference to the concentrations of lead, iron, manganese, zinc and copper in Jacaranda leaf samples. Different methods of sample preparation and analysis are examined. The variation in the trace element concentrations on a leaf and within a tree; temporal variations (daily and monthly); spatial variations (along a road, in different land-use zones); and the effect of meteorological variables (rain and wind) are investigated. Differences between the results from two annual surveys, the distributions and anomalies for each of the examined elements are discussed. The relationship between results from leaf and adjacent air-filter and/or deposit gauges is examined. The linear regression equations for lead, iron, manganese and zinc are used to simulate the atmospheric concentrations of these elements. The application of leaf sampling to augment and clarify the results from the existing Pretoria atmospheric monitoring network is discussed.

It is concluded that the technique can be successfully applied to determine the distributions of trace elements in Pretoria. There is little variation in the concentrations of zinc and copper. The high leaf lead concentrations are found in the City centre and at points of traffic convergence. Anomalies of manganese occur in the southern suburbs, probably derived from the soil, and for iron to the west of the City centre, the possible source of which is industrial activity. The influence of Iscor, the iron and steel works, to the west of Pretoria is clearly shown by the distribution of iron in Pretoria. The comparison with the results from the deposit gauges is poor. The correlation between the air-filter and leaf results is particularly good for lead and iron. The simulated distributions of lead and zinc are very similar, suggesting that traffic is the source of both.

Of the existing atmospheric monitoring stations in Pretoria the site at Munitoria is located in a position well within the overall central area exhibiting the highest lead, iron and zinc concentrations. It is concluded that additional atmospheric monitoring sites are required to determine the sources of the anomalies for iron and manganese, the existence of which were unknown prior to this study.

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AN ODE TO JACARANDA

by Alick M. Hobbs.

Arise ye hosts of Flora; hail the Queen,
And haste ye all to pay the homage due,
For she hath shed her cloak of modest green
And now appears in robe of Royal Blue.

Let honeysuckle's perfume scent the air,
And dainty rose and bougainvillea vie,
With golden-shower and orangeblossom fair,
Her sun-embraced domain to beautify.

Thy Queen; with soft caress her locks to strew
Come summer show'r and gentle breeze to greet
In glorious abundance at her feet,
To shed their beauteous radiance anew.

With wondrous halo now the Queen is crowned;
Before its beauty e'en the sky grows pale.
Come all ye flowers; bow thy heads to ground:
Queen Jacaranda reigns: All Hail! All Hail!

(Bruins-Lich,1967)

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

In the design of a modern pollution monitoring network there is a need to assess the potential concentrations and distributions of pollutants that are likely to occur in a study area prior to the installation of complex monitoring stations. One way of acheiving this is by means of a biological monitor.

Although trace element concentrations in Pretoria have been measured since 1974 (Vleggaar et al, 1980) and information does exist on the possible sources and particle size (Annegarn and Sellschop, 1983), there is to date no detail on the spatial distribution of trace elements in the Pretoria urban area. The results obtained from this study will both compliment and enhance the existing data describing the environment of Pretoria. The focus of attention will be on patterns of trace element distribution.

There were a number of distinct advantages which lead to the use of the Jacaranda tree as a biological monitor for this study. The first is that the trees are widely distributed in Pretoria and only in the outermost and newest suburbs are there no mature Jacaranda trees on the kerbsides. Secondly, the trees are easy to identify, and provide easy access for sampling. Thirdly, the use of a biological monitor enabled the maximum number of samples to be collected economically in the shortest period of time and over the largest area.

Although throughout this study lead, iron, manganese, zinc and copper distributions have been studied by using their relative presence in samples of Jacaranda leaves, this is not to say that this tree is either an indicator or that it preferentially selects or retains these elements. There may exist other more suitable vegetation types with which to study the individual elements. However, it is unlikely that these other species will have either the same or better distributions and be as accessable in the urban areas of the Transvaal as is the Jacaranda.

1.1.1 Aims

The aim of this study is to describe the spatial distribution of lead ,iron, manganese, zinc and copper, as illustrated by their associated concentrations in Jacaranda leaves, throughout the City of Pretoria. To further this aim there are a number of secondary objectives which are addressed to help the interpretation of these data from the surveys. These are :-

a) To examine various collection, preparation and analytical techniques for use in this study.

b) To examine the seasonal variation of trace elements in leaf samples.

c) To examine the relationship between the concentrations of trace elements in the air and the associated levels in the Jacaranda leaf samples.

d) To determine the daily fluctuations in concentrations and the possible influences of rain on these.

1.1.2 Approach

Background information was obtained by conducting an extensive literature survey with the aid of; the South African Retrospective Information System (SARIS), the South African Selective Dissemination of Information (SASDI) and the Department of Agriculture's data base. These provided valuable information for the experimental design and the interpretation of the results.

In the initial stages, a number of small experiments were conducted to establish the factors which would influence the design of the larger surveys. These included the variations in concentrations : on a leaf; within a tree; and along a highway. Temporal variations over daily, monthly and seasonal time scales were investigated. These experiments and surveys were designed to enable the data collected to be used in the interpretation of the results from the larger annual urban surveys.

The same (313) trees were sampled in June 1983 and in April 1984. The results from the analysis of the samples were computerized and with the aid of a standard plotting package, isolines of trace element concentrations in Pretoria were generated. The maps thus produced were examined for visual indications of any influencing factors, in particular meteorological, soil and potential pollution sources within the study area. Experts in these fields were also consulted to assist in the interpretation of the spatial patterns of trace element concentrations.

Air filter and/or deposit gauge samples were obtained simultaneously with leaf samples at four urban sampling sites. The correlation between the results for the air filters and the leaf samples for lead, iron, manganese and zinc allowed the redrawing of the distribution maps to simulate the spatial distribution of atmospheric concentrations in Pretoria for these four elements.

1.1.3 The geography of Pretoria

Pretoria, the administrative capital of the Republic, is located at 25°45' south and 28°14' east at a height of 1370 meters (350 meters lower than near-by Johannesburg). It's siting amongst the eastern spurs of the Magaliesburg Range, which runs east to west, is instrumental to the occurrence of high winter pollution episodes due to the extremely stable atmospheric conditions that develop.

The City centre and oldest parts of the City lie in the southern most valley (figure 1). The majority of this central area's roads are based upon a 24 meter wide, one-way system.

The main residential areas lie in the northern valley and to the east of the centre. Much of this housing is low-density in character, with each house being surrounded by a garden. The high density residential

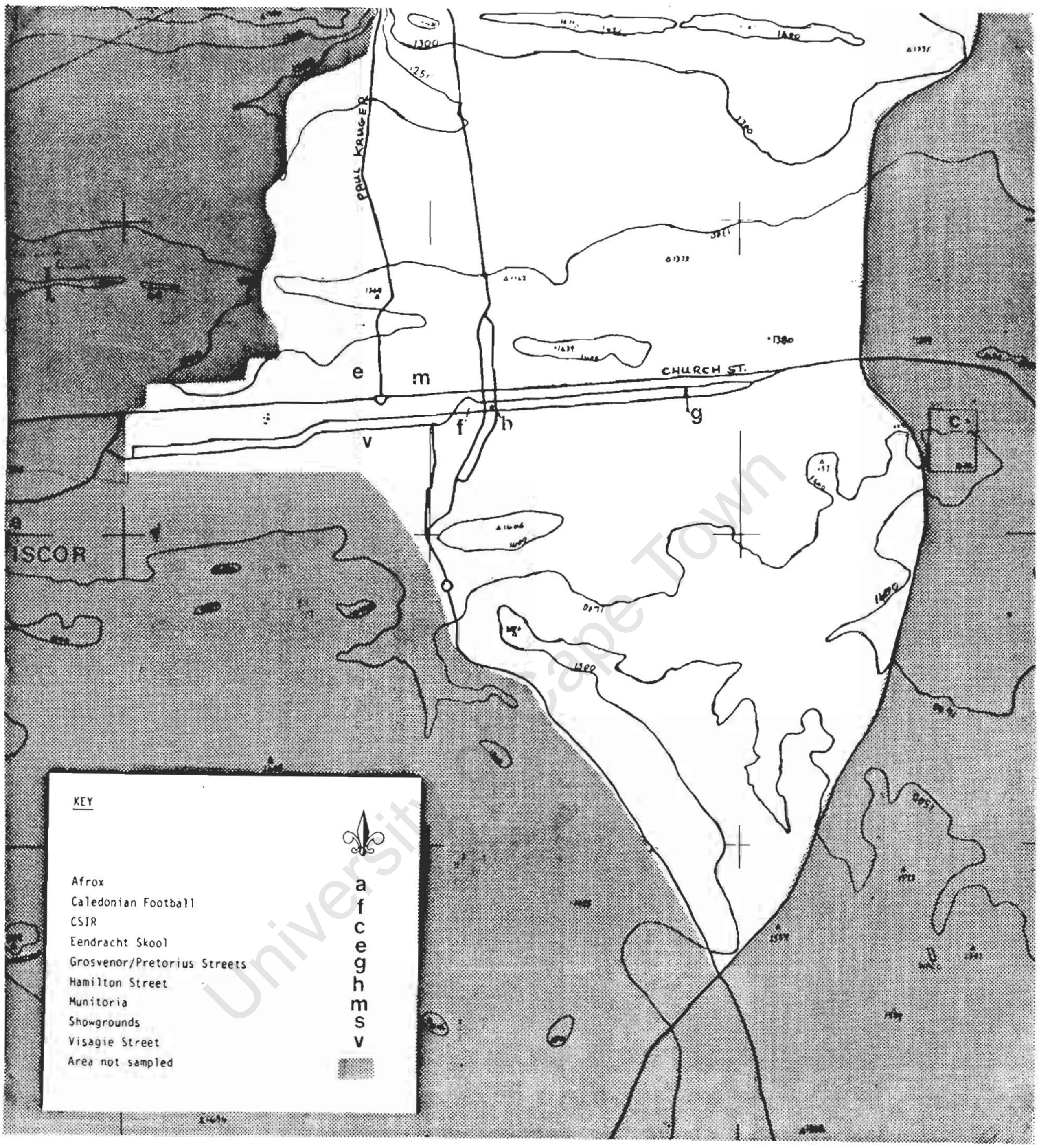


Figure 1. Map of Pretoria.

housing flats occupy the areas immediately to the south and east of the City centre. The black residential areas lie to the east and west of the City, within the northern valley. The total population of the municipal area is approximately 740 000.

The City centre largely consists of commercial and administrative activities, and as such traditional industrial polluters are absent from the area. The centre has the highest traffic density and pollutants from this source can be expected to be higher in the centre than in adjoining areas.

To the west of the centre lies the industrial area, mainly light to medium in character, dominated by warehousing, distribution and service industries, particularly for the motor trade. The heavy industries are located to the southwest of the City. This area is dominated by the large Iscor iron and steel works. This heavy industrial area is located outside and to the west of the study area.

The climate of Pretoria is temperate, with mean winter and summer temperatures of 11.4°C and 22.8°C respectively. Owing to the dryness of the winter and the high altitude, the range of winter temperatures is large (0-21°C). The rainfall is virtually restricted to the summer months, from October to March, and the winter is dry with cloudless skies. The annual mean rainfall is 700mm.

CHAPTER 2

BACKGROUND

2.1 BIOLOGICAL MONITORING, CONCEPT AND EXAMPLES

The requirements of modern technology have lead to the concentration of previously dispersed and rare elements. These elements have usually been removed from their original chemical matrix and altered chemically, and possibly physically. Since the consequences of metal contamination of the environment will almost certainly exist for a considerable period of time, there is a need for any potential problem to be assessed quickly, efficiently and inexpensively. Coupled with this is a growing awareness of the environmental significance of many trace elements and the impact that deficiencies and excesses can have on agriculture, as well as the potential hazards from metal contamination of the food chain. This has stimulated the production of regional and national maps showing the distribution of many trace elements (Webb et al, 1978). These geochemical maps have drawn attention to particular areas where land has been contaminated by past and present industrial activity, as in south-west England.

In many situations there is little justification for using a biological monitor rather than a direct physical or chemical method as the former can achieve the same results as quickly and as cheaply. One major drawback to the use of a biological monitor is that the results obtained are only semi-quantitative in character, due to the complex interactions that occur between plants and animals and their environment. However, Rains (1975) illustrated that the technique can be sufficiently sensitive to register changes in the environment arising from the closure of a smelter, thereby displaying the usefulness of biological monitoring in pollution studies.

Plants have been used as biological monitors in three ways; firstly, as in geobotanical prospecting, a plant species or specialized flora can be indicative of a certain element, having adapted to live in soils containing very high concentrations of that element (e.g. the occurrence of Becium homblei in the Zambian Copper Belt (Drew and Reilly, 1972)). Secondly, the ratio between certain trace elements in a plant becomes a fingerprint. For example, when more lead than copper is found in vegetation, then the presence of either lead mineralization or contamination can be suspected (Warren, 1978). Thirdly, the plant surface may be used as a passive collector, in which case it is important that the species fulfills a number of criteria:

a) It must accumulate trace elements in measurable amounts.
b) It must be widely distributed and accessable.
c) It must clearly show differential concentrations which can be related to exposure.
d) The cost of collection and sampling must be acceptable.
e) The specimen must allow more samples to be collected, if necessary, for repeat analyses.

Many studies have been carried out using plant material to monitor the degree of airborne contamination over large areas, either from existing or past sources of contamination. Little and Martin (1972), Cameron and Nickless (1977), and Gill et al (1975) have examined the South-West of England; Burton and John (1977) and Goodman and Roberts (1971) surveyed the adjoining area of South Wales; Lee and Tallis (1973) conducted a wider survey covering Britain. Hana and Al-bassam (1983) utilized the palm trees of Baghdad to study the distribution of lead, whilst Tanaka and Ichikuni (1982) used the bark of japanese cedar to study heavy metal distribution in the City of Tokyo.

These surveys, among others, either make use of sampling points based upon a large grid, or along transect lines on the prevailing wind direction. In the larger surveys the density of sampling ranged from one sample per 2.64 km^2 (Little and Martin, 1972) to one sample per 13.6 km^2 (Gill et al, 1975). In this study of the Pretoria urban area, the samples were collected on a square grid of 500 meters sides, a density of approximately one sample per 0.25 km^2.

2.1.1 The Jacaranda tree

The species of Jacaranda tree normally found in South Africa is <u>Jacaranda mimosaefolia</u>, a member of the Bignonia family, <u>Bignoniaceae</u>. There has been some confusion, in the past, in regard to the scientific name. In 1822 when Don first described the plant, another botanist, Robert Brown, also described the same plant, but gave it the name <u>J.ovalifolia</u>. The former name is now recognized as the correct one.

Although the tree, a native of Brazil, can grow to a height of 15 meters, most trees in South Africa do not achieve such a height. This is particularly true in urban areas where it is necessary to prune the branches regularly to prevent damage occurring to overhead power and telephone cables. This has had a marked effect on the tree's natural shape.

A deciduous tree, the leaves are lost mainly in July and August. The leaves are large (30-40cm) fern-like, twice-pinnate compound leaves which are divided into 20 or more pairs of pinnae, opposite to each other along each side of a midrib. Each pinnae is further divided into a number of pairs of tiny oval pinnules, figure 2.

The tree is renowned for its flower which appears in late October or November normally prior to, or with, the emergence of the new leaves. The flower itself is about 5cm long and 4cm across and appears in colourful clusters varying between dark to light blue with shades of purple.

There are several cultivars and naturally produced varieties, which may be found in Pretoria. One, introduced in 1961, is a white flowering form originally developed in the Los Angeles State and County Arboretum. There are also pink flowering forms and varieties in which the flower emerges after the leaves.

In India, the bark and leaves are used in folk medicine, either in the form of an infusion of the leaves as a pectoral, or as powdered leaves in a vulnerary. An infusion of the bark can be used as a lotion for ulcers (Prakash and Garg, 1980).

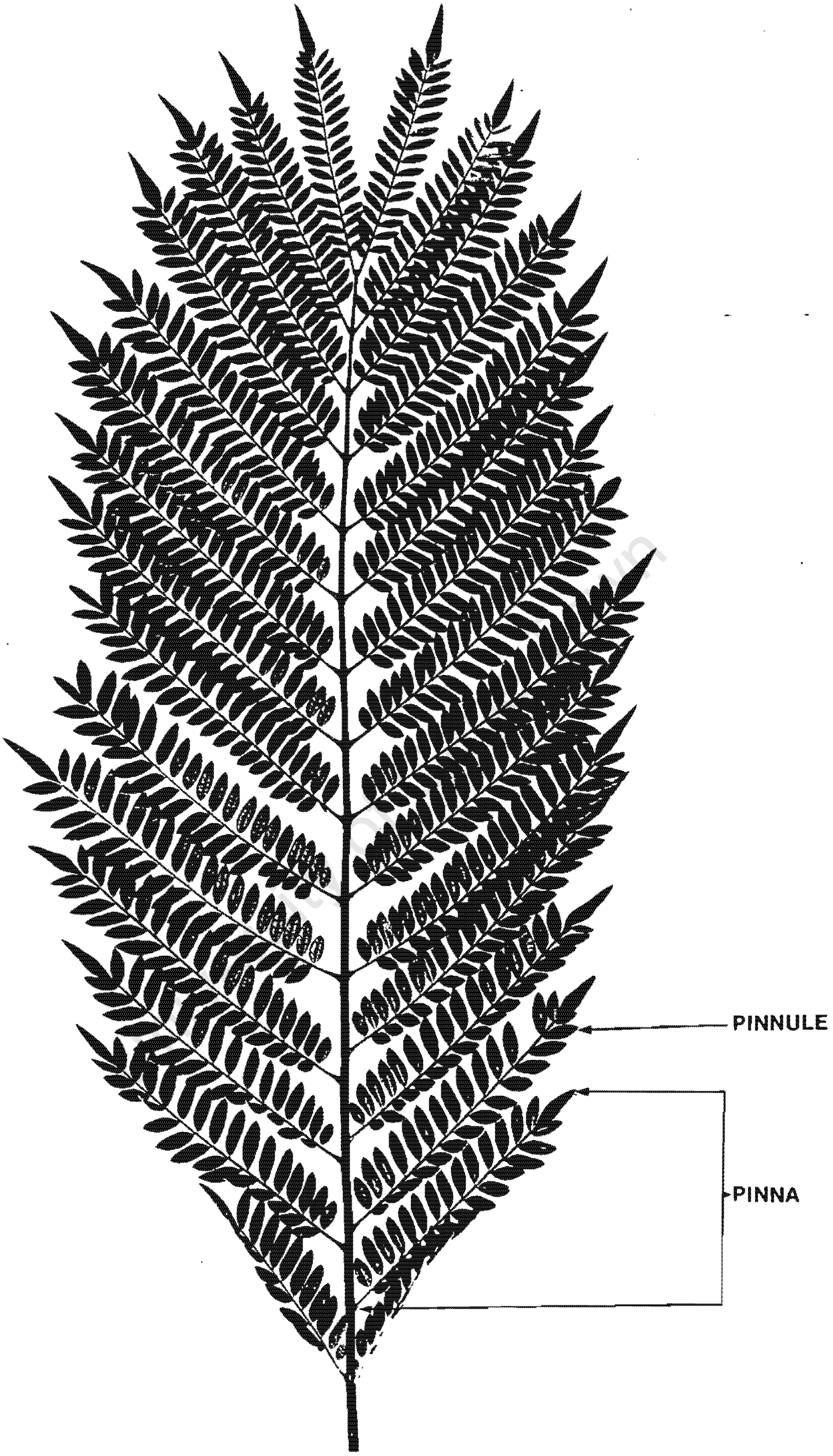


Figure 2. A Jacaranda leaf.

A history of the Jacaranda trees of Pretoria has been fully described by Bruins-Lich (1967) and Anon. (1940, 1947 and 1962). The first pair of trees were planted by a Mr Celliers in Myrtle Lodge, Celliers Street, Sunnyside in 1888 (at the cost of R20.00 each), one of these still survives today. The City Council commenced a planting scheme on the 16 November 1906, when in Bosman Street (which was then Kock Street) and in Arcadia park, two hundred trees, which had been presented to the council free of charge by a local nursery, were planted.

There are now throughout the City of Pretoria approximately 60 000 Jacaranda trees which have been planted along the roads at about 20 meter intervals. The City Council plants an additional 300 new trees a year and 20 as replacements for dead or damaged trees. The profusion of Jacaranda trees in Pretoria has earned the City the name 'The Jacaranda City'.

2.2 TRACE ELEMENTS AND PLANTS

2.2.1 Aerial distribution and foliar uptake

The surfaces of vegetation act as major sinks for airborne particles. The concentrations of these particles will depend upon the distance from the source, the aerosol composition, and wind speed and direction. Nakos (1979) suspected that a combination of these factors was the reason why he found the highest contamination levels in vegetation at a distance of 500 meters from a smelter.

The concentration of elements on or in a leaf will be the result of the net accumulation from the input from both the soil and the atmosphere, and the loss to both of these systems and to the plant's own biological requirements. Enhanced concentrations of any trace element will arise by virtue of retention exceeding loss.

Airborne contamination will be either in a dissolved form (e.g. rain) or as particulate material. The latter can be further divided into the portion of the element that is extractable (either by water or dilute acid) and that which will remain in particle form until its physical removal from the plant, i.e. at leaf fall.

The deposition of airborne particles is dependent on the physical characteristics of both the particle and the plant surface, particularly it's size, shape and surface texture (Chamberlain, 1970., Elias and Croxdale, 1980., Little and Wiffen, 1977, 1978). Thus the cuticle microtopography can be a significant factor in the determination of the collection efficiency of the leaf surface.

Once the particle is on the leaf surface it's retention will be governed by the reactions of the various ions present whilst in solution, which in turn will be dependant upon :

a) the chemical form of the metal
b) the nature of competing ligands
c) the pH of the leaf surface
d) the nature of binding sites
e) the nature of competing metal ions

Thus, as the adsorption of a particle will be dependent upon its chemical form and as many leaf sites are negatively charged, anionic complexes will be poorly adsorbed. In addition, the rate at which this occurs, will be determined by the nature and age of the particle, the conditions of the micro-environment and the chemistry to be found in the intermitent water film on the leaf surface.

The inability of compounds contained in chemical sprays to enter the foliage of plants has been attributed in part to the physical nature of the leaf, e.g. surface fungi and the leaf cuticle. Surfactants added to spray solutions have increased both the rate and amount of absorption because they reduce the surface tension and also increase the wetting of the leaf surface and decrease the adverse effects of air-pockets created by leaf hairs and wax (Neumann and Prinz, 1974).

There have been a number of studies conducted on the methods of leaf uptake and retention of trace elements (e.g. Cantliffe and Wilcox, 1972; Chamel et al, 1982). These have highlighted a large degree of variability between species and the need for further studies. There are many hundreds of references documenting the relationship between foliar fertilizer applications and crop yield, but few which describe the mechanisms involved. In these it has been shown that copper and zinc remain in situ for more than a week and up to several months after foliar application of fertilizer or fungicide. As both elements can migrate to different parts of the plant, the variations between studies may be attributed to the different species of plant tested and the effectivness of the spraying applications. Both elements remain very heterogeneous, but both decrease rapidly with leaf depth (zinc being detectable only in the surface 0-30µm, as compared with the 30-160µm region). Both elements are fixed and retained in the cuticle, fixation being particularly rapid at low concentrations. The removal of the cuticular wax results in higher retention, possibly by promoting access to internal sites (Chamel and Gambonnet, 1979, 1982; Muthappa et al, 1977; Chamel et al, 1982; Mabbett and Phelps, 1983). Of all of the elements discussed in this study, lead is one of the most important as it is wide-spread and is being extensively studied world-wide.

Roberts (1976) used an electron microscope to show that electron dense particles are associated with epidermal cells although some are in sub-stomatal cavities. He also established that lead in solution could not penetrate the stomata because of the high surface tension over the small pores. Previously, (1975), he had shown that some of the deposited particles had become embedded in the cuticular structure; Cataldo et al (1981) suggest that the fine particles adhere to the surface. Arvik and Zimdahl (1974) showed that the cuticular structure acts as a barrier to the foliar uptake of lead and although the penetration of lead seems to be dependent on the plant species, the actual amount was not significant. However, Dorn et al (1975) concluded that in areas of high environmental contamination much of the lead in the foliage and roots entered the plant via foliar absorption. Little (1974) established significant differences between species (hawthorn, willow, elm and oak) for absorbtion and retention of both the soluble and insoluble fractions of zinc, lead and cadmium. Kannan (1969) demonstrated that iron is absorbed through the cuticular membrane in tomatoes and Euonymus japonicus, although the rates differed.

It has been shown by Mann and Takkar (1983) and Chamel and Gambonnet (1979) that zinc absorption is reduced by increasing copper, manganese or iron concentrations in spray solutions. However, Dixit et al (1979) showed no effect on zinc concentrations by the application of iron. As fixation increases rapidly at low concentrations and then tends to a saturation level, the manganese is immobile a low concentration of 750ppm, but at high levels (4 600ppm) may be translocated out of the leaf (Kluthcouski and Nelson, 1979).

2.2.1.1 Effects on plants

Very few particles are required for foliar concentrations to be high. Little (1974) in his work on elm leaves showed that the density of 1 micron diameter particles required to obtain a concentration of 250 $\mu g/g^{-1}$ was only 1.415/cm^2 for zinc oxide and 0.046/cm^2 for lead oxide.

Many authors have reported very high leaf contamination burdens without any evidence of toxicity symptoms, for example Little and Martin (1972) found levels of 8 000 $\mu g/Zng^{-1}$ and 5 000 $\mu g/Pbg^{-1}$ dry weight on unwashed elm leaves, and Ragaini et al (1977) found 11 900 $\mu g/Zng^{-1}$ and 9 990 $\mu g/Pbg^{-1}$.

The absence of toxic effects when there is a high accumulation of trace elements in or on the plant is due to the inert nature of the majority of the burden, and also to the fact that most of the potentially toxic metal ions will be bound to the membrane and cell walls and are consequently unavailable to the rest of the plant. Individual metal toxicity and tolerances in plants, including their pathways and chemical reactions has been reviewed by Woolhouse (1983).

Foliar retention from atmospheric deposition is one pathway by which trace elements may reach the leaf, and the other is via uptake and translocation of the required elements from the soil by the roots. Both pathways are important, as illustrated by both soil and foliar applications of trace elements being benefical in countering deficient soils.

2.2.2 Root uptake and translocation

Leaf analysis for the purpose of advising on the requirements for soil fertilization has been use in South Africa on a commercial basis since 1967. The technique has been further enhanced by the inclusion of soil analysis (in 1976), particularly for citrus and sub-tropical fruits. Leaf analysis will give a good indication of the trace-element status in citrus plants, for zinc, manganese and iron, but not for copper. In the latter case, there have been demonstratable problems in orchards where the soil has become contaminated by the past use of copper based fungicidal sprays (du Plessis, 1977).

As trace elements in the soil are normally only enriched in the top 10-15 centimeters of the profile, shallow rooted grasses and vegetation will consequently be more greatly exposed to surface soil contamination than trees, whose major part of the root system will be in the less contaminated sub-soil horizons. However, in urban areas, buildings, roads and underground structures may restrict a naturally deeper rooting system to more shallow soil, thus allowing root access to contaminated soil.

The soil - trace element - root system is much more complex than that of the leaf surface - atmosphere interface because of the influence of greater biological activity. The root modifies its immediately surrounding soil environment by the secretion of hydrogen ions, chelating agents, reducing compounds and also substances that encourage high concentrations of micro-organisms, which in turn secrete further agents. These biological reactions vary in relation to the depth of root penetration and distribution and the growth activity of the plant.

Martin and Coughtrey (1982, citing Chaney, 1973) listed fifteen factors which are involved in metal uptake by a root system. These are:-

a) The amount of metal in soil.
b) The metal(s) present.
c) The pH of the soil.
d) The organic matter content of the soil.
e) The phosphate content of soil.
f) The cation exchange capacity of soil.
g) Reversion to unavailable forms.
h) The plant species concerned.
i) Characteristics of the metal(s).
j) Presence or absence of competing ions.
k) Phosphate availability.

l) Rooting depth of plant and distribution of metals.

m) Plant age and seasonal effects.

n) Plant part.

o) Soil moisture, aeration and temperature.

Only in certain soil conditions will substantial amounts of trace elements be transported from the roots to the plant's aerial parts. These are low pH, absence of $CaCO_3$, low concentrations of organic matter, phosphorous or sulphur.

Many studies on the uptake and subsequent translocation of trace elements have been conducted with particular emphasis on economic crops. Field experiments have tended to use artifically high applications of the element under consideration and the subsequent effects may thus have little relevance to natural conditions. In addition, the impact of trace elements on plants is normally not the result of the effects of a single, but a combination of a number of elements. Observed pathological symptoms are not often caused by an absolute deficiency of a mineral in the soil but rather by it's biological availablity to the plant. Experiments on the dose/effect relationship are often difficult to design, undertake and interpret, because when examining the interactions between trace elements and plants, it is not appropriate to be restricted to the direct problems of deficiency or excess. The sources, availability, uptake and translocation mechanisms must all be examined.

Actual entry into the plant via the root interface involves the relevant ions passing through an aqueous phase, thus mobility of an ion is dependant upon the characteristics of that ion in it's aqueous phase. Once these characteristics have been established it is possible to account for the availability, capture and the mechanism of uptake for a particular ion by a plant.

Uptake can either be passive or active in nature, for example most evidence of copper uptake indicates that the process is passive, that is it is unaffected by metabolic inhibitors or temperature effects. On the other hand the entry of zinc into the root is by an active mechanism which may be inhibited by both copper and phosphorus.

The actual root uptake of copper is largely influenced by the charge of the applied copper ion, whilst once in the root the chemical form becomes important in the subsequent binding of the ion in the root.

Although root absorption of trace elements from the soil is an important source of element concentration in the whole plant, the translocation to the shoots/foliage is limited for non-nutrients, especially in the higher plants. For example, Malone et al (1974) examined micrographs from studies using an electron microscope which showed that lead is deposited in the cell wall. Schuck and Locke (1970) found no evidence for increasing root absorbance of trace elements in certain crops even though the plants were grown by the side of a major highway. Crump et al (1980) found that the effect of a motorway on the surrounding soil was restricted to a strip twenty meters wide, whilst the vegetation displayed elevated concentrations up to 100 meters from the road, concluding that the contamination was airborne. Rains (1975) also confirmed that in roadside situations the input to plants from the atmosphere via the leaf may be more important than that from the soil.

No biological reaction is known that requires lead to enable it to function. Therefore it is probable that the process of lead uptake is non-metabolic in character. The importance of lead as a universal pollutant and health risk has resulted in a number of studies being carried out to determine the extent of lead mobility within plants (e.g. Rains, 1975; Hampp and Holl, 1974; Mankovska, 1980).

Plants growing near highways may be considered to be usually exposed to more lead than most other locations. The primary source of this lead is automobile exhaust aerosol, generally halides and thus insoluble in water. The non-dissolubility of many lead salts results in very limited mobility in plants. Studies carried out on lead mobility have been conducted using the radioisotopes of lead. Athalaye and Mistry (1972) studied the red kidney bean and Tso and Fisenne (1968) looked at tobacco. Both studies confirmed that the transportation and re-distribution to other parts of the plant from the roots is very limited. It is possible that the root acts as a reservoir for lead. In this manner the effects of contamination may be observed after the source has been removed. Once lead is in the root it moves via the apoplast into the xylem (Tanton and Crowdy, 1971), from where it is transported to the shoots. Work undertaken by Chisholm (1972) and Maclean and Languille (1973) has shown some evidence that some crop plants accumulate lead in their tops rather than their leaves.

Unlike these studies on lead uptake, similar tracer studies on copper have been unsuccessful because of the short half-life of all the natural radioactive copper isotopes (less than twelve hours).

It has also been noticed that there is an internal translocation of elements from the leaves to the stem prior to leaf fall. Guha and Mitchell (1966) demonstrated that back-translocation occurred in sycamore trees for lead and iron and to a lesser extent for manganese. This mechanism may be particlarly active in areas in which nutrients are deficient, although this reason for the mechanism would obviously not explain the situation in regard to lead. This type of translocation is possibly the mechanism by which crop plants benefit from the foliar application of nutrients, however there is very little known about this at the present time.

2.2.2.1 Trace element occurrence in soils

Weathering of the underlying bedrock and the subsequent release and transfer to the soil of trace elements constitute the major source of such elements in an undisturbed ecosystem. The vegetation cover of a geographical area will therefore reflect, to some extent, the trace element concentrations in the underlying soils which are available to the plant. This is the basic principle upon which geobotantical prospecting relies. The extent to which this is evident will be influenced by the rate of foliar adsorption and by surface deposition from the atmosphere.

Whilst studying the relative distribution of trace elements over an area, large or small, the influence of soil type and possible change of biological availability of trace elements should be examined. In the final analysis of the distribution maps of the elements under consideration in this study a comparison was made between the known soil distribution of trace elements and possible ore outcrops. Ideally, to distinguish between the influence of soil type and atmospheric deposition, soil samples should have been taken at each site at which a leaf sample was collected. However, this may not in itself clarify the results because of the difficulties in obtaining, analysing and interpreting the results from soil samples.

Soil analysis was not undertaken as part of this study. However, due consideration has been given to the possible influences of changing soil type and conditions as well as the possiblity of the occurrence of ore bodies, in the interpretation of the results from the leaf analysis. The advice and help of soil scientists at the Department of Agriculture has been sought and used throughout the study.

In the literature there is a great deal of discussion concerning the fraction of the total trace element concentration in the soil that is available, how much of this is taken up by plants, and how best to extract this portion (Lepp, 1981; Nriagu, 1978, 1980). There is no universal soil extractant, the method varies with the element under consideration and the type of soil. In practice, estimates of the amount of available trace elements in the soil are determined by using differing extraction techniques and correlating the results from these with a direct measure of the amount that a plant is shown to take up, rather than measuring it by comparison with plant growth, which is dependant upon many other factors.

It has been suggested that total metal concentration rather than an extractable proportion can be used (Martin and Coughtrey, 1982). Although the sensitivity of the technique would be reduced, it would be compensated by the reduction in the varability in the results obtained from using different chemical extractant techniques.

There is no simple relationship between the elemental content of the soil and the corresponding concentrations in the overlying vegetation, as each plant species will have its own elemental accumulation characteristics. Two different sites which both display similar trace element composition in their soils will not necessarily exhibit the same levels in their corresponding vegetation. A comparison between different studies must be viewed with caution because of the varying sources, species, climate, soil and fertilizer application factors. It also follows that it is not advisable to use different species within the same study without first carrying out an interspecies calibration.

2.2.2.2 Trace element mobility in the soil

Trace elements will accumulate in the surface horizons of a soil (Martin et al, 1982; Rains, 1975). This can be through an enrichment process by which the plant transfers the element from lower horizons, and deposits it on the surface as a residue, or through different forms of aerial deposition. The latter is more evident in areas with a known history of contamination, i.e. surrounding a smelting complex (Martin et el, 1982). The enriched surface layer is normally restricted to the first 15 centimeters. However, this thickness can depend on the type of vegetation cover, particularly the presence and properties of a litter layer, as in a woodland, which can reduce the thickness of the enriched layer considerably.

The majority of available copper in the soil is organically based. In general, shallow peats, sandy loams or leached acidic soils will tend to be copper deficient. Plants grown on soils with heavy nitrogenous fertilizer content may also display copper deficiency. Soil copper excess is normally confined to soils derived from copper-bearing ore bodies, and as such are fairly easily recognized.

The availability of manganese follows the solubility of the various manganese oxides which in turn are very dependant upon the prevailing oxidising conditions and pH of the soil. Both iron and manganese will fix other trace elements (cobalt, copper, zinc, nickel and lead) in the soil. This is a rapid process and the fixed elements subsequently become unavailable to plants.

2.3 CHAPTER SUMMARY

Plants can be used as a biological monitor in three ways. Firstly, because a species has adapted to live in, and possible only in, soils with high concentrations of a particular element, it's presence is indicative of that element. Secondly, a change in the ratio of the elements present in the particular plant material may indicate the presence of mineralization or contamination. Thirdly, the various plant surfaces can be used as surrogate sampling surfaces.

Many regional studies of trace element distributions have been conducted using the analysis of different plants as a measure of airborne contamination (e.g. Little and Martin, 1972). Many of these surveys are based on a large grid or a few transect lines through the study area.

Throughout Pretoria there are in excess of 60 000 Jacaranda trees. These trees are planted along the kerbside in all but the newest suburbs of the City. The distribution, identification and easy sampling, among other criteria, makes this tree suitable for use as a biological monitor.

The leaf concentration of trace elements is the result of the combination of the uptake and subsequent translocation of available soil elements, and the interception and retention of airborne particulates. Leaf surface deposits will be lost due to the actions of the wind and rain. It is only if retention exceeds loss that the plant will be able to accumulate leaf deposits.

The particles on the leaf surface can be an important source of nutrients, particularly in areas of soil deficiency. The surface particles are bonded both chemically and physically to the leaf surface. Surface sprays of nutrients are extensively used in agriculture and many studies have been conducted on the methods of uptake and retention (e.g. Cantliffe and Wilcox, 1972).

Although surface deposits may be a source of nutrients for the plant, very high leaf concentrations can occur without any corresponding evidence of toxicity. This is because most of the potentially toxic metal ions will be bound to the membrane and cell walls, thus becoming biologically unavailable.

The importance of, and mechanisms of, the uptake of elements from the soil and their subsequent translocation have been examined because of the influence that this may have on the interpretation of the leaf data.

There are many factors involved in the control of metal uptake by the root system, Chaney (1973) listed fifteen. The uptake can either be passive or active in character. Passive processes are unaffected by metabolic and temperature effects. The importance of lead as an universal pollutant has resulted in a large number of studies being conducted on the mechanisms of lead uptake and translocation, particularly in crop plants.

The influence of changes in soil type and soil availability of trace elements over a geographical area must be considered when interpreting the results from a regional survey. Throughout this study the advice of soil scientists and geologists has been sought.

No corresponding soil analysis has been undertaken along with the Jacaranda leaf sampling in this study. There is still considerable discussion upon what fraction of the total soil concentrations is available to the plant, how much of this is actually taken up and how best to extract this portion. There is no simple relationship between the element content of the soil and that in the overlaying vegetation.

Trace elements will be accumulated in the surface horizons of a soil. This may be through an enrichment process from the lower horizons or due to surface deposition. The enriched layer is normally restricted to the first fifteen centimeters. The soil's organic content is an important controlling factor because many elements will form insoluble chelates with organic matter and thus become unavailable to plants. Another is the soil's pH.

The combination of these factors may result in the intrepretation of biological data being difficult. In many situations there is no justification for using a biological monitor. In this study the use is justified because although there exists extensive information upon the Pretoria aerosol (Vleggaar et al, 1980; Annegarn and Sellschop, 1983), there is no information on the spatial distribution of trace elements in Pretoria. The use of the leaves of the Jacaranda will result in the distribution of the studied elements being established in a detailed manner. An estimate of how representative the existing monitoring network is, and possible areas in which it may be expanded, will be possible on the completion of this study.

CHAPTER 3

SAMPLE PREPARATION, ANALYTICAL TECHNIQUES

3.1 INTRODUCTION

3.1.1 Washing/not washing samples

Most chemical analysis of leaves which is undertaken is for the determination of the nutrient status of crop plants and is performed on washed samples, in order to minimize the influence of atmospheric deposition and spray residue. On the other hand, in studies which have examined the contribution to food chains of trace element pollutants from leaves, the leaf sample is untreated, since washing would remove contamination that would otherwise have entered the chain.

There are many references in which comparisons between washing and not washing samples have been made. Many of these conclude that washing can remove a significant part of the surface contamination, (Goodman and Roberts (1971); Rains (1971); Ward et al (1974); Wood and Bormann (1975); Beavington (1975) and Little and Wiffen (1977)). These studies also show that the amount of surface contamination removed by washing varies considerably depending upon the actual procedure used. This is probably due to some of the particles on the leaf surface being bonded either physically or chemically to it, and being differentially removed by different washing procedures.

In this study the aim is to illustrate the spatial distribution of certain trace elements due to atmospheric pollution. This is to be done by examining the occurrence of these elements in tree leaf samples collected in an urban area. Washing the leaves, to remove atmospheric contaminants, is therefore clearly inappropriate for the samples collected in this study.

3.2 SAMPLE PREPARATION

In the early stages of leaf collection it became apparent that it would be necessary to dry the samples quickly to avoid decomposition and rotting of leaves which may have had an effect on the concentrations of trace elements. Drying the samples ensured that subsequent analysis took place upon leaf material on a dry-weight basis, thus excluding the variable factors of leaf size and moisture content upon the results.

Since only part of the leaf was required for analysis it was unnecessary to dry all of the collected leaf sample. By applying the conclusions from the initial statistical analysis of the distribution of trace elements on a leaf (section 4.1.1), the centre six pairs of pinnae were removed for analysis, the remaining sample material being discarded. These pinnae were placed in a beaker and dryed at 60-65°C for 24 hours.

After drying the pinnae were gently stirred using teflon coated tweezers to separate the pinnules from their stems, the latter were removed and discarded. In this manner variation due to different types and mixes of plant material is minimised. The results from a pilot study on the potential influence of various washing treatments provided evidence that particles from the stem material were removed and subsequently re-entrapped onto the leaf surface by washing, thus enhancing the leaf concentrations.

The stem free pinnules were thoroughly mixed, and from the resulting five to six grams of material, one gram was weighed into a pre-weighed beaker for acid digestion. Two or three sub-samples were obtained from each sample, (except in the two annual surveys when only representative samples were analysed in duplicate). At leaf emergence and fall the total weight of leaf sample was insufficient to allow for the analysis of sub-samples.

3.2.1 Acid extraction and digestion techniques

Two methods were used to dissolve the leaf samples: cold extraction and hot digestion. The latter method was not used in the large annual urban surveys.

By using the cold extraction method it was hoped that the time involved in sample preparation would be reduced, particularly in the case of the large annual surveys. It was also envisaged that by reducing the number of preparative steps the risk of contamination or error would be reduced. The cold extraction technique may also allow the removal of the surface contamination and leaving the internal leaf structure undamaged; thus reducing the influence of internal leaf concentrations and possible changes in soil concentrations on the results. Hot digestion was used to obtain total concentrations in a leaf for comparative purposes.

The hot digestion technique used is the same as that for the National Study of Trace Elements in Airborne Particulates in South Africa (Vleggaar et al, 1980) in which deposit gauges and air-filters are used. The technique is as follows: 10 ml of concentrated nitric acid is added to the sample. The sample is then heated on a hot plate until the solution is nearly dry, at which point 5 ml of 30% hydrogen peroxide is added. This is again reduced to near dryness, and 5 ml of concentrated hydrochloric acid is added and the solution is further reduced to near dryness at which point 5 ml of $CsNO_3$ (5 000µg Cs/cm^3) is added and the mixture is heated to reduce the volume to about 5cm^3. This solution is then filtered, washed with 0.25M nitric acid, and made up to a volume of 25 ml by the addition of 0.25M nitric acid.

For the cold extraction method the weighed samples were placed into a beaker and 25 ml of 3.5M nitric acid was added. This was covered and left to stand for 24 hours, during which the beaker was occasionally agitated gently. The solution was then filtered and made up to volume (25 ml) by the addition of distilled water.

Initial results (table 1) indicated that the cold extraction method using the higher strengths of acid agreed favourably with the hot digestion. As the study progressed it became increasingly obvious that the percentage of the trace elements in the leaf samples recovered by the cold extraction did vary to a small extent with locality but to a larger extent with time. Figure 3 illustrates the mean and the standard deviation of the

Table 1. Comparison between the use of different nitric acid concentrations. Determination of lead (ppm)

location	Hamilton St.		Edison Rd.(a)	
		%		%
hot digestion	27.75	100	11.86	100
cold extraction,				
3.5M	27.00	97	8.50	72
1.75M	25.50	92	9.00	76
0.8M	27.50	99	7.75	65
0.25M	16.25	59	8.00	67

	Hot digestion	Cold extraction (3.5M)
Delfos Rd.	6.50	7.50
Edison Rd.(b)	8.00	8.50
Research St.	12.50	12.75
Paul Kruger St.	16.25	16.50
Struben St.	25.00	23.25
Proes St.	43.75	42.75
Frederika St.	15.00	14.25
Ben Swart St.	8.00	8.00
Haarhoff St.	3.75	5.25

percentage of recovery for the cold extraction verses the hot digestion for the elements under consideration at the four Pretoria sampling sites in June 1985. It can be seen that the mean recovery percentage changed very little through the range of different acid strengths, from dilute (0.25M) to concentrated (14M), although the percentage did vary from element to element.

Apart from the beginning of the seasonal study in 1983, all samples were treated by both hot and cold digestion. This allowed a comparison to be made between the seasonal results obtained by hot digestion and cold extraction for the four urban measuring sites from October 1984 to August 1985. The results are illustrated in figure 4.

There are a number of observations that can be made from figures 3 and 4:

a) It is apparent that the recovery percentage varies from one element to another, with iron having the lowest rate (15%) with other elements displaying recovery rates of between 55-65%.

b) The variation in the recovery rate, as measured by the standard deviation, over the geographical area of Pretoria is within ±10% throughout the sampling period for all of the elements under consideration, except for lead which displayed a much wider variation in the recovery rate.

c) The recovery rate varied with time at all of the sampling sites. Zinc and manganese showed increasing trends, lead and copper showed greater variability. The samples for December and January were collected and prepared by different personnel. Despite them being given specific details on the

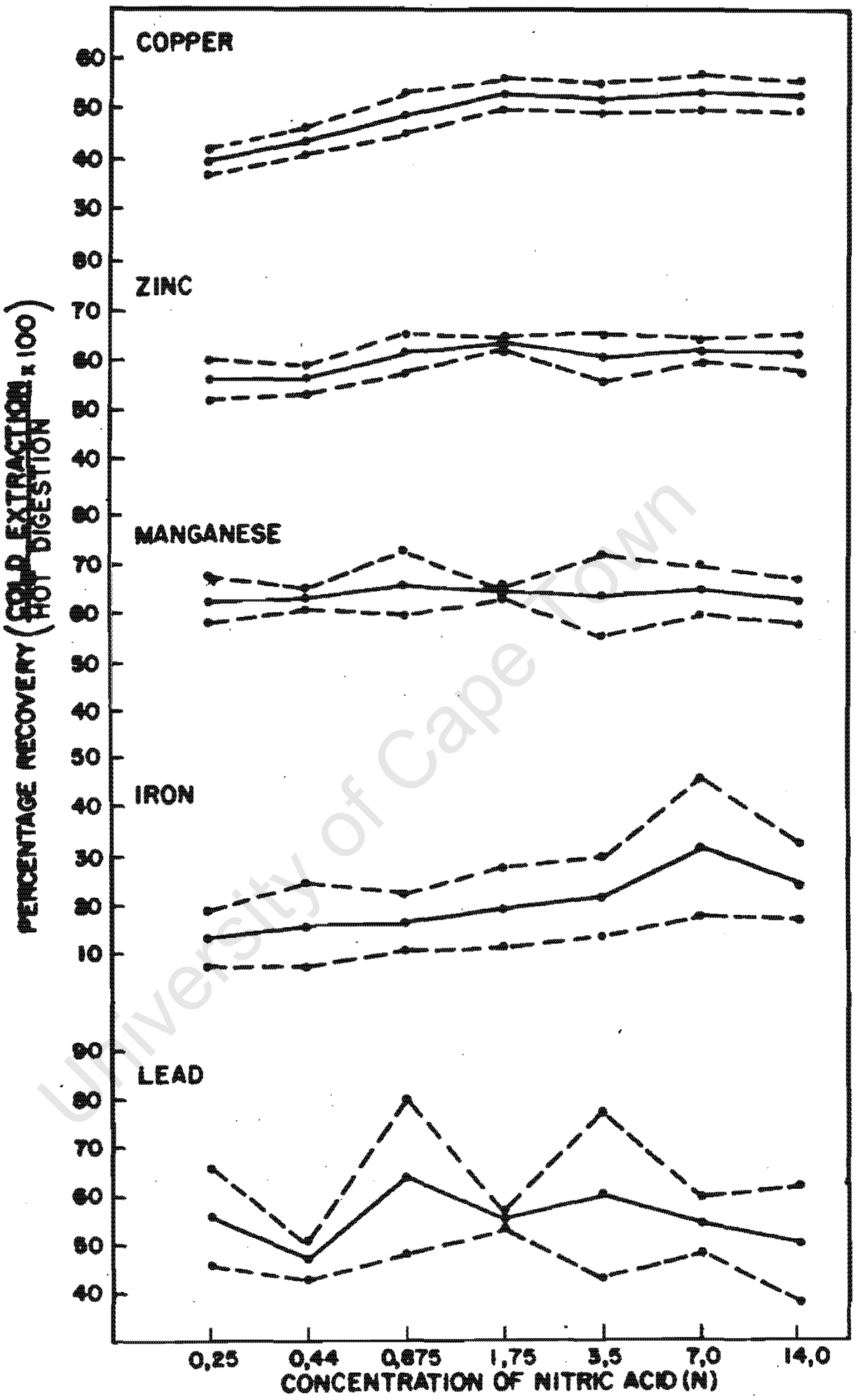


Figure 3. Variation in element recovery with differing acid strengths.

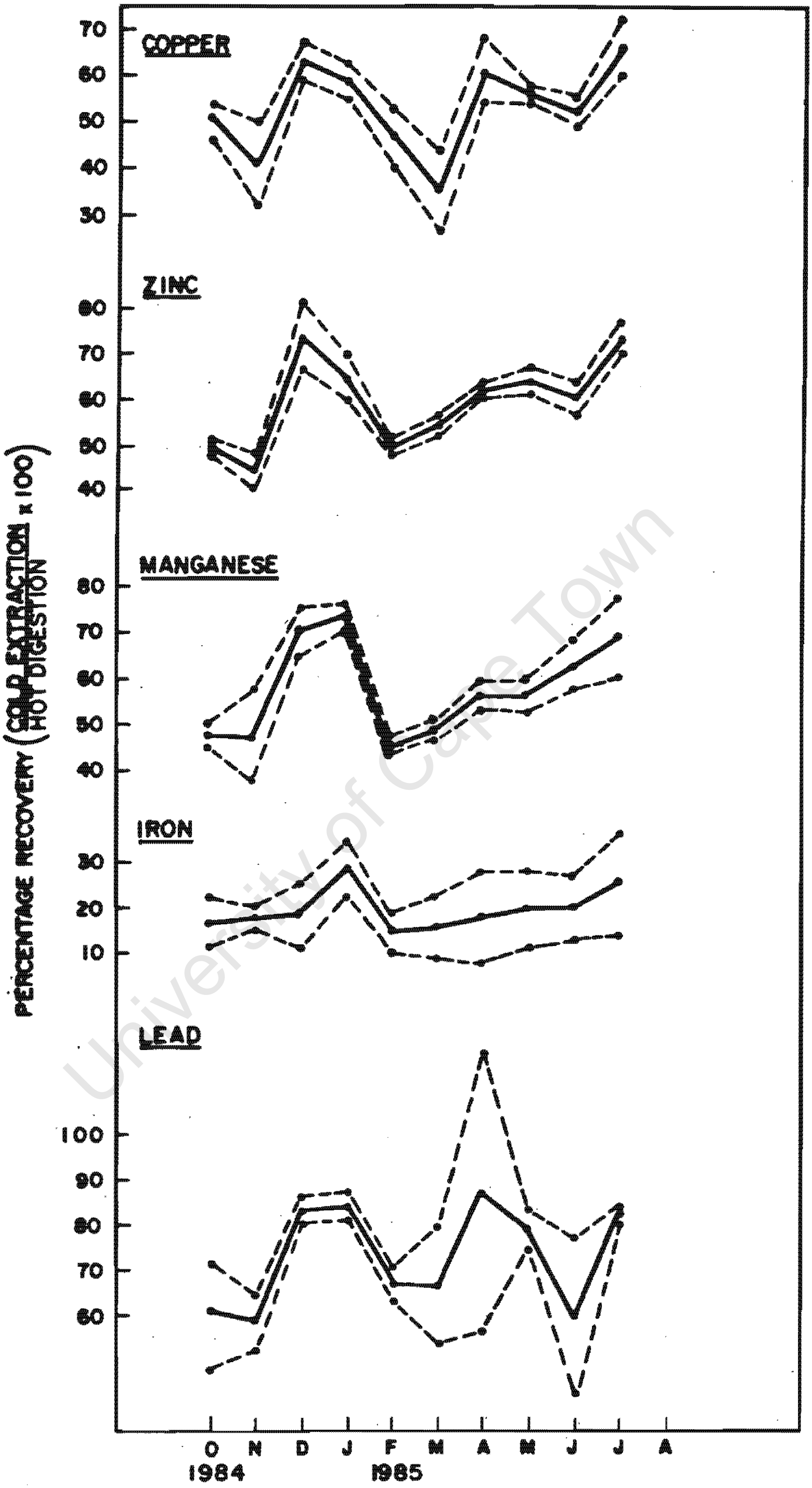


Figure 4. Seasonal variation in element recovery at urban sampling sites.

techniques to be used, it is possible that the variation in the rate of recovery for these two months might be attributed to a slight variation in individual techniques.

d) The use of varying strengths of acid for the cold extraction had little effect on the recovery rate. Except for lead, the other elements all displayed stable standard variations with changing acid strength. Iron and copper displayed a slight tendency for the recovery percentage to increase with increasing acid strength.

e) With the exception of copper, the leaf concentrations of the studied trace elements determined by the cold extraction and hot digestion methods significantly correlate at all of the sampling sites (table 16).

The cold extraction method was varied at the end of July 1985, so that in addition to the normal cold extraction a further cold technique, which included the use of hydrogen peroxide was used. Gutknecht et al (1981) concluded that the addition of hydrogen peroxide is necessary for the dissolution of the Pb^{+4} species (i.e. lead dioxide). In the modified technique 5 ml of H_2O_2 was added to the 25 ml of 3.5M nitric acid, prior to the sample being left to stand for 24 hours. In table 2 the results from the two cold extraction techniques are presented. It may be concluded that the addition of hydrogen peroxide did not increase the recovery rates, and it is possible that in the case of iron the rate was decreased.

The addition of hydrogen peroxide in the cold extraction method was not adopted for use in this study.

Table 2. The effect of the addition of H_2O_2 on the cold extraction technique (ppm).

	Cold extraction			Hot digestion
	without	with	difference	
LEAD				
Hamilton	56.0	55.0	-1.0	68.2
Munitoria	75.5	73.5	-2.0	90.5
Visagie	67.5	67.5	0.0	81.0
IRON				
Hamilton	70.0	61.3	-8.7	459.0
Munitoria	250.0	135.0	-115.0	797.5
Visagie	330.0	290.0	-40.0	870.0
MANGANESE				
Hamilton	29.1	29.0	-0.1	45.5
Munitoria	40.3	36.0	-4.3	52.3
Visagie	33.5	32.3	-1.2	45.0
ZINC				
Hamilton	12.1	12.4	0.3	17.6
Munitoria	19.3	18.4	-0.9	25.3
Visagie	23.3	23.3	0.0	30.3
COPPER				
Hamilton	6.4	6.5	0.1	10.4
Munitoria	9.8	9.4	-0.4	13.8
Visagie	11.0	10.8	-0.2	15.2

3.3 ANALYTICAL TECHNIQUES

Atomic Absorption Spectrometry (AAS) is extensively used for the routine analysis of trace elements. Numerous modifications, improvements and refinements have been made to the 'standard' technique. The major drawback of AAS is that it essentially only analyses a single element at a time, thus considerable time is involved in multi-element analysis.

For this study the instrument initially used was a Varian AA6 with a Bc-6 background corrector, however in January 1985 this instrument was replaced by a Varian AA-1475. Commissioning tests conducted within the Atmospheric Sciences Division on the change-over of instruments indicated that there was no difference between the results obtained on the two instruments.

A nitrous oxide/acetylene flame was used for the analysis of iron, whilst an acetylene flame was used for the remaining trace elements (lead, manganese, zinc and copper).

3.3.1 Analytical reproducibility

Throughout the duration of the study the samples collected were analysed either in duplicate or triplicate, the only exceptions being the samples collected during the two annual surveys, for which only a few of the total number of samples were analysed in duplicate. The standard

Table 3. Standard Deviation for leaf analysis, March to July 1984. (ppm).

(standard deviation of differences/mean of the differences).

	Hamilton St.	C.S.I.R.
lead	1.09	0.70
iron	0.86	0.57
manganese	0.94	0.65
zinc	0.91	1.59
copper	1.33	1.21

deviations for the concentrations of trace elements for March to July 1984 at the two sampling sites are shown in table 3, (the samples were collected twice a month, giving a total of ten samples).

The results from the C.S.I.R. site (background location) display lower standard deviations for the elements than those from Hamilton street, with the exception of zinc. At the Hamilton Street site it is probable that the tree leaves are affected by the close proximity of the highway. The reason for zinc being the exception is that the C.S.I.R. site experiences episodes of short-lived, localized zinc pollution resulting from fires generated for research purposes. This has increased the leaf concentrations considerably (in excess of any concentrations found to exist throughout the whole Pretoria area) and has thus had the observed effect on the statistics (Section 4.4.1.3).

3.3.2 Inter-laboratory test

Apart from establishing the variability of the results due to analytical reproducibility it is desirable to know whether these data are comparable with those from other laboratories undertaking similar work, possibly using other techniques. As part of the routine analysis for trace elements collected on air filters the laboratory in which this work was undertaken sends sections of filters to the Atomic Energy Board at Pelindaba, for duplicate analysis by Particle-Induced X-ray Emission

(PIXE) Analysis. The results indicate that there is satisfactory agreement between the results obtained by the different techniques and laboratories (Vleggaar et al, 1980). No leaf material was sent to other laboratories for duplicate analysis.

3.4 CHAPTER SUMMARY

The selection of a method for sample collection, preparation and analysis will be dependant upon the type and quantity of information which is required. Since differences in surface particulate deposition will contribute to the spatial distribution of the trace element leaf concentrations throughout the study area, the Jacaranda leaf samples were not washed prior to the analysis.

Two methods were used to digest the leaf samples. The first, and subsequently most commonly used, was a cold extraction with 3.5M nitric acid over 24 hours. The other, a hot digestion technique, is used in the National Survey of Trace Elements (Vleggaar et al, 1980). The former provided information on the surface and near surface, easily dissolvable particles; the latter on the total leaf concentrations.

Varying the concentration of the cold nitric acid, from dilute to concentrated, revealed that there was little variation in the subsequently released trace element concentrations. However, the percentage of the available elements recovered by the cold technique did vary between different sampling localities. This is expected because of the different local aerosol compositions.

Lead was the most variable of the five studied elements (figures 3 and 4). The addition of hydrogen peroxide to the cold technique did not reduce this variability, as might have been expected if the cause was varying lead dioxide concentrations in the total lead deposit (table 2).

The samples were analysed by Atomic Absorption Spectrometry. The reproducability of the results was found to be acceptable (table 3), with iron having the largest standard deviation, and zinc and copper having the lowest at the urban sampling sites.

Routine comparison tests are conducted with the laboratory of the Atomic Energy Board at Pelindaba on air filter samples. The results indicate a satisfactory agreement between the parallel analyses undertaken by the two laboratories.

The next step after the determination of the analytical technique was to design a suitable and representative collection method. It was essential to determine the natural variations in trace element concentrations so as to be able to differentiate between those areas in which the tree leaves had enhanced concentrations and those which had not.

CHAPTER 4

VARIATIONS IN TRACE ELEMENT OCCURRENCES

4.1 VARIATION WITHIN AN INDIVIDUAL TREE

In the design of a suitable and representative collection technique it was necessary to establish the variation in trace element concentrations within a leaf; in a tree and along a highway. Little (1974) demonstrated the large variations and subsequent complexities in the occurrence of trace elements on a leaf surface by showing that zinc concentrations on elm leaves, close to a smelting site, varied between 3 477 to 6 246ppm on the same twig. Photographs taken of the surface of a Jacaranda pinnule, as viewed under an electron microscope showed a higher density of particles in the region of the midrib on the upper leaf surface than any other location on the leaf.

When determining the technique for sample collection, the following questions were considered:

a) What is the variation in concentrations on/in a leaf?

b) What is the variation within an individual tree?

c) What would be a representative sample from an individual tree?

d) What is the expected range of concentrations throughout the Pretoria urban area?

e) What local influences would cause a tree to be unsuitable for sampling by making it unrepresentative of the immediate local area?

4.1.1 Variation on a leaf

There are a number of possible reasons for a natural variation in the trace element concentration on a leaf; the young tips may exhibit elevated levels due to the local increases of nutrients essential for growth; high concentrations may exist on pinnae at the base of the leaf, due to a longer exposure to atmospheric aerosol. It is therefore important to establish the degree of variation, if any, for the concentration of trace elements on/in a leaf.

Samples were collected from a typical kerbside Jacaranda tree on Cusson Road, situated in the eastern suburbs of Pretoria, close to the C.S.I.R.. Two paired pinnae from each side of the midrib were collected from the same leaf on twelve consecutive days. Four leaves, one from each quarter of the tree were analysed. The samples were prepared by cold extraction and analysed in the standard way (section 3.2.1).

The results (table 4) are from an insufficiently large sample to enable a statistical analysis to be undertaken. Nevertheless it can be observed that in general, no section of the leaf (tip, middle or base) has a consistently different degree of contamination than any other section of the leaf.

Table 4. Results from analysis of paired pinnae (ppm).

Element	Leaf section										
Sector	base			middle			tip				
Pinnae pair	1	2	3	4	5	6	7	8	9	mean	s.d.
LEAD											
north	17.7	20.0	20.6	18.4	17.7	20.0	-	-	-	19.5	1.3
east	22.5	19.4	18.2	17.3	20.4	20.5	31.0	29.4	-	22.3	1.5
south	16.7	13.0	12.5	17.5	15.2	11.2	14.7	14.2	14.2	14.4	2.0
west	16.3	14.7	12.5	15.9	13.5	12.5	13.0	-	-	14.1	1.6
IRON											
north	97.1	125.0	110.3	111.8	110.3	141.7	-	-	-	116.0	15.4
east	187.5	91.7	85.2	100.0	96.3	118.2	196.4	152.9	-	128.5	44.5
south	78.3	71.7	88.5	106.3	92.4	98.7	97.1	78.3	95.0	89.6	11.3
west	70.0	69.1	71.3	85.2	72.1	71.3	81.5	-	-	74.4	6.3
MANGANESE											
north	22.1	23.3	22.8	24.6	22.8	22.0	-	-	-	22.9	1.0
east	31.0	23.6	21.3	21.6	23.2	22.2	28.0	32.4	-	25.4	4.4
south	22.0	21.2	22.9	23.4	23.9	21.7	25.0	23.3	20.8	22.7	1.4
west	28.8	22.1	20.6	23.3	21.6	18.8	15.2	-	-	21.5	4.2
ZINC											
north	33.8	13.3	33.8	25.0	11.8	25.0	-	-	-	23.8	9.6
east	20.0	16.7	4.6	11.5	13.9	21.6	22.6	22.1	-	16.6	6.3
south	13.3	13.0	12.5	15.0	4.4	15.8	11.8	20.0	20.0	14.0	4.7
west	n.d.	n.d.	10.0	4.6	3.9	10.0	16.3	-	-	6.4	6.0
COPPER											
north	22.1	16.7	32.4	6.6	17.7	8.3	-	-	-	17.3	9.4
east	10.0	-	13.6	14.4	13.9	5.7	14.3	7.4	-	11.3	3.4
south	8.3	n.d.	5.2	-	18.5	9.2	10.3	8.3	8.3	9.7	5.2
west	5.0	10.3	12.5	5.7	6.7	6.3	37.0	-	-	11.9	11.4

n.d. not detectable

In a further experiment, the leaf samples taken at the four city study sites (as part of the seasonal study, representing May, June, and July 1985) underwent additional preparation and analysis. Apart from separating the centre six pairs of pinnae in the normal course of preparation, the remaining pinnae located at the tip and base of the leaf were also seperately removed, thus allowing analysis to be undertaken on samples representing the three different sections of the leaf. The results are shown in table 5. Again there is no distinguishable trend in the concentrations of the studied elements between the different leaf sections (tip, middle or base). Thus any section of a Jacaranda leaf appears to be representative of the total leaf. To minimise any undetected effects of sampling different sections of the leaf, and to conform to a standard method it, was decided to remove and analyse only the center six pairs of pinnae, the rest of the leaf being discarded.

4.1.2 Variation within a tree

A single tree, located in the City centre was selected for the purpose of investigating the variation in concentrations of trace elements in leaf samples taken from different positions around a tree. For this part of the study it was necessary that the tree had not been pruned so that leaves would be accessible for sampling by hand. As hand sampling of kerbside trees would be difficult due to the dangers from traffic the selected tree was not typical of the majority of other trees sampled in this study, since it was not located on a kerbside. The tree

Table 5. Monthly results from the different sections of a leaf (ppm).

sample site	Hamilton St.			Munitoria		Afrox		Visagie St.	
	May	June	July	May	June	May	June	May	June
LEAD									
base	55.6	68.3	61.8	55.0	71.3	19.5	-	59.8	52.8
middle	54.5	65.3	56.0	52.8	60.5	19.9	21.0	53.3	54.4
tip	51.3	75.0	56.0	53.6	65.8	19.0	15.8	50.9	51.3
IRON									
base	67.6	115.0	90.0	102.0	210.0	268.8	-	230.0	345.0
middle	67.9	145.0	70.0	101.5	177.5	290.6	467.5	206.9	411.3
tip	66.1	162.5	72.5	99.4	177.5	273.0	422.5	205.5	362.5
MANGANESE									
base	20.6	32.5	29.0	19.0	32.3	53.8	-	20.3	31.0
middle	18.9	39.3	20.1	18.4	28.5	61.4	90.5	18.6	37.0
tip	18.8	39.3	30.5	17.3	28.0	53.8	101.5	20.1	33.5
ZINC									
base	11.6	14.8	12.8	12.3	19.0	30.5	-	19.5	21.0
middle	10.0	16.5	12.1	11.6	15.3	29.1	24.0	16.4	22.8
tip	10.0	18.5	13.5	11.3	14.5	26.8	25.8	16.8	21.8
COPPER									
base	5.5	7.5	6.5	5.5	8.0	9.3	-	8.0	8.0
middle	5.5	8.0	6.4	5.3	6.8	8.5	8.0	6.8	8.4
tip	5.8	9.0	7.0	5.3	7.3	7.8	9.5	7.1	8.0

selected was located within the grounds of the Eendracht School, in the centre of Pretoria. The relationship between the tree, the adjacent roads, the nearest buildings and the leaf sampling points is shown in figure 5.

The samples, each consisting of a single leaf, were taken from the same position, at the same time of day, on twelve consecutive days from the fifteen positions shown on figure 5. Each sample was prepared by cold extraction and analysed by the methods already described.

The statistical analysis of the results (table 6) indicate that for each of the five trace elements there is a highly significant positional effect. To determine which positions differed from which, a multiple comparison test was conducted, (SAS, 1985; citing Miller, 1981) the results of which are given in table 7. The results are in order of increasing concentrations in the second column, the first giving the day of sampling. The vertical lines next to the columns are used to indicate those means which do not differ significantly from each other. No positional effect could be established in relation to distance from the kerbside.

The division of the tree into quarters was undertaken to obtain a variance of concentrations per sector, these were then used to calculate the expected standard deviations of these data as one or more leaves were sampled, from one or more positions in each sector (table 8).

By sampling two leaves, rather than one leaf at each position in each sector, (therefore a composite sample consists of eight leaves) the precision of the mean can be increased (e.g. for lead by 74%). Further

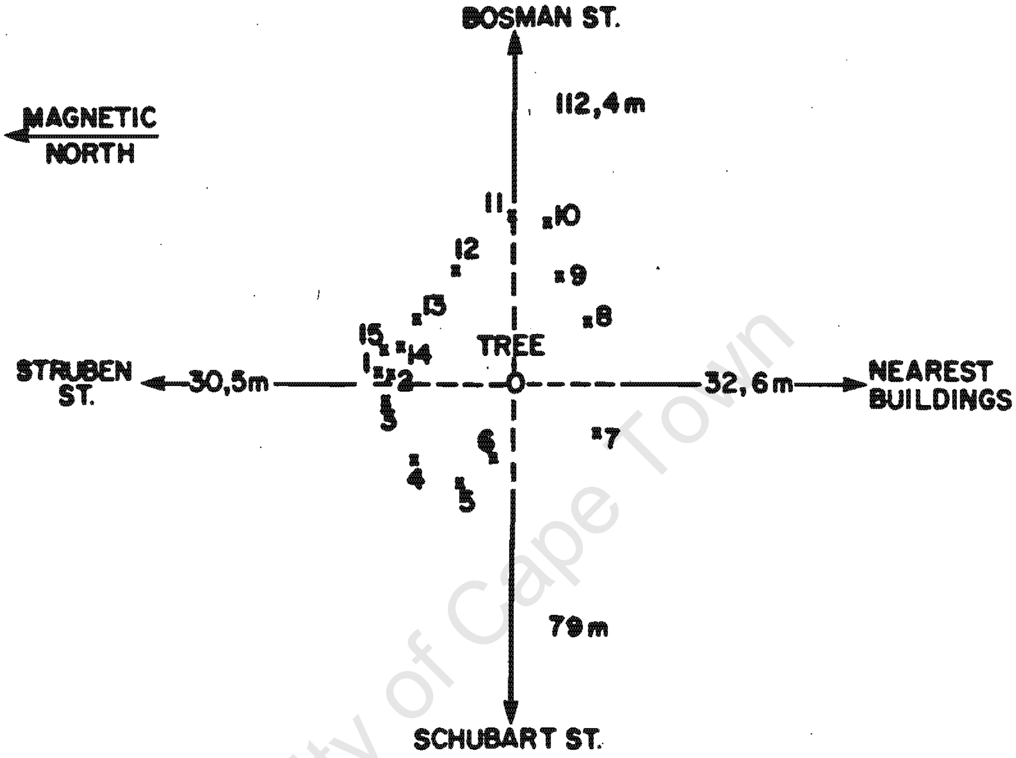


Figure 5. Sample points on the study tree, Eendracht School.

Table 6. Analysis of variance tables - Eendracht School.

	Source	DF	sum of squares	mean square	F value	PF > F
LEAD	day	11	3344.742	304.067	35.76	<0.0001
	position	14	854.288	61.021	7.18	<0.0001
	error	152	1292.636	8.504		
	TOTAL	177	5491.665			
IRON	day	11	11570.447	1051.859	13.32	<0.0001
	position	14	6550.257	467.876	5.93	<0.0001
	error	152	12000.445	78.951		
	TOTAL	177	30121.150			
MANGANESE	day	11	496.889	45.172	7.47	<0.0001
	position	14	614.237	43.874	7.26	<0.0001
	error	152	918.562	6.043		
	TOTAL	177	2029.688			
ZINC	day	11	221.146	20.104	10.74	<0.0001
	position	14	176.505	12.607	6.74	<0.0001
	error	152	284.412	1.871		
	TOTAL	177	682.062			
COPPER	day	11	43.817	3.983	8.69	<0.0001
	position	14	29.495	2.107	4.60	<0.0001
	error	152	69.645	0.458		
	TOTAL	177	142.957			

Table 7. Multiple comparisons test for positional effect.

LEAD		IRON		MANGANESE		ZINC		COPPER	
Position	Mean	Position	Mean	Position	Mean	Position	Mean	Position	Mean
10	8.666	3	34.763	10	11.017	4	6.268	15	3.320
5	9.429	10	37.758	7	11.718	7	6.888	1	3.354
9	9.523	8	38.522	11	11.965	3	7.019	3	3.449
7	9.528	1	38.563	4	11.978	15	7.156	4	3.544
8	9.654	15	39.045	15	12.570	8	7.181	10	3.590
3	10.593	9	39.509	9	12.577	1	7.292	8	3.691
4	10.712	7	39.951	1	12.854	10	7.439	7	3.723
15	11.054	4	40.498	3	12.887	6	7.629	11	3.770
11	11.747	11	43.696	5	12.894	11	7.846	14	3.866
1	11.833	5	43.918	8	13.332	5	8.216	9	4.003
6	12.874	6	45.907	12	14.588	9	8.322	13	4.092
12	13.186	13	48.614	6	15.158	12	8.378	12	4.367
13	13.788	2	50.854	13	15.592	14	8.541	6	4.427
14	15.142	12	53.305	14	16.158	13	9.348	2	4.480
2	16.358	14	55.716	2	17.863	2	10.237	5	4.589

Table 8. Expected standard deviations for varying sample composition.

Number of leaves	Number of positions	Pb	Fe	Mn	Zn	Cu
1	1	1.7641	5.4465	1.5245	0.8552	0.3729
2	1	1.4314	4.4492	1.2525	0.7053	0.2860
2	2	1.2474	3.8512	1.0780	0.6047	0.2637
4	1	1.2318	3.8550	1.0914	0.6168	0.2305
4	2	1.0121	3.1460	0.8856	0.4987	0.2022
4	4	0.8820	2.7232	0.7623	0.4276	0.1864

small increases in precision may be obtained by taking more leaves in several different positions within each sector. These results verified the sampling procedure which was used in the annual surveys, i.e. two leaves from the same position from each of the four sectors.

Although no positional effect was established in relation to the surrounding roads, this is probably due to the study tree being located at least 30 meters from the nearest road. Table 4 shows that another particular tree sampled in this study did display a positional effect in relation to the road; the easterly side of the tree being the closest to the road and displaying the highest concentrations of lead.

4.2 VARIATION ALONG A HIGHWAY

4.2.1 Variation along a highway

It has been well established that there is an inverse correlation between distance from a highway and the concentration of lead in the associated soil, vegetation and atmosphere. This reduction measured at 100 meters is of the order 80% of the concentration measured at the source, with a decrease of about 50% within 20 meters of the highway. Lead concentrations are directly related to traffic density, although peak concentrations are not necessarally related to the peak traffic flow (Crump et al, 1980).

It is possible to calculate the theoretical kerbside lead concentration from a given road and thus predict the road's potential impact (Chamberlain et al, 1979). Factors such as distance from traffic lights and the light cycle times (Kinard et al, 1976), as well as local meteorological conditions, particularly wind, are known to be important and have been taken into account.

The samples collected for this study were from trees adjacent to roads, within three meters from the kerbside and with many of the higher branches overhanging the road. Under these conditions it was expected that the close proximity of the road would have a particularly dominant effect on the concentration of lead. The sampling of leaves was undertaken from all sides of the tree, thus reducing the positional effect on the results (section 4.1.2). The uniform manner in which Jacaranda trees are planted on the kerbside throughout Pretoria reduces the influence of varying distance on the relative spatial distribution of lead. However, because of the close relationship between the sample point and the source, (the road), the concentration of lead will be influenced by changing traffic volume. The interpretation of the resultant distribution maps for lead should therefore take into account varying traffic volumes.

One of the pilot studies examined the variations in leaf lead concentrations along a major road, and at right-angles to it. The site, in the east of the City was along Pretorius Street, a west bound one-way street with a traffic volume of 18 000 vehicles a day. The side road, Grosvenor Street, provides access to a limited part of a very quiet suburb with minimal traffic flow (probably less than a thousand vehicles per day).

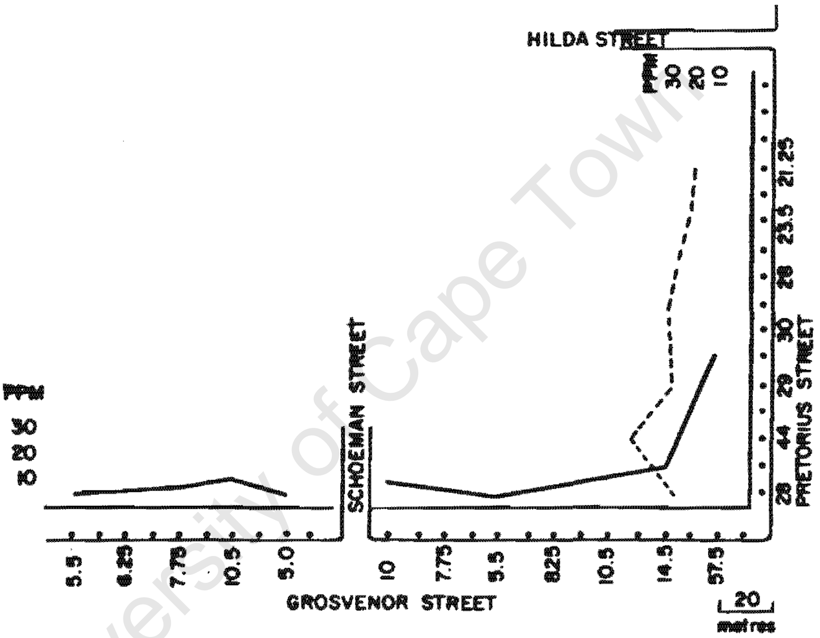


Figure 6. Lead concentrations along a highway.

The variation in concentrations between trees adjacent to each other along each of the roads is illustrated in figure 6. The mean lead concentrations along the side road, Grosvenor Street, was 8.3 ±2.9 ppm. Excluded from the calculation is the last tree in the road, which exhibited an elevated concentration compared with the other trees in the road. At this point Grosvenor Street joins Pretorius Street at a compulsory stop. There is thus a localised traffic build-up at this point, which, when accelerating away would increase lead emissions.

The leaf lead concentrations along Pretorius Street are both higher and exhibit a larger range of values, (29.1 ±7.3 ppm) than in Grosvenor Street. An elevated concentration occurs at a bus stop, where localized congestion may occur whenever a bus stops and the flow of traffic is thus restricted to three, rather than four lanes.

These observations illustrate the influence that minor, very local, traffic congestion points may have on the leaf concentrations of lead. Any single tree selected for sampling along either Pretorius or Grosvenor Streets, away from the above mentioned points of congestion, would have been representative of that particular section of road. Comparative samples also indicate the obvious difference between the concentrations along the two different types of roads, although very close to each other.

4.3 VARIATION IN AN URBAN AREA

There are many different elements which may be considered as potential urban pollutants. It was important to establish from the outset of the study which of these elements would be studied. It was decided to eliminate rare elements, those which would be unlikely to display enhanced concentrations due to pollution in Pretoria, and those elements whose concentrations which were below the limits of detection for the analytical equipment which was available.

To establish the possible range of concentrations in the Pretoria urban area using knowledge of areas of relatively high and low pollution, thirteen samples were taken. These covered the industrial (I), City center (C), and residential areas (R). The locations of the trees sampled are listed below:

C	Hamilton St.	between Pretorius and Schoeman streets, next to tennis courts, Arcadia.
C	Paul Kruger St.	next to lamp post no.c64, outside special court rooms, Pretoria Central.
C	Struben St.	no.262, next to post office, Pretoria Central.
C	Proes St.	c/o Van der Walt St., next to the barracks, Pretoria Central.
I	Edison Rd,(a)	outside the 'Afrox' works, Industria.
I	Edison Rd.(b)	opp. no.280, Industria.
I	Delfos Rd.	opp. power station, lamp post no.35, Industria.

I	Research Rd.	next to lamp post no.29, Industria.
R	Amos St.	rear of 234 Amos Street, Colbyn.
R	Lindfield Rd.	rear of 12, Lynnwood Manor.
R	Frederika St.	c/o 18de laan, Villieria.
R	Ben Swart St.	no 956, Villieria.
R	Haarhoff St.	c/o 27 Avenue, Villieria.

The results (table 9) from the samples show that the concentrations varied from site to site for all the elements analysed, although the variations in concentrations are not always as large for one element as for another. The analysis shows that chromium, cadmium and nickel were either often not-detectable or at very low concentrations. Potassium, sodium, magnesium and calcium are major plant nutrients and are not recognized as atmospheric pollutants in Pretoria. In the case of calcium and potassium this conclusion is supported by Annegarn and Sellschop (1983). In the same study these authors show that there is a marked enrichment of lead and zinc, and to a lesser extent iron and manganese, in Pretoria. Copper was recorded only intermittently above the PIXE detection limits, although it is readily found on the monthly air-filter samples from Pretoria. Leaf concentrations of iron, manganese, zinc and copper are seen to be enhanced in the industrial area compared to the residential areas. As expected leaf lead concentrations were highest in the City centre.

For these reasons it was decided to restrict the present study to the determination of the lead, iron, manganese, zinc and copper concentrations in Jacaranda leaves.

Table 9. Variation of trace elements in Jacaranda leaves due to variations in locality, (ppm).

classification & location	Pb	Fe	Mn	Zn	Cu	Mg	Cr	Ca	K	Na
C Hamilton	28	275	25	11	8	3300	1.5	6250	5087	4
C Paul Kruger	16	250	22	11	11	329	-	4250	4250	26
C Struben	25	2875	19	13	7	258	-	2375	4125	5
C Proes	44	500	27	19	9	411	-	5975	5250	9
I Edison a)	12	1327	59	18	12	3205	2.9	5994	4455	10
I Edison b)	8	1050	50	17	10	326	-	6100	4750	11
I Delfos	7	313	16	11	7	228	-	3450	4125	8
I Research	13	2275	120	21	10	360	-	6600	4625	23
R Amos	7	175	33	8	6	3300	0.75	8000	4025	8
R Lindfield	3	175	15	4	4	2525	0.75	4450	4000	-
R Frederika	15	243	17	11	8	290	-	4525	4250	4
R Ben Swart	8	218	21	10	7	343	-	5700	3750	14
R Haarhoff	3	130	19	6	8	348	-	4900	5250	15

- not detectable, C = central site, I = industrial site, R = residential site

4.4 TEMPORAL VARIATION

4.4.1 Daily variation

The collection of the necessary samples for a large survey was not possible within a single day. It was therefore necessary to investigate the effects and influence of extending the sampling over a longer period, in particular:

a) is there a daily variation in measured concentrations?

b) if so, is this within an acceptable range so that any possible spatial variation is not masked?

and c) is there an influence due to rainfall?

Further analysis of the data obtained to establish the variation of concentrations within a tree (section 4.1.2) showed that there was a significant difference, between the daily samples collected on the twelve consecutive days (table 6). The difference was not related to the small amount of rainfall that occurred (0.3,0.1,0.9 and 0.3mm on days 5,6,8 and 9 respectively). Table 10 indicates the day, mean concentration and, by use of vertical lines, those means which do not differ significantly from each other. As can be seen, the situation is complicated and varies according to the element under consideration.

Although no regular pattern for the daily variation in trace element concentrations was established, it was thought prudent to keep the number of days for sampling to a minimum.

Table 10. Multiple comparisons test for daily variation.

LEAD		IRON		MANGANESE		ZINC		COPPER	
Day	Mean	Day	Mean	Day	Mean	Day	Mean	Day	Mean
6	3.177	1	33.040	1	10.559	1	6.095	12	3.023
7	6.073	3	35.667	2	11.575	3	6.583	5	3.483
5	9.571	2	36.237	3	11.690	2	6.644	7	3.503
1	10.183	6	36.831	5	12.651	5	7.027	1	3.616
2	10.396	5	37.065	4	12.996	4	7.600	3	3.700
3	10.489	4	37.987	7	13.054	7	7.881	8	3.728
4	10.543	7	41.179	6	13.658	8	7.965	6	3.765
8	10.797	12	48.979	10	14.371	6	8.030	11	3.852
12	16.119	11	51.544	12	15.143	9	8.223	4	4.025
10	16.912	9	52.412	8	15.507	12	8.843	2	4.571
9	17.184	10	52.863	9	15.559	11	9.476	9	4.574
11	17.825	8	56.699	11	15.757	10	9.869	10	4.773

The natural daily variation in trace element concentrations will be the result of variations in the rates of deposition and loss. The loss may be due to biological utilisation or chemical fixation of the elements or the influence of rain or wind.

4.4.1.1 The influence of rainfall

Rentschler (1977) noted a variation in the concentration of trace elements in <u>Oxalis acetosella</u> with rainfall. Long dry periods allowed substantial build up of particles, whereas a thunderstorm would reduce the concentrations dramatically. Little and Wiffen (1977) found that small amounts of rainfall could remove 30% of the deposited lead, and up to 50% could be removed by heavy or repeated rainfall. However, Rains (1975) in his work on wild oats found that rainfall of up to 90mm did not wash the lead from the dead tissues of the plant at the end of the season. Carlson et al (1976) concluded that mist was more effective in the removal of surface deposits than rain. This was because mist coalesced into large drops, ran towards the leaf edges, collecting surface deposition on the way and fell off. Raindrops, on the other hand, splash off on impact. Muthappa et al (1977) showed that the maximum loss of copper occurred during the first 60 days of weathering (850mm of rain and severe winds) after the spraying of copper nutrient solution. The upper leaf surface deposits are eroded more quickly than lower ones, however the latter also suffered severe losses under heavy rainfall conditions, in response to the canopy becoming saturated (Mabbett and Phelps, 1983).

The sampling of tree leaves has an advantage over samples taken from ground vegetation, because the former are remote from the ground and are therefore not affected by deposition of surface soil carried by splashing rainwater.

Two attempts were made to measure the influence of rainfall on the trace element concentrations of Jacaranda leaves in Pretoria (section 4.1.1, variation of concentrations on leaves; and section 4.4.1, daily variation). Both of these failed to produce sufficient data because either no rain fell, or insignificant falls were recorded. In the latter case the difference in leaf concentrations before and after the rain events could not be statistically differentiated from normal daily variations.

The possibility of the occurrence of a rainstorm during the annual sampling periods was considered. In such an event, all of the samples which had been collected prior to the storm would have been repeated, thus ensuring that all of the samples would have been influenced by similar environmental conditions. This would have provided the opportunity to study the influence of such a rainstorm. No rainfall was recorded in either of the annual surveys conducted in 1983 and 1984.

4.4.1.2 The influence of wind

Ratcliffe (1975) showed that in a moss bag survey, lead correlated significantly with wind direction and speed over monthly periods. However, over weekly periods only 40% of the variation could be explained by these parameters. Harriss and Lindberg (1981) correlated dry deposition on leaves with periods of air stagnation and the associated high concentrations of elements in the aerosol. Carlson et al (1976) found re-entrainment of mono-dispersed lead particles from leaf surfaces at windspeeds up to 6-7 m/s.

The data from the samples collected on a daily basis at the Eendracht School (18-2-85 to 1-3-85; section 4.1.2) was examined to determine if the daily variations in concentrations could be attributed to either wind speed, direction, or a combination of both factors, as described by a wind vector. The meteorological data was obtained from the Weather Bureau, for the Forum Building monitoring station. This site is within 200 meters of the study tree, the instruments being located on the roof, at a height of approximately 32 meters.

Table 11, shows the mean vectored wind direction for each day. The days are in the order of ascending trace element concentration. The vertical lines beside the columns indicate those days for which the mean concentration of a particular element is not significantly different from it's concentration on any other day.

With the exception of day 9, it appears that the highest concentrations of lead, iron and manganese are associated with a southwest, west or northwest wind. For zinc or copper no similar relationship is observed. Iscor is situated to the west-south-west of the study tree and the emissions from this steel works may be the source for the airborne iron and manganese which is then deposited on the leaves. Figure 5 shows the relationship between the study tree and the nearest roads, the numbers indicating the positions from which the samples were taken. No explanation for the apparent higher concentration of lead when the vectored wind direction is from the northwest to the southwest can be found. The influence of periods of calms should be investigated.

Table 11. Comparison between mean vectored wind directions and daily variations.

LEAD		IRON		MANGANESE		ZINC		COPPER	
Day	Wind	Day	Wind	Day	Wind	Day	Wind	Day	Wind
6	319.4	1	60.9	1	60.9	1	60.9	12	248.3
7	236.2	3	68.4	2	84.7	3	68.4	5	216.9
5	216.9	2	84.7	3	68.4	2	84.7	7	236.2
1	60.9	6	319.4	5	216.9	5	216.9	1	60.9
2	84.7	5	216.9	4	30.8	4	30.8	3	68.4
3	68.4	4	30.8	7	236.2	7	236.2	8	264.3
4	30.8	7	236.2	6	319.4	8	264.3	6	319.4
8	264.3	12	248.3	10	279.0	6	319.4	11	318.3
12	248.3	11	318.3	12	248.3	9	52.2	4	30.8
10	279.0	9	52.2	8	264.3	12	248.3	2	84.7
9	52.2	10	279.0	9	52.2	11	318.3	9	52.2
11	318.3	8	264.3	11	318.3	10	279.0	10	279.0

4.4.1.3 The effect of local zinc emissions

During the 1983/4 seasonal study of the variations of trace element concentrations in leaf samples from the C.S.I.R. study tree, it became apparent that an unexpected source of zinc was periodically affecting the results. Detailed examination of the site established that the source was a series of burning tests being conducted to establish the properties of various fire retardent chemicals applied to telegraph poles, and the burning characteristics of PVC insulated armoured cables. The zinc concentrations over the relevant period are shown in figure 7. Although copper was also applied to the telegraph poles, no corresponding rise in leaf copper was found (figure 8).

Surface wind data is available for the C.S.I.R., unfortunately the exact times for the fire tests are not available (although in general these were carried out between 10H00 and 14H00. The wind directions between these hours for the days upon which tests were carried out (either on telegraph poles or armoured cable) are also shown in figure 7.

The rise in leaf zinc concentrations after a test can not be attributed directly to a particularly critical wind direction. The direction between the tree and the test house being southwest. Rainfall data was also examined because of the possibility that the deposits may be washed off the leaf. There are no apparant links between either the frequency or amount of rainfall and the rise or fall of zinc concentrations.

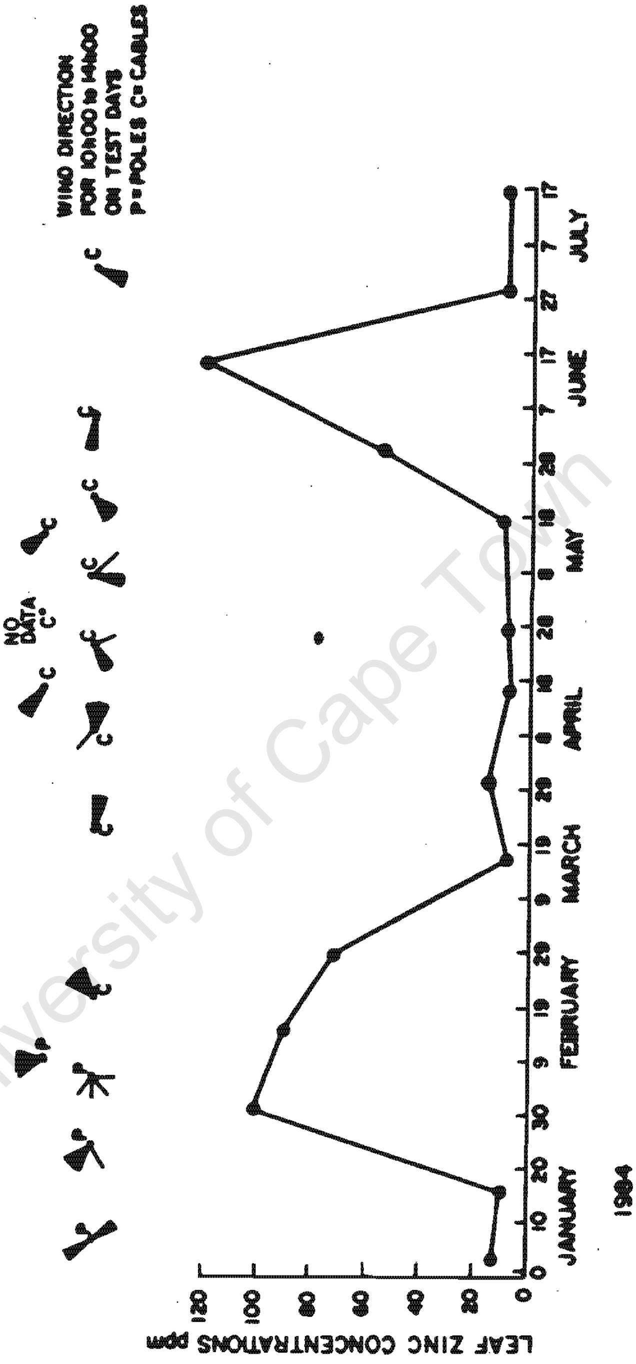


Figure 7. <u>C.S.I.R. study tree's leaf zinc concentrations.</u>

Two major zinc pollution episodes occurred. During the first, the concentrations rose from 10 to 100ppm between two sample days (16 and 31 January). A test, conducted on eight telegraph poles, was held on the 24 January, thus the maximum response period was eight days. Further tests were conducted on the 6 and 9 of February; the former with eight poles, the latter with only one pole. Only on the 6 February was there a south westerly wind. On the 21 February a test was conducted, however the wind was north easterly. By the 16 March (71.6mm of rain in eight events, one of 46.4mm) the leaf concentrations had returned to the level that was recorded prior to January, 52 days after the first test (74.1mm of rain) and 35 days after the last test.

The second rise in zinc concentrations, from 10 to 55ppm, was within 12 days (18-30 June; 14.4mm of rain in one event) and then from 55 to 120ppm in 16 days (30 June to 15 July; 19.0mm of rain in three events). The concentrations dropped dramatically from 120 to 5ppm over the next 13 days (15-28 July; 0.0mm of rain). The only test for which the wind was directly from the south west was on the 21 May (performed on armoured cables).

Although the rise in leaf zinc is probably directly the result of the wind carrying the smoke from the fire tests directly to the tree, the available evidence can not conclusively prove this. The existing wind data is collected on the other side of the hill on which the tree is located. This is probably unrepresentive of the micro wind regime surrounding the study tree, and is insufficiently sensitive for the required analysis. The mechanism of transportation suggests that the zinc will accumulate within a single day, although the sampling undertaken show a maximum response of eight days.

4.4.2 Seasonal variation

An examination of the seasonal trends in trace element concentrations is necessary in a number of situations:

a) if sampling is undertaken throughout the year

b) if the results are used to predict pollution levels

c) if it is necessary to establish the optimum period for sampling

The study of the trends of trace element concentration in vegetation throughout the year is fraught with problems. The influence of the weather, the plant's growth rate, age, and any changes in leaf size, shape or surface characteristics may disguise seasonal trends.

The plants' growth rate during the sampling period can be important in the interpretation of biological data, because of the effects that changes in the leaf area throughout the year (as new leaves become mature) may have. Increasing the leaf area will produce a change in the dry weight of a leaf, or in the case of the Jacaranda, reduce the total number of pinnules required for a predetermined weight.

Some authors have found that concentrations increase throughout the growing season, peaking just prior to leaf fall, or the death of the upper parts of the plant (Rains, 1971). Crump et al (1980) showed a winter maximum and summer minimum for the trace element concentrations on grass growing near to a motorway. Mitchell and Reith (1966) also found a rise from late autumn to early spring, but only for lead and iron; zinc, copper and manganese showed little or no change. Guha and Mitchell (1966) agreed that zinc and copper remained at a constant concentration, or fell slightly, after the initial maximum. However, in their study manganese increased continually throughout the season, whilst the concentrations of both lead and iron fell after leaf emergence, and then increased to an autumn maximum. In a study by Smith et al (1978) the levels of nickel and zinc remained constant throughout the season (May to November); aluminium, iron, manganese and lead accumulated during the spring and early summer and decreased in the late summer and autumn.

Starting in October 1983 leaf samples were collected at the beginning and midway through the month until August 1984. Two sites were selected for study. Firstly, a tree in Hamilton Street, in a high density housing area near the City centre of Pretoria. The tree was five meters from the kerbside, with some of its branches overhanging the road. Hamilton Street has an estimated traffic flow volume of 20 500 vehicles a day. The second tree was within the C.S.I.R. site, on the side of a road with less than one hundred vehicles a day passing within 50 meters.

These two sites represent a suspected polluted and a relatively clean area. The samples were prepared initially only by the cold extraction technique, however late in the 1984 season the hot digestion method was also used on duplicate samples.

The results of the cold extractions are presented in graphical form in figure 8. At the C.S.I.R. site zinc pollution was unexpectedly found (section 4.4.1.3). For all of the other elements the concentrations in the leaf samples were in general lower at the background site than at Hamilton street. There was no apparant significant change in the concentrations of lead, manganese or copper. The concentrations of iron did increase during August, prior to which the concentrations showed little variation.

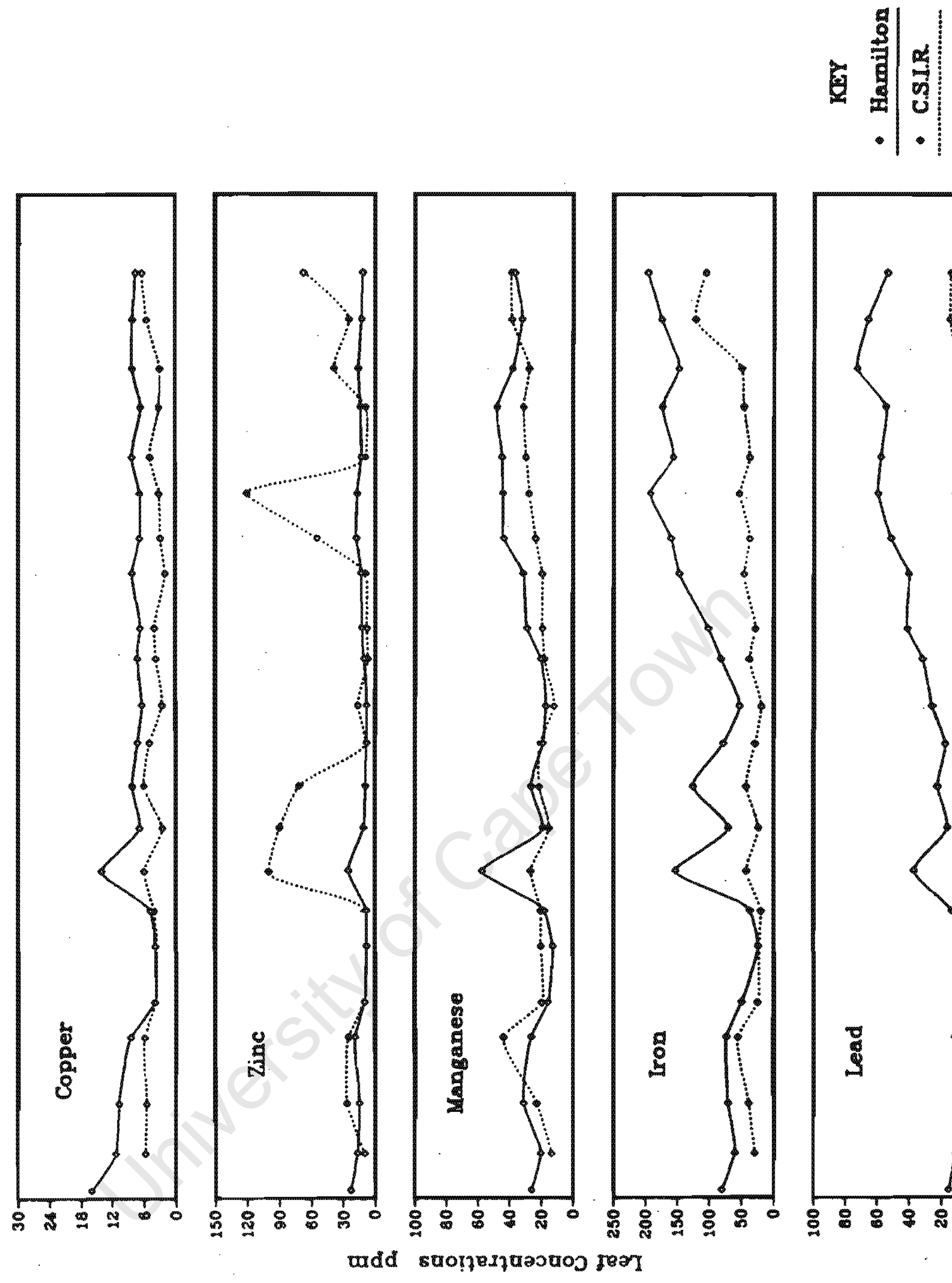


Figure 8. Seasonal trends in leaf sample concentrations at Hamilton st. and C.S.I.R. October to September 1983/4- cold extractions.

At the Hamilton Street site all of the elements displayed a temporary peak at the end of January, for no apparant reason. Zinc concentrations remained constant throughout the period, whilst lead and iron displayed increasing trends after the initial four months. Copper showed an initial decrease, whilst during the rest of the year the concentrations remained constant. Manganese was very variable throughout the period.

These results prompted continuation of this study. The C.S.I.R. site was suspended due to the contamination problem, but three other urban sites were established. These were at Munitoria in the City centre; at Afrox in the industrial area; and at Visagie Street a mixed industrial and central site.

At all of these sites air-pollution monitoring stations consisting of an air-filter unit and/or a deposit gauge were already in operation. Leaf samples were collected on a monthly basis, to coincide with the collection of air pollution samples. The leaf samples were prepared by both the cold extraction and hot digestion techniques. Since only one sample per month was collected compared with the previous two, it was expected that some of the previous variability shown at Hamilton Street during the first season would be smoothed out.

Figure 9 illustrates the concentrations of the studied trace elements over the two years of study (October 1983 to August 1985) for the Hamilton Street site, for the cold extraction method of preparation. Essentially the results in the second year are less variable than in the first. The concentration of zinc did not vary throughout the period and remained the same in both years. The concentration of manganese and iron appear to be closely related, with only a slight increase at the end of the

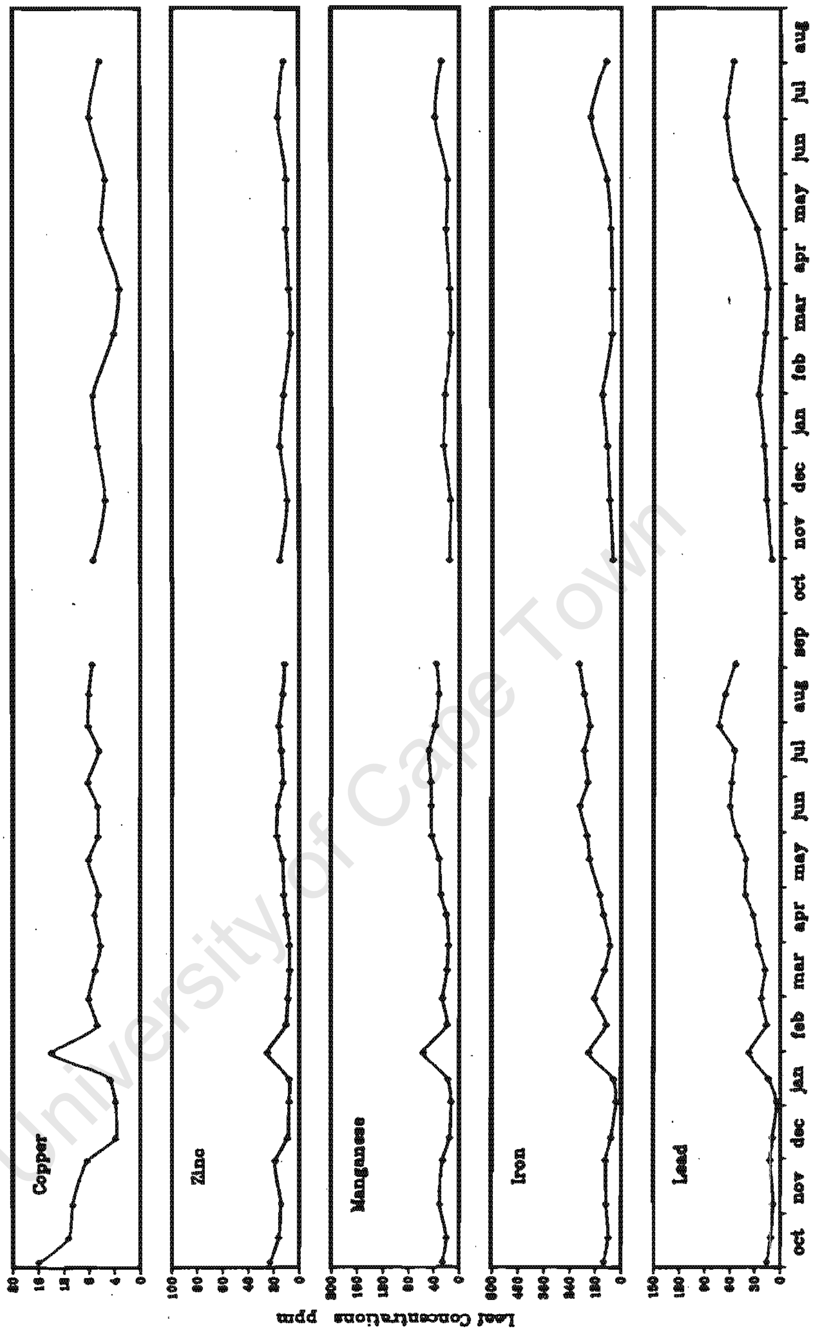


Figure 9. Seasonal trends in leaf sample concentrations at Hamilton st. October to August 1983/5 - cold extractions.

second year, compared with a steady rise observed in the first year. Lead displayed similar patterns in both years, with a steady increase from April to August. The concentration of copper varied throughout each year, without showing any clear tendency.

Figure 10 shows the concentrations at Hamilton Street as determined by the hot digestion method, for 1983 and 1984. Although the leaf concentrations of the studied trace elements are higher when determined by this method, the observations made above in regard to the cold extractions apply equally well to the results from the hot digestions.

Figure 11 illustrates the concentrations of trace elements (as determined by the cold extraction method) for the four urban study sites (Hamilton Street being the same as in figure 9). In general the same seasonal characteristics for each of the elements are exhibited at each of the study sites. There are some exceptions. In the latter part of the year the lead concentrations recorded at Afrox did not rise as did the three other sampling sites. A possible reason for this is the minimal traffic volume at this site. As a consequence of this, there is only a relatively small amount of lead emitted which is insufficient to build up to a larger local atmospheric pool during the unfavourable winter meteorological conditions.

The Afrox site displayed the highest iron and manganese concentrations, this is to be expected because the large Iscor iron and steel works is only some 500 meters away from the sample tree. The iron concentrations in general decrease with distance from Iscor (Afrox, Visagie Street, Munitoria and Hamilton Street).

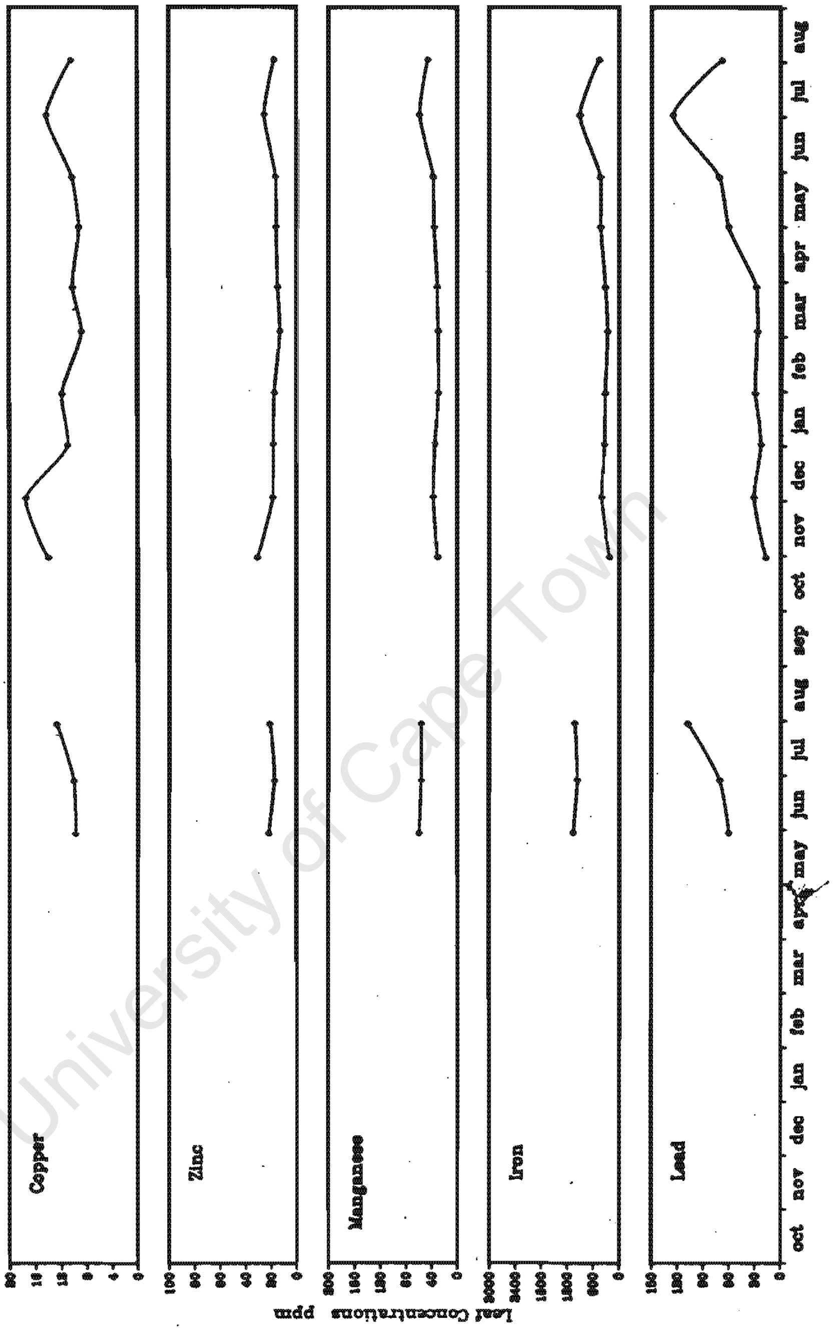


Figure 10. Seasonal trends in leaf sample concentrations at Hamilton st. June to August 1984/5 - hot digestions.

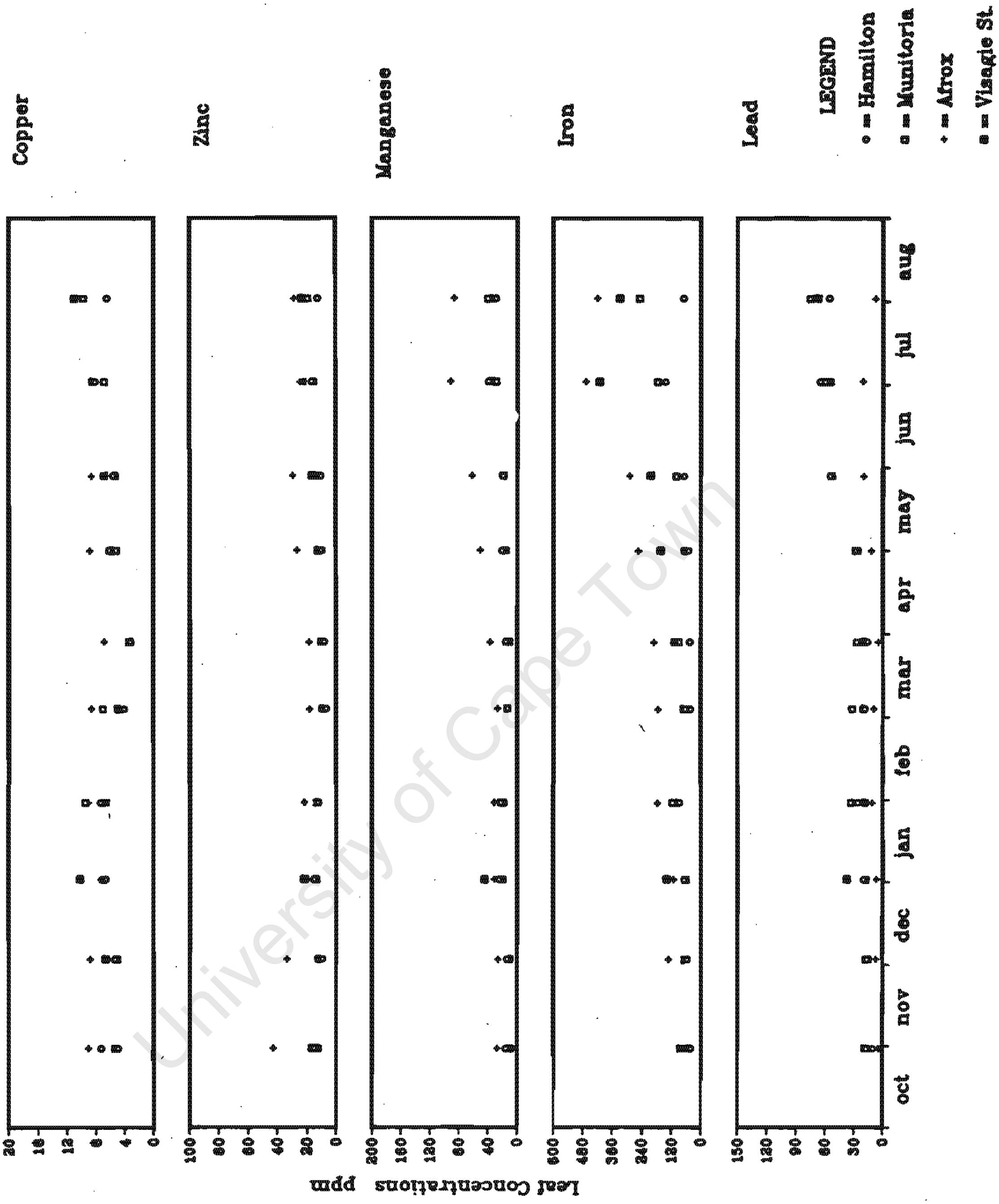


Figure 11. Seasonal trends in leaf sample concentrations: October to August 1984/5 - cold extractions.

The concentrations of trace elements, as determined by the hot digestion method, at each of the urban sites are illustrated in figure 12. Although the concentrations are higher, the same observations as made in the previous paragraph can be applied.

4.4.2.1 Possible biological seasonal influence

The Jacaranda trees of Pretoria are infected by the Jacaranda Wax Scale, Ceroplastes sinoiae. These insects, although harmless to the tree, (Bruins-lich, 1955) do excrete a sticky substance which may influence the collecting efficency of the leaf.

The insect has been studied in great detail by Bedford (1968), who suspected that as the insects squirted out drops of excreta and honeydew, most of it would be carried away by the wind, thus preventing the leaves from becoming covered with the substance. During September and October, as the insects mature, the excretions are at their highest, and it would be during this period that any possible effects upon the seasonal survey would be observed. From figures 9, 10, 11 and 12 no influence upon the leaf concentrations of the studied trace elements can be detected.

The City Council of Pretoria does not use any form of insecticide to control these insects. It is thus improbable that, for any of the trace elements of interest to this study, insecticide or fungicide sprays are a source of contamination.

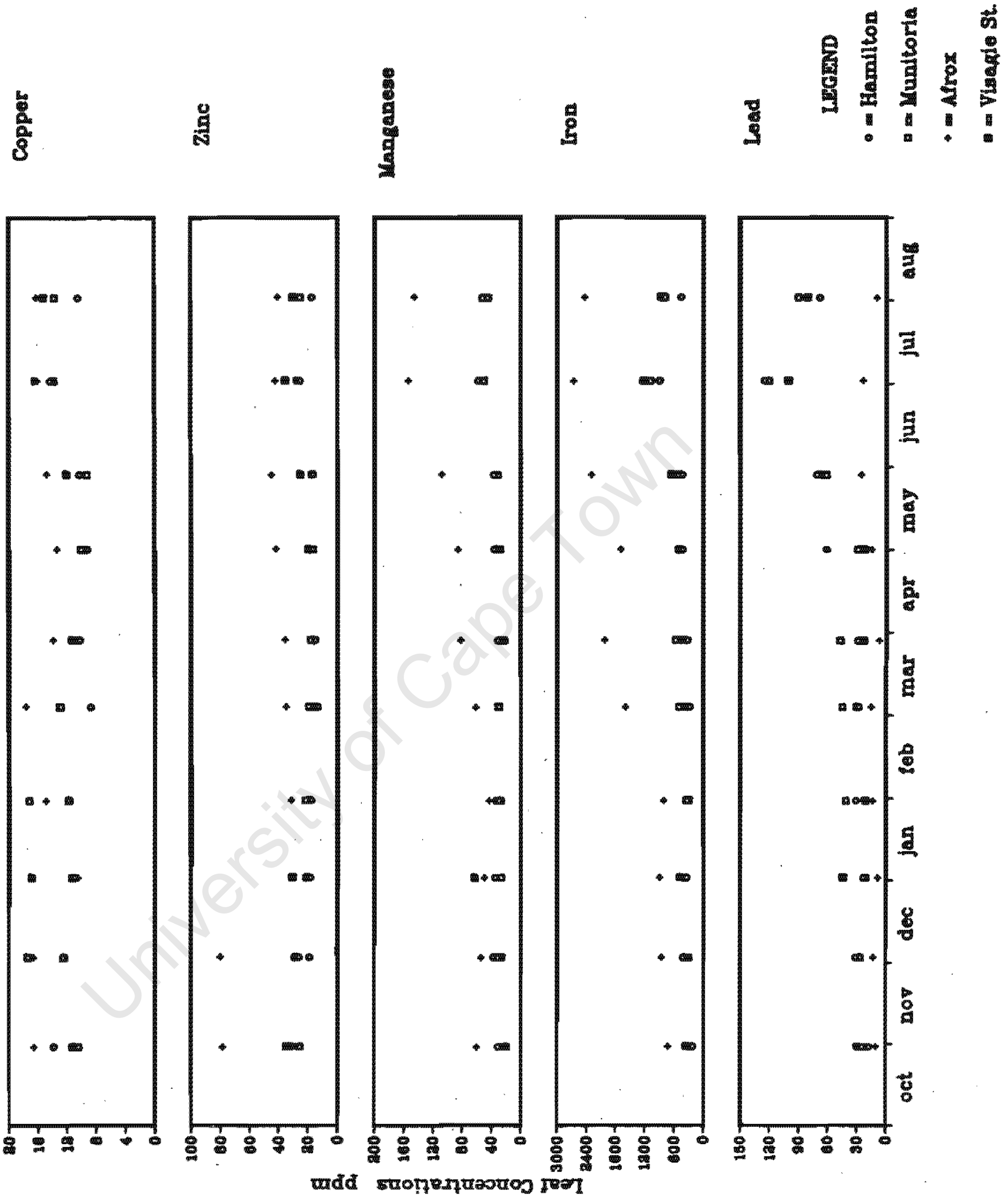


Figure 12. Seasonal trends in leaf sample concentrations: October to August 1984/5 - hot digestions.

4.5 CHAPTER SUMMARY

To be able to successfully interpret the data from the geographical collection of tree leaves throughout Pretoria it is necessary to examine in detail the variation in trace element concentrations in a leaf, a tree and between trees. The causes of these variations and the impact that they have on the sampling technique and data interpretation have to be examined.

No consistent difference between the trace element concentations of the different regions of a leaf (tip, middle or base) was established. For the purpose of this study, the centre six pairs of pinnae were normally sampled. It was established that there was a natural variation in the trace element concentrations within a tree. The concentrations may be influenced by the direction of the source. From the collected data it was possible to calculate the positions and the number of leaves to be collected to achieve an optimum sampling procedure.

The influence of local traffic congestion points (e.g. bus stops and stop streets) on increasing leaf lead concentrations was established. The sampling for the 1983 and 1984 surveys avoided trees in such localities. The differences in the leaf lead concentrations between trees on a major and a minor road, separated by less than 50 meters was marked and the two sites could be easily distinguished from each other (figure 6).

Of all of the possible elemental pollutants that could have been analysed for, it was decided to work on lead, iron, manganese, zinc and copper. Other elements, such as cadmium and nickel, were found to be either not detectable or at extremely low leaf concentrations; others, such as sodium and magnesium are not recognised as potential pollutants in Pretoria.

Since the collection of leaf sample material for the annual surveys would almost certainly span a number of days, it was necessary to examine the natural daily variations in leaf concentrations. A very complicated picture was established in which the daily variation was different for each of the studied trace elements, and was not apparently influenced by the very little rainfall that occurred (table 10).

The seasonal study of the leaf concentrations commenced in October 1983 at a site in Pretoria and another (to provide background information) at the C.S.I.R.. The study was continued upon leaf emergence in October 1984 until August 1985 at three additional urban sites, but suspended at the C.S.I.R. because of a zinc contamination problem due to fire research on telegraph poles and armoured cables (section 4.4.1.3).

The zinc concentrations at the C.S.I.R. did provide information on the rapid accumulation of relatively high leaf concentrations and the subsequent loss over an equally short space of time (two weeks).

The concentrations of iron and manganese appear to be closely related, increasing at the end of both seasons (e.g. figure 9). The leaf lead concentrations also increased, but from April onwards. These increasing trends may be due to the marked atmospheric stability during the winter months, and the lack of rain. No influence on the seasonal variations can be attributed to Ceroplates sinoiae, an insect pest which infests the Jacaranda trees, particularly during September and October.

CHAPTER 5

PRETORIA SURVEYS

5.1 INTRODUCTION

Prior to, and after, undertaking the first annual survey in 1983, it was necessary to conduct the series of experiments and studies, which have been described in chapters three and four, to establish which parameters influence the leaf concentrations of trace elements. Before undertaking the first survey the density at which the samples were to be collected had to be determined.

5.1.1 Choice of sampling grid

A consideration in designing a survey is the density at which the samples are collected. The choice of sampling grid will be dependant upon the use to which the results will be put and also upon the available resources. A sparse grid (one sample per $10km^2$) is often all that is required for a national survey. A finer grid is required for the investigation of a local pollution source.

An arbitrary maximum limit of seven days was set for the collection of all the samples for an annual survey. These consecutive days would have to be rain-free, because of the factors discussed in section 4.4.1.1. The available manpower allowed for two teams, each with two people, to be deployed. From experience gained in the pilot studies it was estimated that 35 samples could be collected daily by each of the teams. The total area to be sampled was 108 km^2, with a potential maximum of 490 samples. A square sampling grid based on 500 meter sides was consequently selected.

An appropriate grid was drawn on transparent film and overlaid on a map of Pretoria, thus predetermining the location of the sampling sites, from which a list was compiled. The sites were divided into two groups, those to the north and those to the south of Church Street: one sampling team was assigned to sample each group. The teams were free to make their own decision on the order in which the samples were to be collected. In this manner the samples were collected throughout Pretoria in no pre-determined order. This eliminated the systematic influence of the natural daily variations in leaf concentrations (section 4.4.1).

5.1.2 Comparison between different grid densities

After the 1983 survey had been completed and the results plotted, it was possible to simulate the effect that the density of sample collection had upon the results. Figures 13 and 14 allow for visual

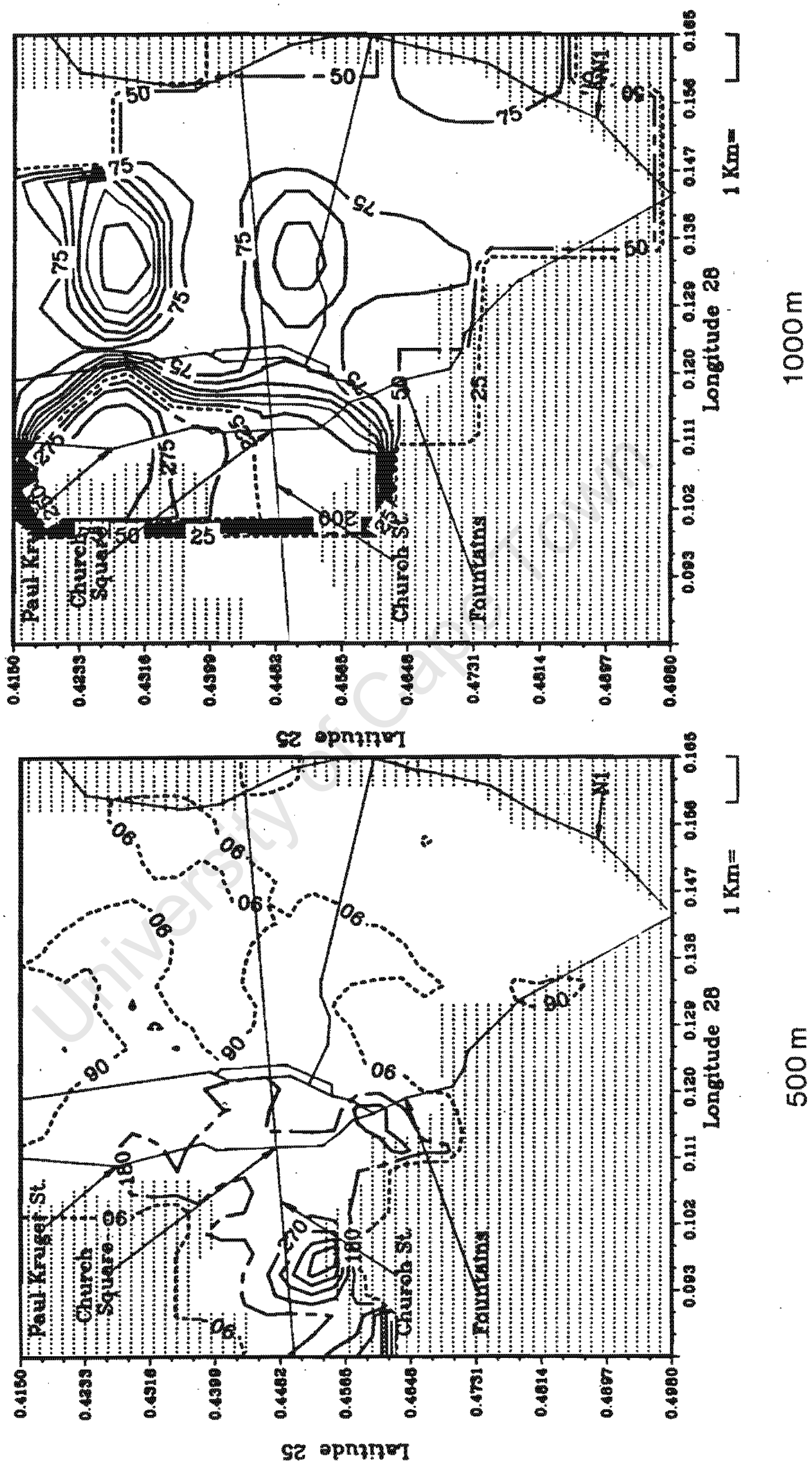


Figure 14. <u>Effect of varying grid density's - iron (ppm).</u>

comparison of the distributions of lead and iron (for example) based on sample grids of 500 and 1000 meters. In the latter case, the study area is covered by 80 samples as compared with the original 313. A grid based upon 2000 meters was also tested, but the sample points (only 18) were insufficient to allow isolines to be drawn without extensive computer interpolation.

As can be seen, as the sample density becomes less, the maps become more simplified. Many of the smaller areas of enhanced concentrations disappear and the overall impression is that essential detail for the purpose of interpretation is missing. Only the basic distributions can still be determined (i.e. for iron the high concentrations are in the west of the area, and for lead in the City centre).

The map based on the 1000 meter grid shows isolines at certain localities which depict higher concentrations than the corresponding point on the map based on 500 meters. The reason is that in the former case there are fewer sampling points, therefore the neighbours are further apart and the algorithm (section 5.2) used to calculation the concentrations at the grid nodes is not affected by the concentrations of the neighbouring sampling point to the same extent as those in the 500 meter grid.

It appears that a grid based on 500 meters provides adequate information to determine the distribution of trace elements in Pretoria. To establish the extent of local high concentrations more intense sampling, either by biological or conventional means, would have to be undertaken.

5.1.3 The collection of samples

The location for a sample was predetermined, but the choice of the actual tree to be sampled was left to the individual sampling team. This was because local points of traffic congestion and access to suitable trees could only be determined on site. It had already been shown (section 4.2.1) that trees in certain positions are not representative of an area, and as such should not be sampled. To ensure that the sampling teams were aware of such limitations the teams were involved in a practice sample collection. The purpose of which was to ensure a uniform sampling procedure was used by both teams. The same personnel were used for the sampling in both 1983 and 1984.

Guha and Mitchell (1966) showed the importance of a consistent sampling height when they established that both lead and iron concentrations were lower at the top of the tree; and that zinc, copper and manganese all showed a slight (less than 20%) reduction with increasing height. Consequently, leaves were collected, using an extendable pruner, from the outermost edges of the tree, thus avoiding contamination due to rainwater run-off from the leaves above the specimens being collected. Four sub-samples were taken at ninety degrees to each other, on a horizontal plane, at a height of between four and five meters. Each sample consisted of two leaves from each of the sampling points. The composite sample was placed into a plastic bag, marked with a code for the location, and sealed.

Samples for the 1983 survey were collected from the 18th to the 23rd of June. Within the week 402 samples were obtained, including samples for both north-south and east-west transects (the results of which were inconclusive). In addition, 88 other sites were visited at which no samples were collected because of the absence of suitable trees. The breakdown of the samples collected on individual days is shown in table 12.

At the sampling sites where there were no Jacaranda trees, another species of tree was sampled. These samples were not limited to a single tree species, a number of different species were sampled, some of which were not identified when sampling. These results (totalling 28 cases) were omitted from subsequent statistical analysis.

The sampling for the 1984 survey of Pretoria was undertaken from the 12th to the 16th April. It was unfortunately impossible to arrange the collection of these samples to coincide with the corresponding period of sampling in 1983.

For the 1984 survey only samples from Jacaranda trees were collected. At the locations at which other trees were sampled in 1983, no sample was taken in 1984. A total of 320 samples were obtained in 1984, of which 313 were from the identical trees sampled in 1983.

From the experience gained in the two surveys it is possible to conclude that the technique can be successfully applied and carried out within three weeks from the start of sampling. This includes sample collection and processing, and the production of the map of the spatial distribution of a particular trace element in the study area.

Table 12. <u>Breakdown of the number of leaf samples collected for the annual survey's of Pretoria.</u>

Date	Team A		Team B		Daily	Total
June 1983	Daily	Total	Daily	Total		
18	32	32	22	22	54	54
19	39	71	29	51	68	122
20	34	105	57	106	91	213
21	34	139	39	145	73	286
22	16	155	32	177	48	334
23	37	192	12	189	49	383
24	-	192	19	208	19	402
April 1984						
12	22	22	-	-	22	22
13	31	53	30	30	61	83
14	34	87	63	93	97	108
15	41	128	40	133	81	261
16	24	152	35	168	59	320

5.2 MAP PREPARATION

The results for each of the annual surveys were filed onto a mainframe computer (Cyber 750), and processed using the computer package DISSPLA (DISSPLA).

In using DISSPLA'S plotting routines the array containing the element concentrations must contain a value at each node of the specified grid. Although the samples were collected on a grid of 500 meters, there are a number of points within the grid for which no data is available.

DISSPLA supplies a series of routines which will generate an evenly spaced grid from irregular data points. The algorithm used is a mathematically weighted technique based on the distance from a grid node to the irregular spaced data points in a specified search area according to the following formula :

$$Z_{jk} = \frac{\sum_{i=1}^{n} \frac{1}{D_i^{w}} Z_i}{\sum_{i=1}^{n} \frac{1}{D_i^{w}}} \qquad [1]$$

where Zjk	is the value to be computed for node jk of the grid
Di	is the distance from node jk to irregular point zi
w	is the weighting factor (2.0 by default)
n	is the number of irregular points which fall in the search area for the irregular point zi

The collection of samples was planned to coincide with the nodes of the 500 meter grid. In only a few instances within the area of sample collection are there missing values. Outside the boundary of the collection area the computer program identified missing values at the nodes and calculated values from the data available from inside the collection area, hence the isolines are drawn extending outside the collection area.

On the maps the areas outside the collection area are shown stippled, in these areas the isolines may be considered to be unreliable.

DISSPLA'S contour plotting routine allows for any isoline interval to be selected and for the line characteristics to be modified. In general the larger the concentration range for an element, the larger the selected isoline interval. The data collected from the annual surveys are presented in a visual form, therefore the isoline interval, which was eventually selected, could not be so large that few lines were drawn, nor could the contour interval be so small that the map became a jumble of lines, which were hard to distinguish. A further criterion was that the selected isoline interval for a particular element would have to be suitable for both the 1983 and 1984 data sets, so as to facilitate the comparison and interpretation of data for the particular element. The selection of a particular isoline interval was not based upon any health or environmental criteria, but only on the resultant map's visual impact.

5.3 RESULTS AND DISCUSSION ON ELEMENT DISTRIBUTIONS

The results for both the 1983 and 1984 surveys from the samples prepared by the cold extraction method are tabulated in the appendix. It has not been possible to find any work which has previously been undertaken on the trace element concentrations in Jacaranda leaf samples, therefore no reference to previously determined levels can be made.

To determine if any of the locations with high trace element concentrations were associated with industrial sources the trace element concentration maps were compared with the distribution of pollution sources maintained by the Air Pollution Control Officer of the Pretoria City Council. Except for Iscor none of the remaining pollution sources corresponded to the locations of the areas of high trace element concentration on any of the maps.

5.3.1 Lead

For both 1983 and 1984 the lower lead concentrations are found in the south of the study area and in the northern suburbs (figures 15 and 16). The main impression from the maps of the 1983 and 1984 distributions of lead is their similarity. An area of higher concentrations (greater than 30ppm) lies on an east-west axis through the City centre, with an extension to the north-west. The two north-south

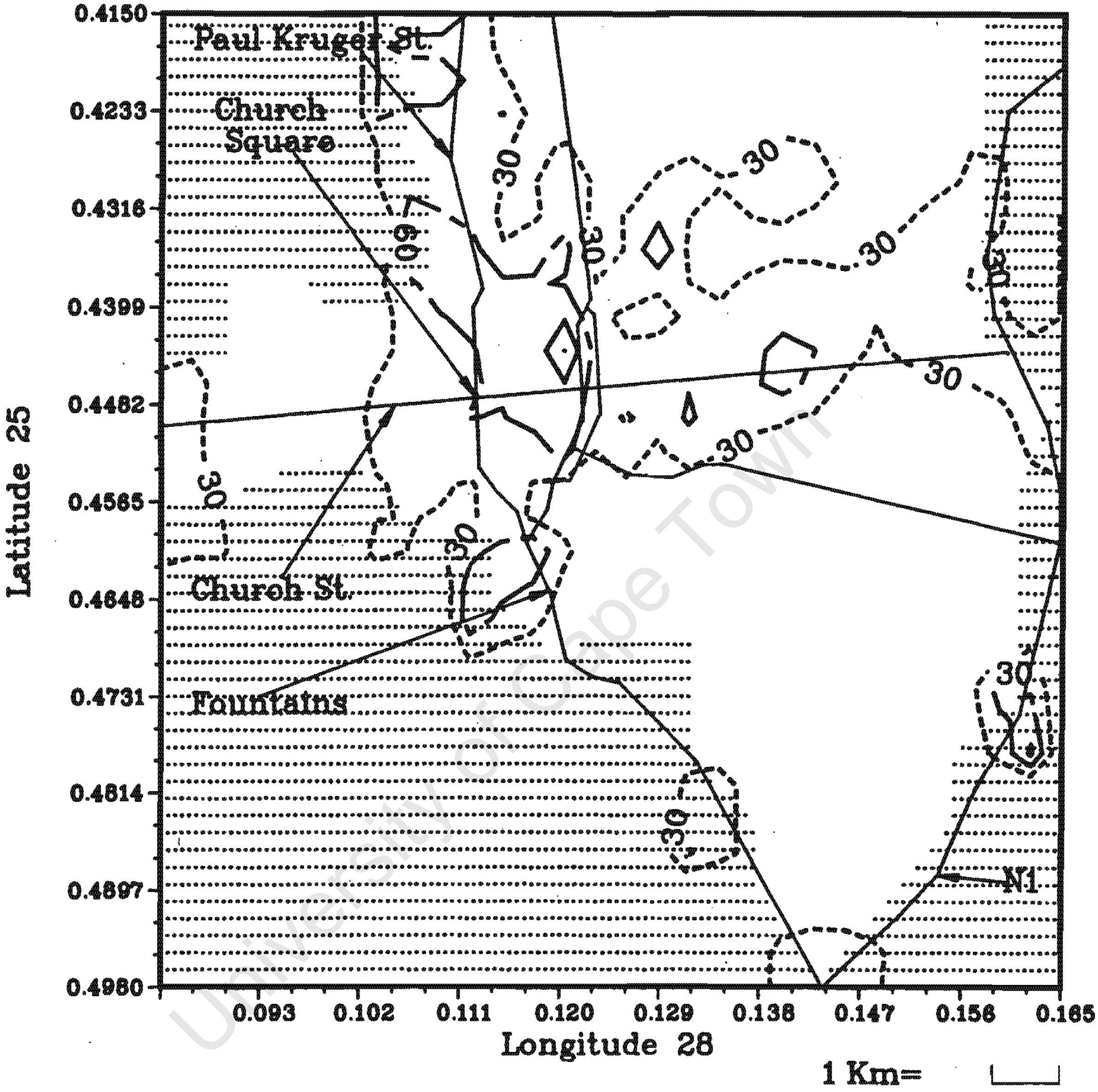


Figure 15. Spatial distribution of lead in Jacaranda leaf samples : Pretoria 1983 (ppm).

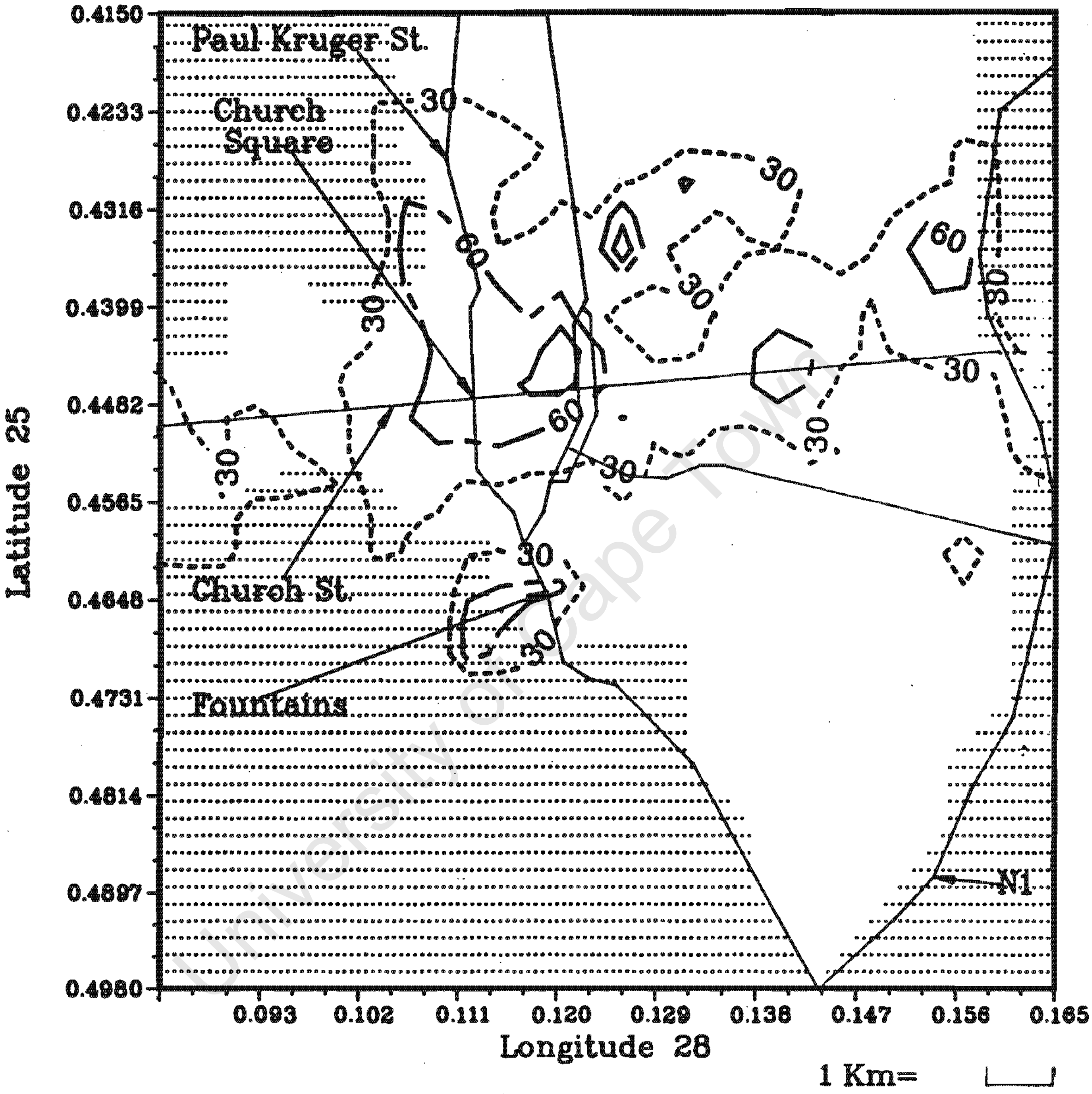


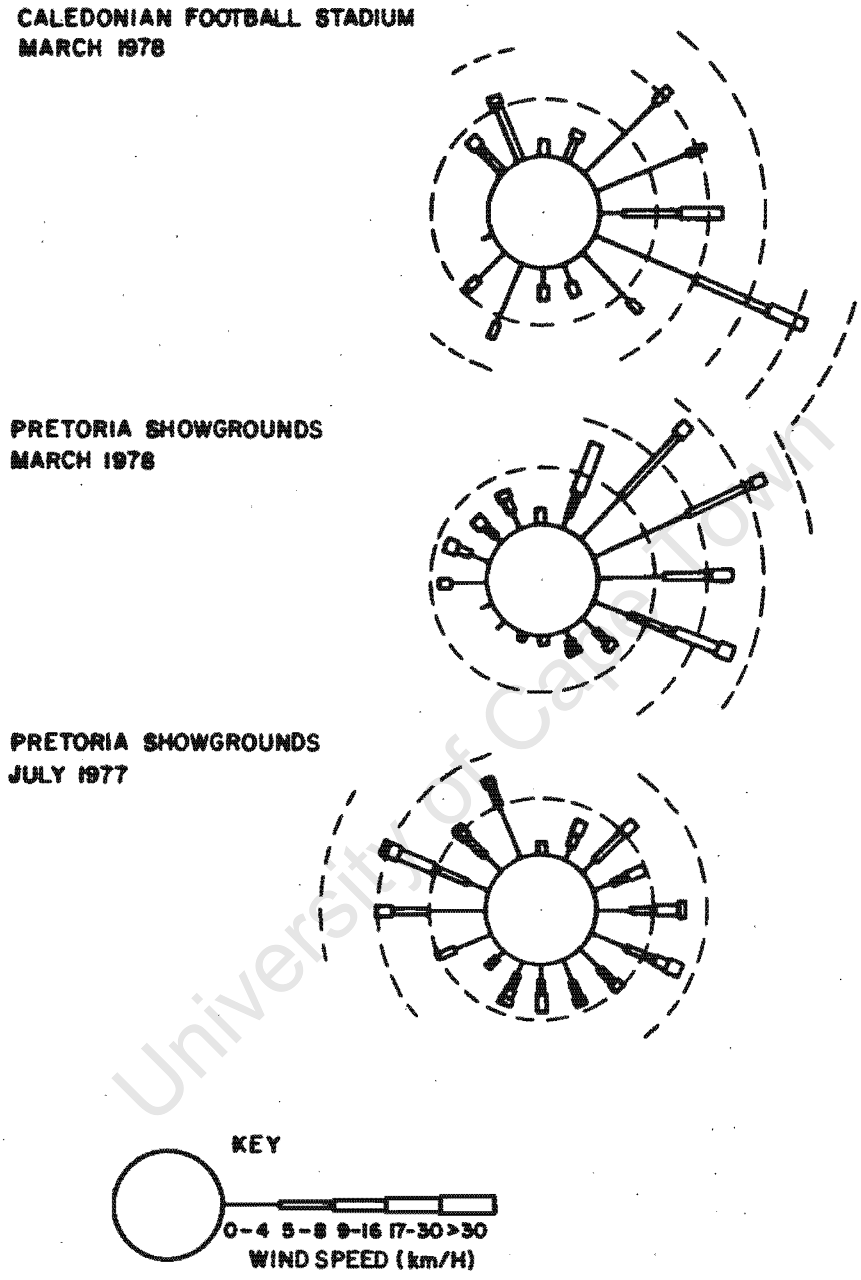
Figure 16. Spatial distribution of lead in Jacaranda leaf samples : Pretoria 1984 (ppm).

orientated lobes in the northwest of the study area correspond to the two major northern traffic routes in and out of the city (Paul Kruger Street and Voortrekker Road). The curved lobe in the north of the picture corresponds to Michael Brink Street (another major traffic route), and between this and the main east-west area is an area of lower concentrations. This is an area of high ground, with no transecting roads, which is mainly occupied by private residences.

The area of higher concentrations of lead to the southwest represents the Fountains Circle, an intersection of four vehicular routes from the south and southeast of the City. The other much smaller areas of high concentration which exist in the southern suburbs of the City in the 1983 survey correspond with off-ramps from the N1 freeway. During the 1984 survey these small features did not appear. A possible reason for this is that any feature on the boundary of the collection area which is based on only one or two samples will be greatly influence by their 'no data' neighbours because of the nature of the algorithm used in the plotting program (section 5.2).

The other areas depicting concentrations greater than 60ppm of lead in leaf samples which are shown on the maps all correspond to major junctions in the City's road system (Kilnerton Circle; corner of Duncan Street and Church Street; corner of Michael Brink and Voortrekker Roads).

This is clear evidence that the source of the lead found in the tree leaf samples is the lead, in its various forms, that is added to petrol. Leaf lead is expected to be correlated with traffic volume and it can be expected that the City centre, with the heaviest traffic, will have the highest leaf lead concentrations. In the situation of a small town, with radially radiating roads, a circular distribution pattern of lead concentrations can be expected (Turner et al, 1984).



CALEDONIAN FOOTBALL STADIUM
MARCH 1978

PRETORIA SHOWGROUNDS
MARCH 1978

PRETORIA SHOWGROUNDS
JULY 1977

Figure 17. Representative Pretoria wind roses for 1978.

Dashed lines indicating 5% frequency intervals.

The distribution of lead as depicted in figures 15 and 16, show that there is an extension of the central high (+60ppm) towards the northwest. In this area the traffic density would be less than in the City centre, however both areas appear to have similar leaf lead concentrations. The reason may be because of the influence of the southeasterly winds which are common at this time of the year.

The wind data for the Caledonian Football Stadium (southeast of the City centre) was examined. This monitoring station was originally part of a larger network which was eventually closed in 1978. As shown by the mean 24-hour wind rose for March, (figure 17), the predominate wind for this time of the year is from the east south east (20% of the total occurrences). It is possible that the lead containing aerosol from the City centre is being transported to the north-western suburbs, where it is being deposited.

5.3.2 Iron

The two maps showing the distribution of iron in the leaf samples for 1983 and 1984 (figures 18 and 19) are similar; the small separated areas of concentrations greater than 90ppm in 1983 have merged together in 1984 to form a larger unified area. The immediate impression from the maps is that higher iron concentrations are to be found in the west, centre and northwest of the City. Within this area the concentrations are seen to have increased between 1983 and 1984.

A major feature of both the 1983 and 1984 maps is the existence of an area of very high leaf concentrations in the west of the City. This area some 1.5 kilometers in diameter, is bounded to the south by the railway line to the Pretoria station; the Pretoria West yards and the Iscor works. Through the centre of the area another rail line runs north via the major Capital Park yards. Although the Iscor iron and steel works were originally placed close to iron deposits, the geology of this small area does not indicate the existence of a small ore body (Mr G.Stone, personal communication). The cause of this area of high leaf iron identified in both the 1983 and 1984 surveys is unknown, it could be local industrial activity or derived from the soil. The area requires further investigation.

The general distribution of leaf iron concentrations appear to be controlled by the topographical features of the area, being restricted to the valley systems of Pretoria (figure 1). The major polluting source of iron in the Pretoria region is the Iscor iron and steel works to the west of the City. Wind measurements were extensively conducted in the years prior to 1978 as part of a larger Pretoria study. The nearest monitoring station to the industrial area was at the Pretoria Showgrounds the location of which is shown in figure 1. The mean 24-hour wind rose for March, (figure 17), shows the predominate winds from the east south east to the northeast.

During the early winter period it is possible that the emissions from Iscor are being transported away from the City. Although some iron is still being transported to the City by local winds of relatively short duration, which follow the local geographical features.

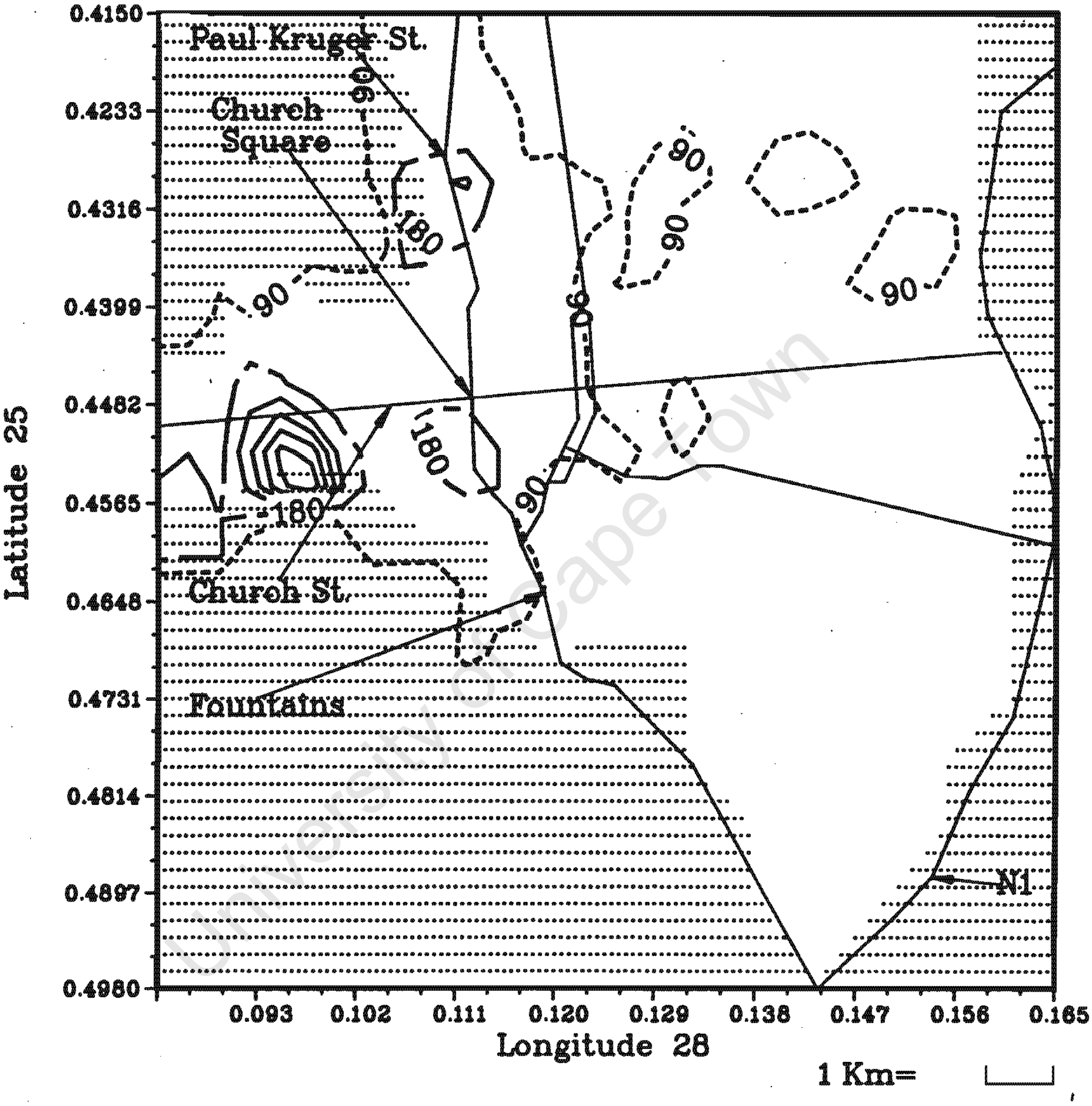


Figure 18. Spatial distribution of iron in Jacaranda leaf samples : Pretoria 1983 (ppm).

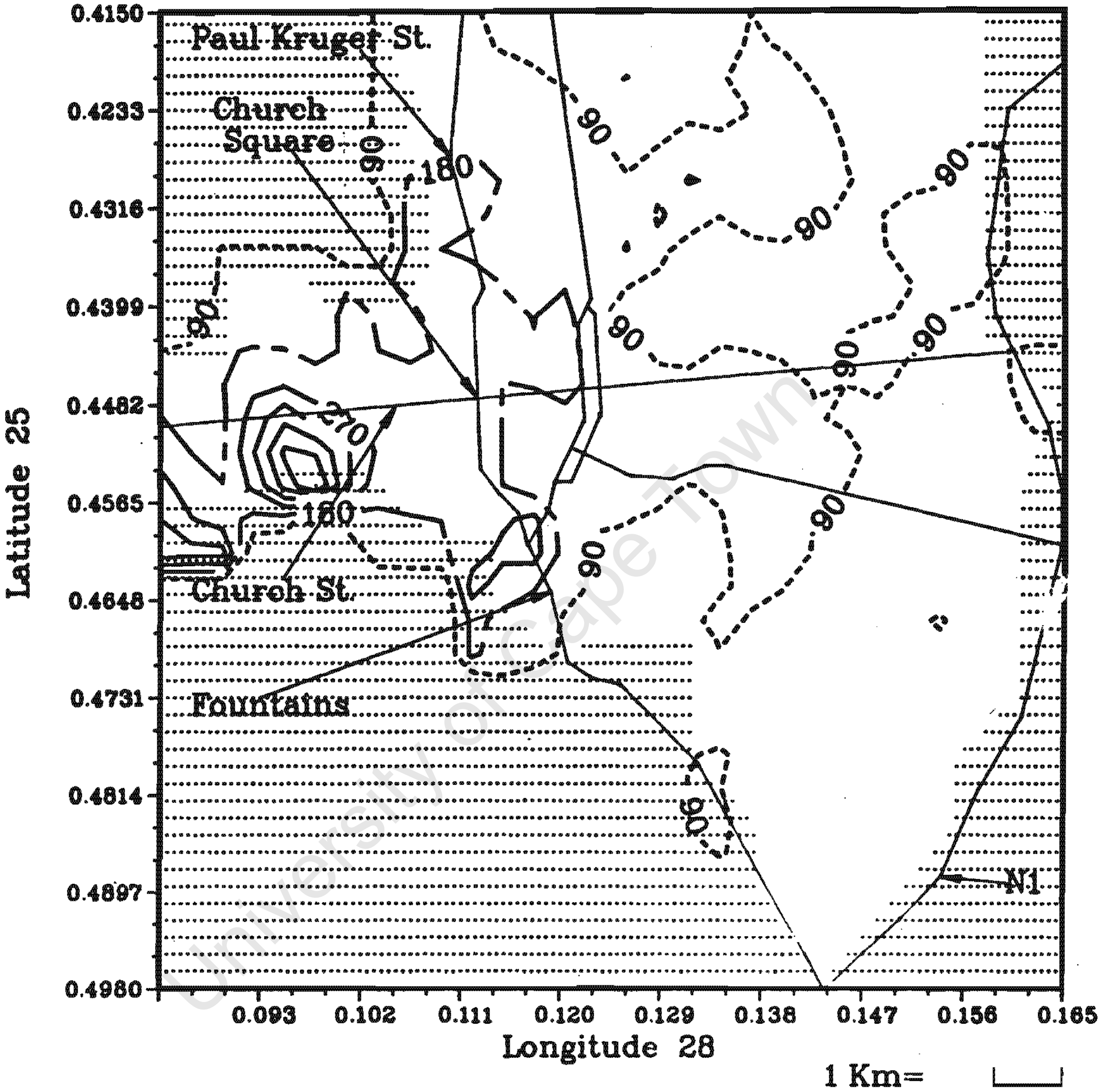


Figure 19. Spatial distribution of iron in Jacaranda leaf samples : Pretoria 1984 (ppm).

From the seasonal study (section 4.4.2), it has been shown that the leaf iron concentrations rise substainually in July and August (figure 11). An examination of the mean 24-hour wind rose for the Showground site for July shows a substantial increase of winds from the west and northwest. These may be transporting iron and manganese containing aerosols into the City area, and in conjunction with the unfavourable winter dispersion meteorology, increases in the resultant leaf concentrations of these two elements are observed.

5.3.3 Manganese

Figures 20 and 21 illustrate the spatial distribution of manganese in the Jacaranda leaves of Pretoria for 1983 and 1984 respectively. There appears to be a widespread increase in manganese concentrations over the two years period; particularly in the centre, west and north of the study area. In general, lower concentrations are found in the northern and central areas of the City.

In the southern part of the study area a number of small areas of high concentration of manganese occur, surrounded by a larger area of enhanced concentrations. This southern area is residential, and therefore the source of manganese can not be industrial activity. The absence of associated high iron concentrations (figures 18 and 19) suggests that the high manganese concentrations cannot be attributed to emissions from the iron and steel works in the west of the study area.

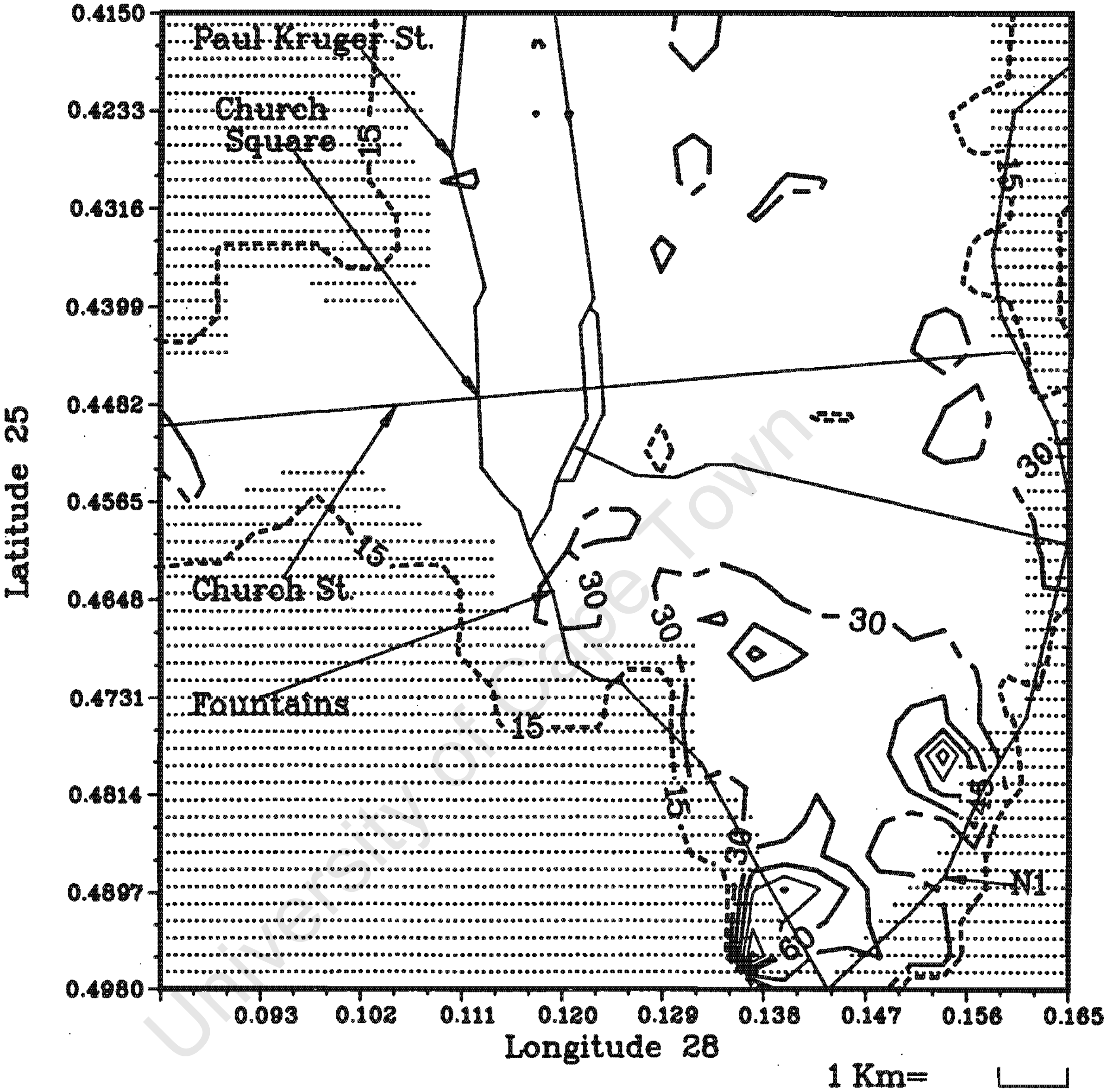


Figure 20. Spatial distribution of manganese in Jacaranda leaf samples : Pretoria 1983 (ppm).

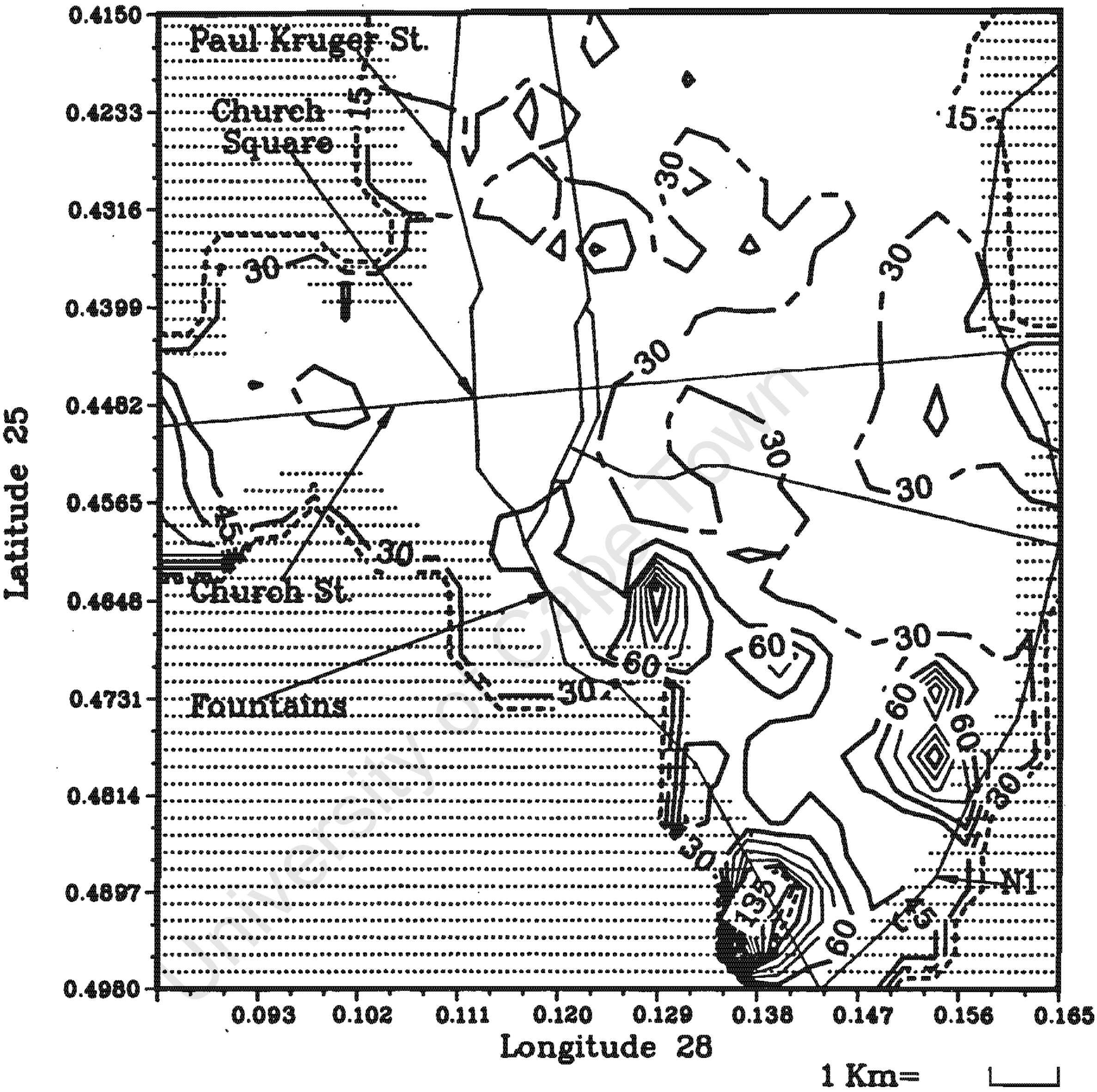


Figure 21. Spatial distribution of manganese in Jacaranda leaf samples : Pretoria 1984 (ppm).

Consultation with the staff from the Geological Survey of the Department of Mineral and Energy Affairs suggested no correlation between the geology of the area and the anomalous points. Nevertheless, the southern most area of high manganese concentrations is situated on the contact between the Karoo sequence and the Transvaal sequence of rocks. In such contact zones, water infiltration has a tendency to form wad (hydrated manganese oxides, usually containing iron oxides) from the dolomite. It is possible that in this location the concentrations of manganese in the Jacaranda leaves are influenced by the rock and soil concentrations of manganese.

This does not explain the occurrence of all of the small areas of high manganese concentrations nor the generally higher concentrations of manganese found in the leaf samples from the south of the study area. Since to some extent the features exist for both 1983 and 1984 this warrants further investigation to establish whether the leaf concentrations are related to geological features or atmospheric deposition.

5.3.4 Zinc

The two maps (figures 22 and 23) depicting the 1983 and 1984 distribution of zinc in the leaf samples differ considerably. The range of zinc concentrations is smaller than for the previously descibed elements. Within the study area the 1983 distribution of zinc is very uniform, with only isolated instances of concentrations above 16ppm, and one case in the south of the area in which the concentration for a single sample rose to

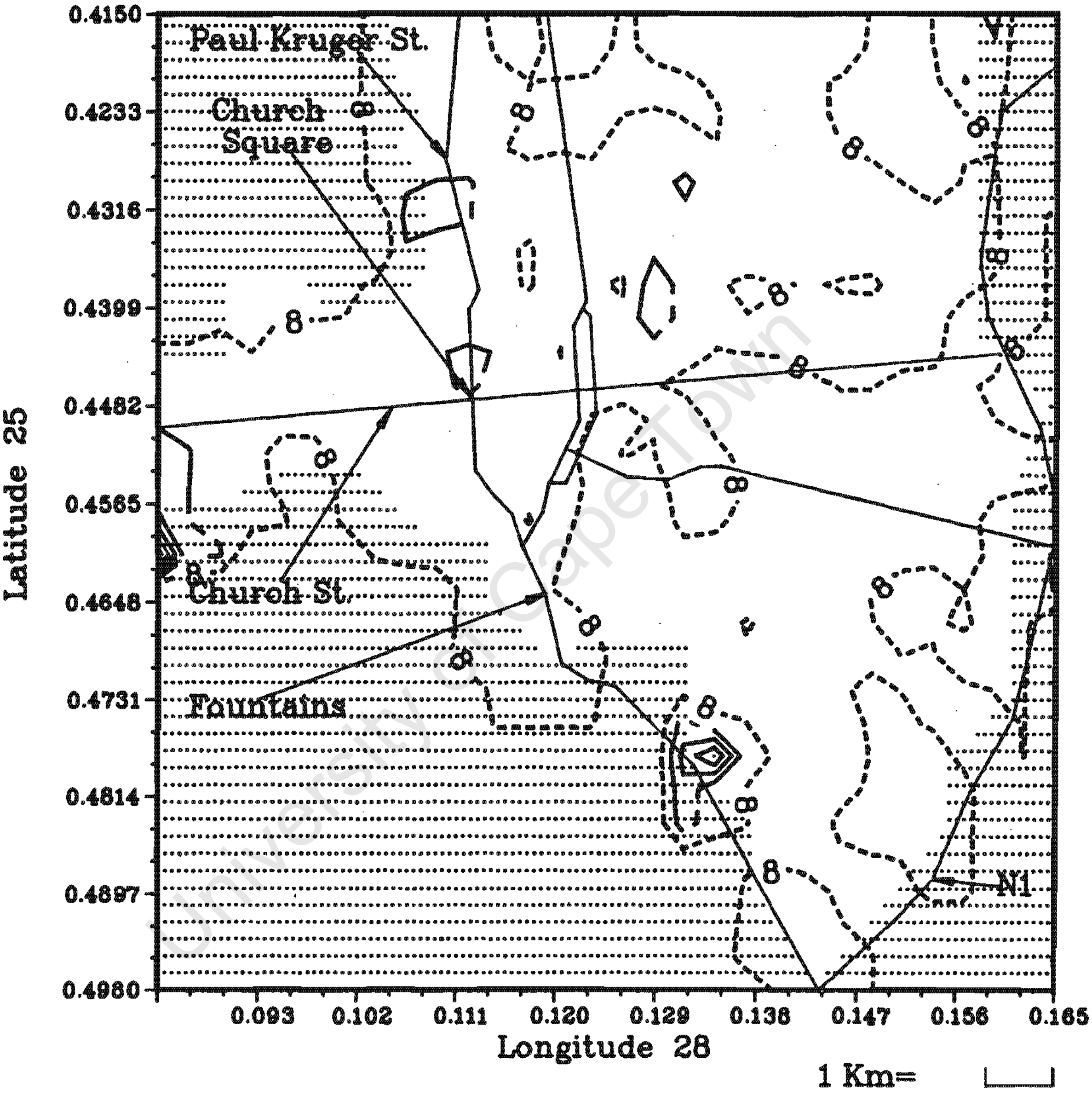


Figure 22. Spatial distribution of zinc in Jacaranda leaf samples : Pretoria 1983 (ppm).

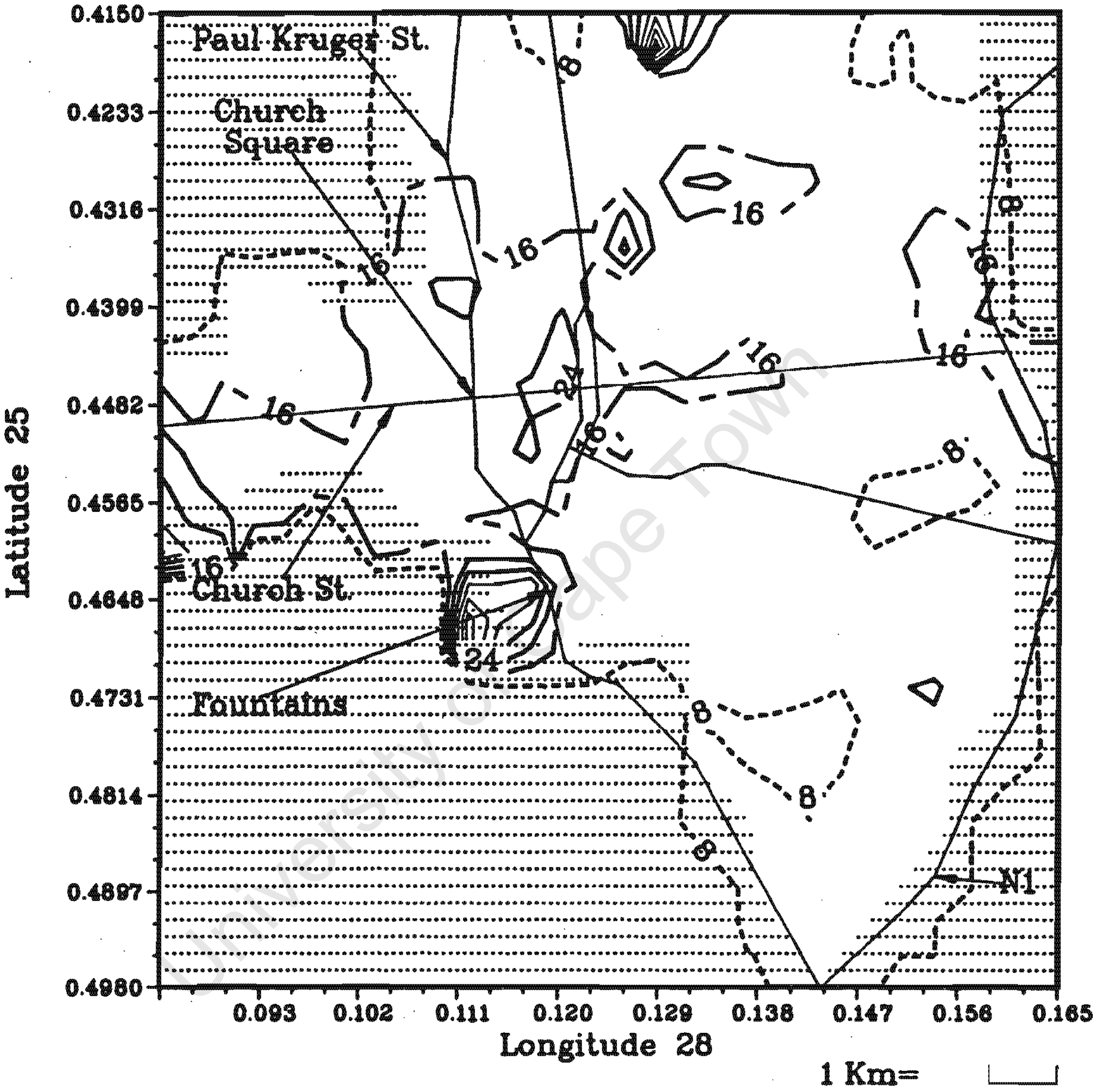


Figure 23. Spatial distribution of zinc in Jacaranda leaf samples : Pretoria 1984 (ppm).

54ppm. (Higher concentrations were also found in the heavy industrial area which is located just outside the study area.)

In 1984 the distribution pattern clearly illustrates the increase in zinc concentrations that occurred between 1983 and 1984. In 1984 there was a single large area corresponding to concentrations greater than 16ppm. This area covers the west and central areas of the city, the small lobes coincide with the major traffic routes. There are two small areas of high concentrations, one corresponds to the Fountain Circle an area of very high traffic density. The other area in the north of the Pretoria and is based on a single high leaf sample. None of this sample's neighbours are high nor was the concentration from the same tree in 1983 high. Therefore this result could be caused by sample contamination and should be verified.

The similarity between the distributions for the urban concentrations of leaf zinc and lead (figures 23 and 16) indicate that they probably share the same major source, although derived from different components. The source of zinc is the motor car in which zinc is used extensively in the tyres and oil.

Why there was a general increase in concentrations between the two years is unknown, if the source is the motor car, since no significant change in the city's vehicle population occurred at this time.

5.3.5 Copper

In both 1983 and 1984 copper displayed the smallest standard deviations of the five elements examined, (4 to 5 ppm). The selection of a suitable isoline interval is difficult in such situations. The maps (figures 24 and 25) show that there was in general a small increase in leaf copper concentrations over the two years. There appear to be no areas of enhanced or high concentrations within the study area. In 1983 the distribution map shows that the highest concentrations that existed occurred in the City centre and in adjoining areas of high traffic flow. Although in general all the 1984 concentrations increased slightly, the areas of higher concentration are found in the City centre. It is therefore probable that the source of the leaf copper are the various components (electrical and oil) of the motor car.

5.4 STATISTICAL ANALYSIS OF SURVEY RESULTS

The data for the 313 Jacaranda trees is significantly skewed in both 1983 and 1984. Tests for the analysis of variance assume that the data is normally distributed (SAS, 1985). In order to apply these tests it was required that the data is first logarithmically transformed. The means and standard deviations for the raw and logarithmically transformed trace element data, for both 1983 and 1984, are presented in table 13.

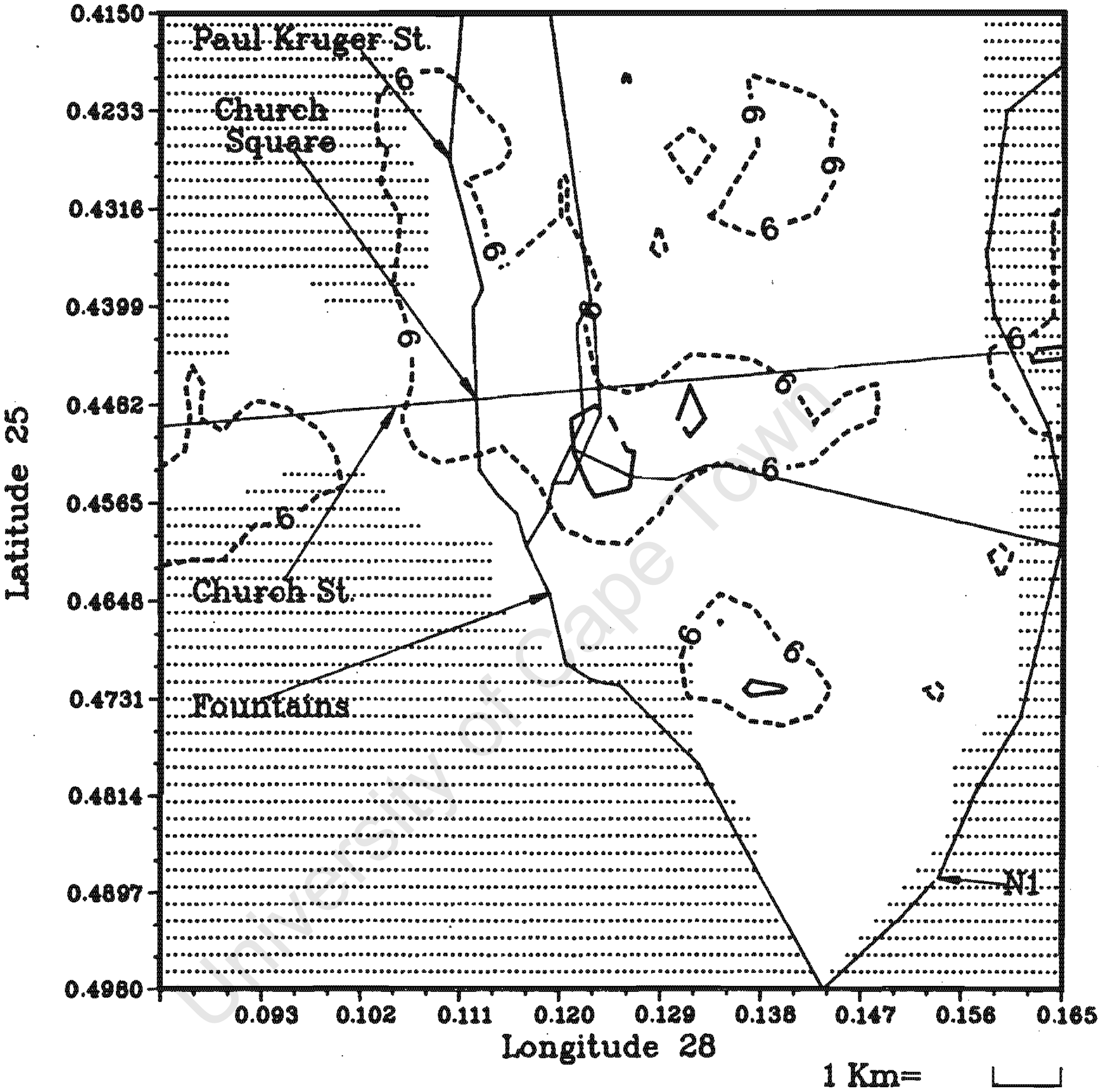


Figure 24. Spatial distribution of copper in Jacaranda leaf samples : Pretoria 1983 (ppm).

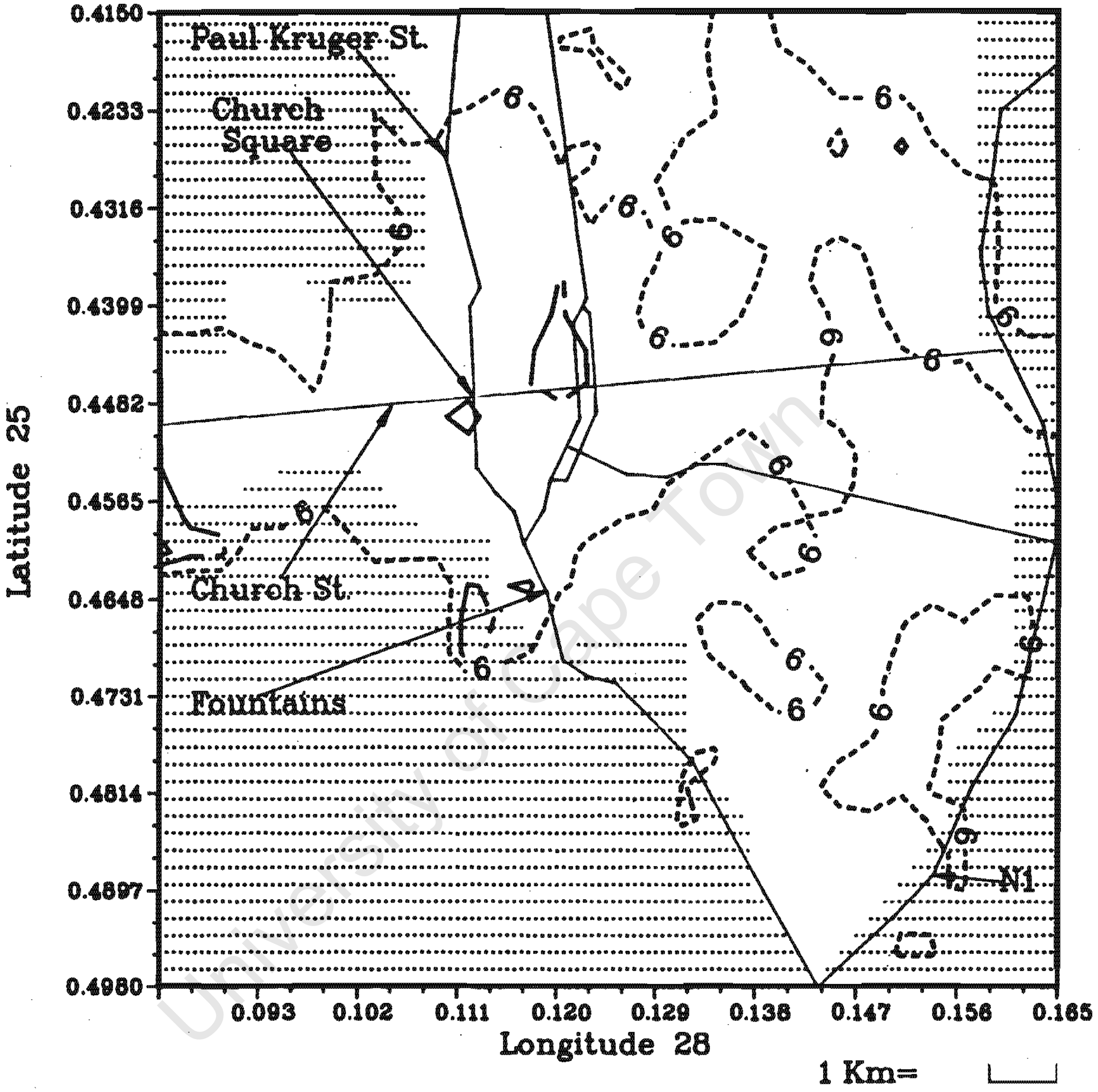


Figure 25. Spatial distribution of copper in Jacaranda leaf samples : Pretoria 1984 (ppm).

The transformed data was used to test for a significant difference between the 1983 and 1984 data. A change in the variance between the two years would show up as a correlation between the sums and differences of the concentrations.

The mean differences between the 1984 and 1983 data sets and the correlation between the mean differences and sums, with the significance for each test is shown in table 14. These results show that the trace element concentrations in the 1984 survey were significantly higher than those in the 1983 survey. The variance in the range of concentrations was higher in 1984 than in 1983 for iron, but did not change for the other trace elements.

There is no apparent reason (the collection, preparation and analysis of all of the samples being the same) why the trace element concentrations were higher in 1984 than in 1983. The study into the seasonal trends of leaf concentrations (section 4.4.2) indicated that none of the five elements leaf concentrations would be higher in April than in June. Therefore the reason for the increase can not be because the 1984 samples were collected earlier in the year than those in 1983 (mid-April rather than mid-June).

5.4.1 Inter-elemental leaf correlations

As the study progressed it became apparent that the leaf concentrations of iron and manganese were related. The study on the effects of varying acid strength (section 3.2.1; figures 3 and 4)

Table 13. Statistical analysis of annual survey data.

	1983		1984	
	mean	standard deviation	mean	standard deviation
RAW DATA				
lead	26.33	27.40	28.83	24.41
iron	87.61	87.58	118.40	96.06
manganese	26.33	14.88	36.96	26.39
zinc	9.91	11.75	14.25	10.71
copper	5.48	4.81	6.90	4.47
LOG-TRANSFORMED DATA				
lead	2.92	0.80	3.02	0.79
iron	4.22	0.65	4.58	0.57
manganese	3.15	0.47	3.47	0.48
zinc	2.11	0.53	2.50	0.51
copper	1.49	0.60	1.77	0.56

Table 14. Statistical study of log-transformed data.

	mean difference	s.d.	sig.	correlation	sig.
lead	-0.102	0.415	<0.0001	0.024	<0.667
iron	-0.371	0.484	"	0.216	<0.0001
manganese	-0.318	0.451	"	-0.020	<0.729
zinc	-0.395	0.498	"	0.042	<0.456
copper	-0.283	0.572	"	0.086	<0.129

Table 15. Correlation coefficients for elements, 1983 and 1984 survey data. (n=313).

1983	lead	iron	manganese	zinc	copper
lead		0.416	0.020	0.322	0.354
iron			0.193	0.487	0.417
manganese				0.373	0.150
zinc					0.502
1984					
lead		0.411	0.072	0.535	0.545
iron			0.307	0.628	0.647
manganese				0.345	0.328
zinc					0.752

Table 16. Inter-elemental correlations at the four urban sampling sites.

		lead	iron	manganese	zinc	copper
AFROX n=10	lead		0.6685	0.6260	-0.0825	0.0414
	iron			0.9722	-0.1070	0.1661
	manganese				0.0182	0.1733
	zinc					0.5796
	copper					
HAMILTON n=22	lead		0.7175	0.6255	0.1376	0.0203
	iron			0.8646	0.4227	0.3894
	manganese				0.6764	0.5747
	zinc					0.8374
	copper					
MUNITORIA n=10	lead		0.9207	0.8621	0.7070	0.5040
	iron			0.9605	0.8641	0.6166
	manganese				0.9073	0.7193
	zinc					0.6466
	copper					
VISAGIE n=10	lead		0.8841	0.6891	0.7981	0.7342
	iron			0.6591	0.7624	0.6058
	manganese				0.8258	0.8645
	zinc					0.8636
	copper					
ALL n=52	lead		0.2585	0.1311	-0.1264	0.0899
	iron			0.8014	0.5346	0.3746
	manganese				0.5914	0.5215
	zinc					0.6234
	copper					

indicated that iron and manganese reacted in a similar manner. In the study of the seasonal variations (figure 9) the trends of leaf iron and manganese also appeared to be closely related to each other.

The 1983 and 1984 distributions for the leaf concentrations of iron and manganese are markedly different from each other (figures 19 and 21). The high leaf iron concentrations in the west and centre of Pretoria, and the high manganese in the southern suburbs, dominate their respective maps. The correlation analysis between each of the elements for the 1983 and 1984 data sets (table 15) revealed no strong correlation between any of the elements. This data was collected on a predetermined grid throughout Pretoria covering approximately 100 square kilometers. Over this area local influences such as wind direction and distance from sources, as well as changing particle deposition rates, will change the local aerosol composition and hence reduce a wide geographical correlation between the deposited particles on a leaf surface.

When the data from the four urban sampling sites was analysed, rather than the data from the annual surveys, the leaf concentrations of iron and manganese were found to be correlated for all of the individual sites and for the combined data set (table 16). This confirmed the visual observation that there was a similarity between the trends of the concentrations of these two elements. The correlations between the leaf concentrations of the other elements varied between sampling sites from poor to strong. None of the concentrations of these other elements were correlated for the combined data set.

The Pretoria trace element aerosol must vary considerable throughout the urban area. At specific localities the existence of a correlation between elements is dependant upon the source, and distance from the source to the sampling point. As these factors change so does the local aerosol characteristics and consequently the composition of the leaf surface deposits.

5.5 CHAPTER SUMMARY

After considering the sampling requirements and the available resources, a sampling grid based on 500 meter sides was selected. This was used to determine the sampling sites. The 500 meter grid provided sufficient data for detailed isolines to be constructed. A 1000 meter grid could only provide information on the basic trace element distribution, however this lacked essential detail.

Leaves from the same 313 trees were sampled between the 18 and 23 June 1983 and the 12 and 16 April 1984. Trees which were unduly influenced by local pollution were not sampled. Four sub-samples, each of two leaves, were taken at ninety degrees to each other, from the outermost edge of the tree, on a horizontal plane at a height of between four and five meters.

The isolines were generated from the available data by the use of the mainframe computer package DISSPLA. None of the high areas for trace element leaf concentrations were shown to correspond with known pollution sources.

The high concentrations of leaf lead were found in the City centre and along the main traffic routes. It is possible that the predominant south easterly wind for the period of sampling, transports the lead loaded aerosol from the City centre to the northwest suburbs of

Pretoria. The concentrations of iron are influenced by Iscor, the iron and steel works, to the west of the study area. The highest leaf iron concentrations were found in the west, centre and northwest of the City. There is one area of high leaf iron concentrations which existed in both 1983 and 1984 in the west of Pretoria for which a source, either geological or industrial, could not be determined.

The concentrations of leaf manganese are at the lowest in the northern and central areas of the City. The southern part of the area is characterised by high concentrations of leaf manganese, which because of the absence of associated high iron concentrations cannot be attributed to Iscor. No direct link between the soil and outcrop geology of the area and the leaf manganese distribution could be established. However, it is still probable that the high leaf manganese is due to local soil or sub-soil manganese, possibly at the contact boundary of the Karoo and Transvaal geological sequences.

Both leaf zinc and copper concentrations show little variation over the study area. The highest copper concentrations are found in the City centre. There appears to be no areas within Pretoria of enhanced concentrations of these two elements due to specific pollution sources.

The leaf concentrations for all of the studied trace elements were higher in 1984 than in 1983. In both years the range in concentrations for each element was the same except for iron, for which the range was higher in 1984 than 1983, (table 14).

Contrary to the indications from the seasonal study, no correlation was established from the combined data set between any of the elements, (table 15). In the seasonal survey, the leaf concentrations of iron and manganese for the four urban sampling sites are shown to be correlated at each of the sampling sites and for the combined data set, (table 16). At these sites there are reasonable correlations between some of the other studied elements. However, because of varying aerosol composition and deposition across the City, none of these inter-element correlations can be applied collectively to all of the sites.

At each of the urban sampling sites a deposit gauge and/or air-filter unit was operational. The results from these sampling mediums in relation to the adjacent leaf concentrations are discussed in the next chapter.

CHAPTER 6

CORRELATION WITH OTHER SAMPLING TECHNIQUES

6.1 INTRODUCTION

The aim of this study was to illustrate the distribution of five trace elements in the Pretoria urban area by reference to the concentrations of these elements in Jacaranda leaves. The generated maps provide a visual indication of the relative high and low areas of leaf concentrations. There would be considerable advantages for the interpretation and practical use this information if an indication of associated atmospheric concentrations could be obtained. One way to achieve this would be by establishing the relative contribution from either the soil or the atmosphere to the leaf concentrations.

For reasons outlined in section 2.2.2 no soil analysis was undertaken simultaneously with leaf sampling during this study. Thus the relative contribution to the leaf concentrations from the soil could not be determined.

At each of the four urban sampling sites from which samples were regularly taken, an air-filter unit and/or deposit gauge was operational. In this manner, an estimate of the relative contribution from the atmospheric aerosol to the leaf concentrations could be made.

6.1.1 Correlation with deposit gauges.

Deposit gauges have been in operation at the Afrox and Visagie Street sampling sites since the mid 1970's. An additional gauge was set up at Hamilton Street in October 1983. The gauges were adjacent to, but not under the trees being sampled. The monthly samples were prepared and analysed by the same techniques as used for the air-filter samples (Vleggaar et al, 1980).

Plots of the relationship between the deposit gauge results and those for the leaf concentrations, determined by the cold extraction and hot digestion methods are shown in figures 26 and 27 respectively. The leaf concentrations, as determined by the hot digestion method, are higher than those from the cold extraction.

The Afrox site has a dominant effect on the overall correlation between the results from the deposit gauge and leaf concentrations because of the close proximity of Iscor, the iron and steel works. Only at the Afrox site are the leaf concentrations of iron and manganese correlated with the deposit gauge results (table 17). In addition the correlation for zinc and copper, although poor, is higher than for the other sites. Any relationship between the results from the deposit gauges and associated leaf concentrations is valid only over a small area. For example the correlations for iron and manganese at the Afrox site does not apply at the Visagie Street site, a distance of only six kilometers.

If the data points for the Afrox site are ignored in the figures 26 and 27, the leaf concentrations do not increase with increasing

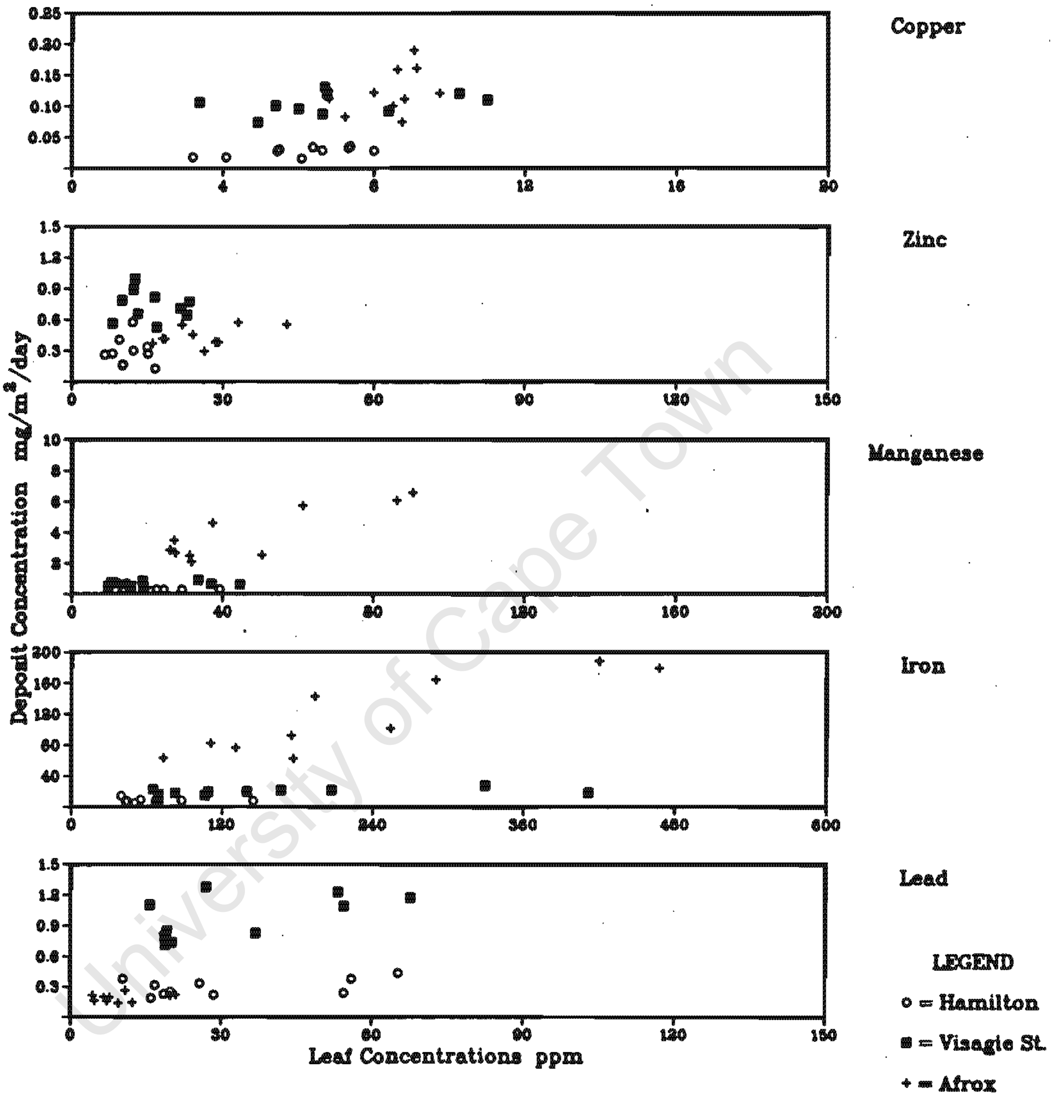


Figure 26. Comparison between leaf and deposit gauge concentrations. October to August 1984/5 - cold extractions.

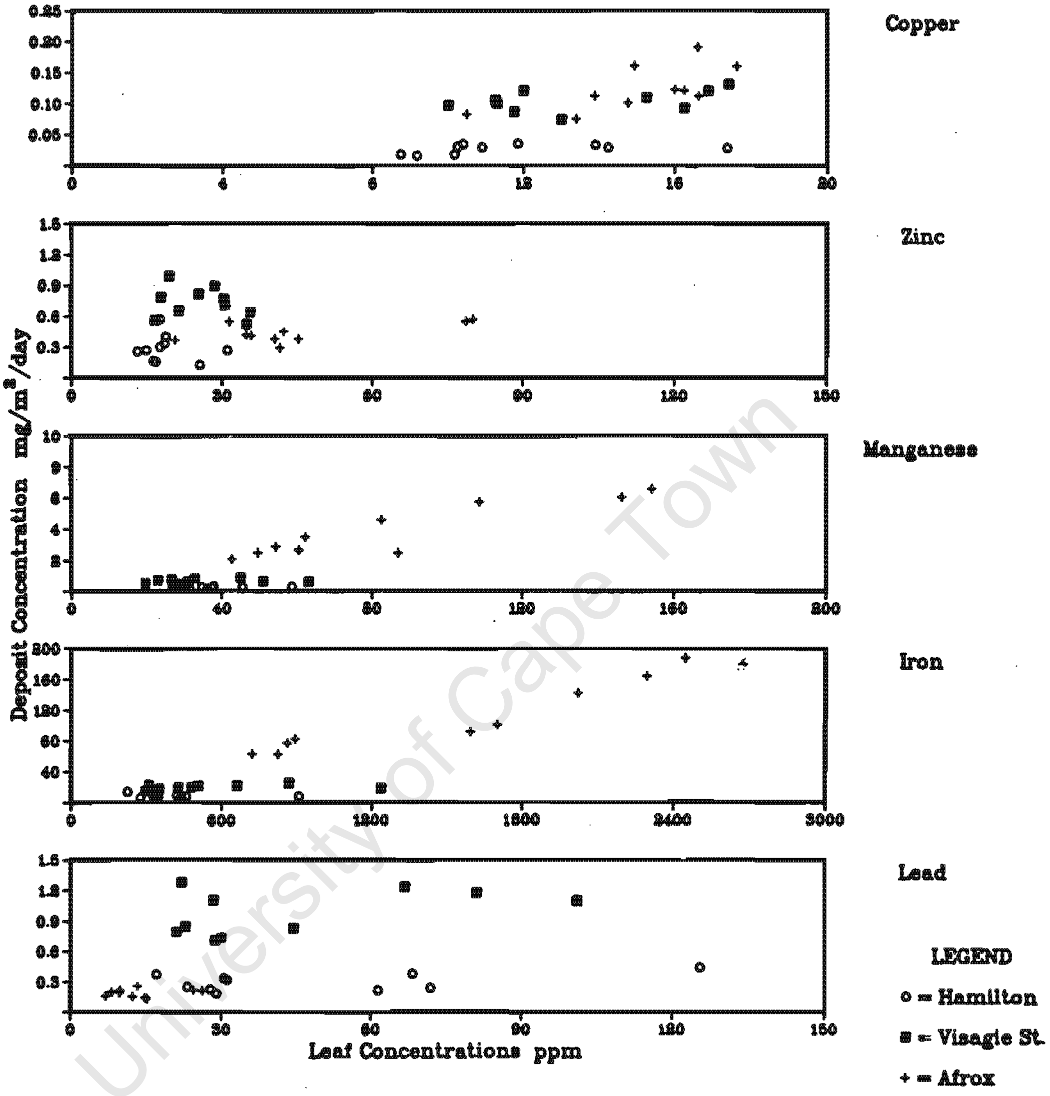


Figure 27. Comparison between leaf and deposit gauge concentrations. October to August 1984/5 - hot digestions.

Table 17. Correlation statistics for leaf, air-filter and deposit gauge data, r.

LEAD	ALL SITES	AFROX	HAMILTON	MUNITORIA	VISAGIE
Lc v Lh	0.9245	0.9653	0.8994	0.8913	0.9124
Lc v F	0.9156	0.3689	0.8984	0.8386	-
Lh v F	0.8915	0.3230	0.8726	0.7759	-
Lc v D	0.3575	0.3035	0.4267	-	0.5786
Lh v D	0.2832	0.2588	0.4913	-	0.4609
F v D	0.6372	-0.0228	0.5768	-	-
IRON					
Lc v Lh	0.8251	0.8993	0.9604	0.7576	0.9838
Lc v F	0.8386	0.7568	0.6544	0.6008	-
Lh v F	0.8955	0.7605	0.8661	0.8707	-
Lc v D	0.6836	0.8865	0.3490	-	0.4327
Lh v D	0.9101	0.9633	0.4564	-	0.3736
F v D	0.8555	0.7290	0.4368	-	-
MANGANESE					
Lc v Lh	0.9553	0.9735	0.9332	0.8708	0.9761
Lc v F	0.8482	0.8695	0.6369	0.4941	-
Lh v F	0.9347	0.9114	0.8278	0.7712	-
Lc v D	0.7162	0.8564	0.2703	-	0.1308
Lh v D	0.8803	0.9184	0.5347	-	0.1835
F v D	0.8496	0.8587	0.2805	-	-
ZINC					
Lc v Lh	0.9132	0.8942	0.7476	0.6210	0.8241
Lc v F	0.7058	0.4549	0.0681	0.5036	-
Lh v F	0.7959	0.6643	0.0752	0.3832	-
Lc v D	0.1483	0.4534	-0.2299	-	-0.1236
Lh v D	0.1439	0.6091	-0.2058	-	-0.2697
F v D	0.6013	0.5908	-0.2811	-	-
COPPER					
Lc v Lh	0.6496	0.5957	0.2737	0.7789	0.6641
Lc v F	0.0877	0.4036	0.0116	0.1050	-
Lh v F	0.2731	0.8028	-0.1359	0.0915	-
Lc v D	0.3146	0.4047	0.3666	-	0.3338
Lh v D	0.6374	0.6710	0.2724	-	0.4486
F v D	0.1717	0.5618	0.5077	-	-

Lc - leaf cold extraction
Lh - leaf hot digestion
F - air filter
D - deposit gauge

deposit gauge concentrations, as would be expected if there was a workable correlation between the two sampling mediums that could be applied for Pretoria.

The lack of agreement between the leaf concentrations of trace elements and the associated results from adjacent deposit gauges may be due to the design of the gauge minimising the loss from the collection bowl. The deposited particles on a leaf surface will be continually lost to the environment. Rainfall will wash from the leaf surface the easily removed deposits, however the same rain would aid the collection and retention of deposits in a gauge.

The results from the Jacaranda leaf analysis can not be used to augment the information collected from the current network of deposit gauges throughout Pretoria. The collection of leaf samples can not substitute for the deployment of these gauges.

It is possible however that if an area of interest was small and was close to a dominant source of particulate pollution (e.g. the Afrox site and the iron and steel works) that leaf analysis could yield valuable information.

6.1.2 Correlation with air-filters

Monitoring stations of airborne particulates are in operation in Pretoria at the Munitoria, Afrox and Hamilton Street sites, the locations of which are shown in figure 1. The method of sample collection and analysis is described by Vleggaar et al (1980).

Figures 28 and 29 show the relationship between the trace element concentrations, as determined by the air-filters, and those from the leaf analysis, for the cold extraction and hot digestion techniques respectively.

It is apparent from an examination of the plots that there is no relationship between these two sampling methods for copper. In the case of lead, iron, manganese and zinc there is a possible relationship between the two different analytical techniques.

In table 17 the correlation coefficent, r, is given for each individual site and for the combined data set for both the cold extraction and hot digestion techniques. In the case of Hamilton street the data from 1983 has been included with that from 1984.

The leaf concentrations from the combined data set, determined by either the cold extraction or hot digestion methods, significantly correlate with the results obtained from the air-filters for lead, iron, manganese and zinc. The correlation at each of the four sampling sites varies due to the different aerosol composition. Except for lead, the leaf concentrations are the highest at the Afrox sampling site because of the surrounding industrial sources. Unlike the situation with the deposit gauges the range of concentrations at the sampling sites normally overlap each other. If the data points from the Afrox site are ignored in figures 28 and 29 the visual correlation between the two sampling mediums is still observed. At the Hamilton Street and Munitoria sites the correlations between the leaf and filter concentrations for iron and manganese are better for the hot digestion than the cold extraction method of sample preparation. For zinc, the correlation is poor at each of the individual sampling sites but considerably improves for the combined

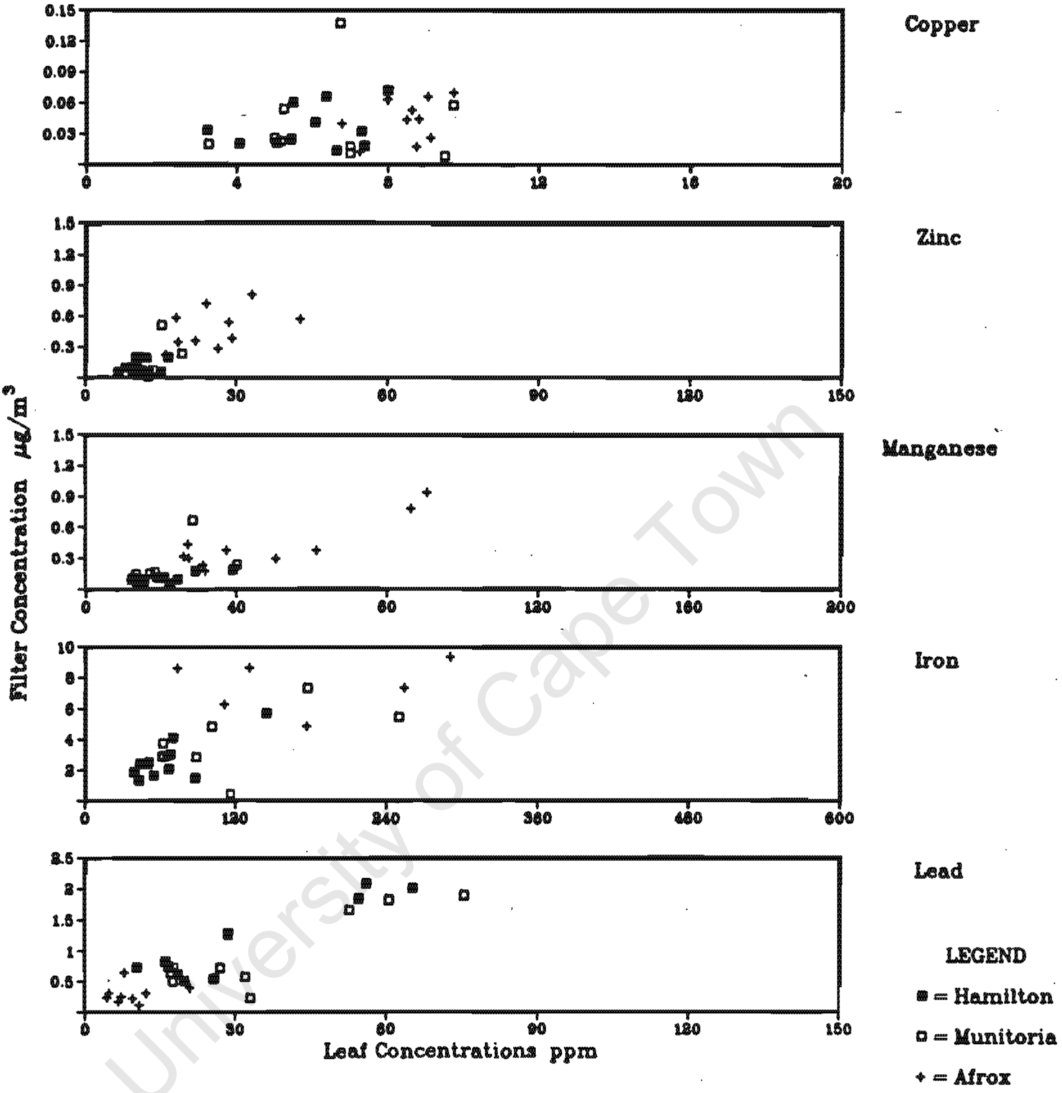


Figure 28. Comparison between leaf and air filter concentrations. October to August 1984/5 – cold extractions.

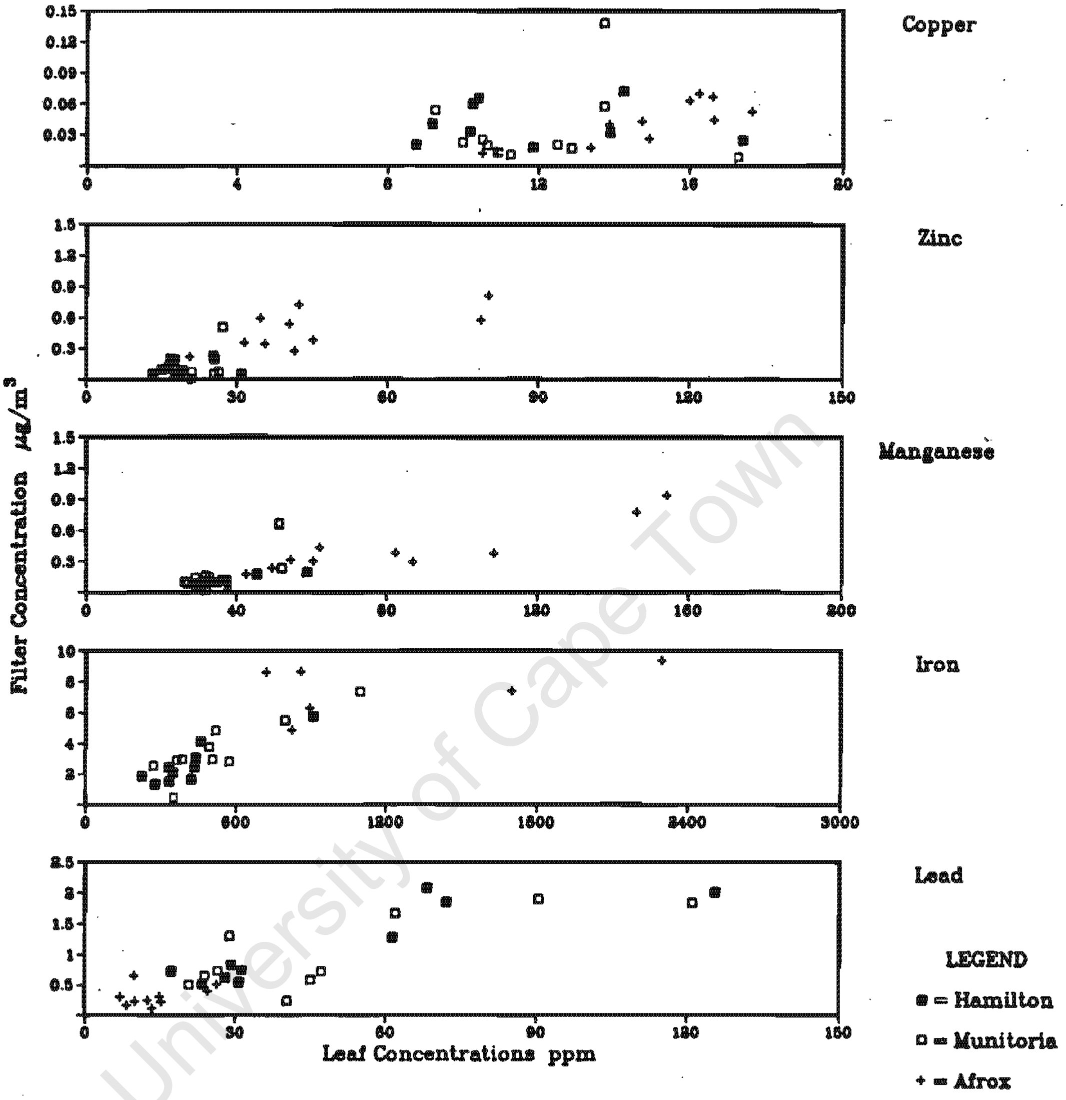


Figure 29. Comparison between leaf and air filter concentrations. October to August 1984/5 - hot digestions.

data set. The reason for this is that at each sampling site the range of concentrations is small and do not overlap each other, thus by plotting the data together the range of concentrations is enlarged.

The effect that the results from the Afrox site has on the correlations is not evident for lead because at this sampling site there is minimal traffic and consequently the lead concentrations are very low.

In the next section the regression equations for the correlations between the air-filters and leaf samples are used to make a preliminary assessment of the atmospheric concentrations of lead, iron, manganese and zinc.

6.2 SIMULATED ATMOSPHERIC CONCENTRATIONS

The correlation coefficents for the linear relationship between the results from the air-filter units and adjacent Jacaranda tree leaves (table 17), suggest that it is possible to transform leaf concentration collected in the 1984 survey into corresponding atmospheric concentrations. Such data can easily be replotted.

The advantage of presenting the data in this form is that the distribution maps of the trace element concentrations now highlight areas of airborne contamination. These can be compared with emission data from known sources. It is possible that areas of past contamination which are presently unknown could be identified. The maps could also be used to provide information on the optimum geographical location for airborne particulate monitoring stations, so that these can be shown to be representative of the area.

It is not appropriate to compare these estimated concentrations directly with published health criteria as a means of control or as a stimulus for control, since the determination of the concentration is indirect. Nevertheless the values can be used to determine areas which may give rise to concern on the basis of public health and in which further monitoring is required.

6.2.1 Lead

The linear regression equation [2] used to transform leaf concentrations of for Pretoria with, in brackets, the standard errors is :

$$Conc_{air} = 0.0936 + 0.0280{*}Conc_{leaf} \qquad [2]$$

$$(0.0668)\ (0.0020) \qquad R^2 = 0.838$$

Where $Conc_{air}$ is lead concentration in the air, µg/m^3

$Conc_{leaf}$ is leaf concentration of lead (ppm), determined by the cold extraction method

Taking into consideration the standard errors, the range of simulated atmospheric concentrations from leaf concentrations of 30, 60 and 90ppm are 0.8068 to 1.0004, 1.5868 to 1.9604 and 2.3668 to 2.8604 µg/m^3 respectively.

The map (figure 30) highlights areas of enhanced concentrations in the City centre, at the Fountains Circle; at the junction of Duncan and Church Streets and also at the Kilnerton Circle. The latter three areas correspond to major points of traffic convergence.

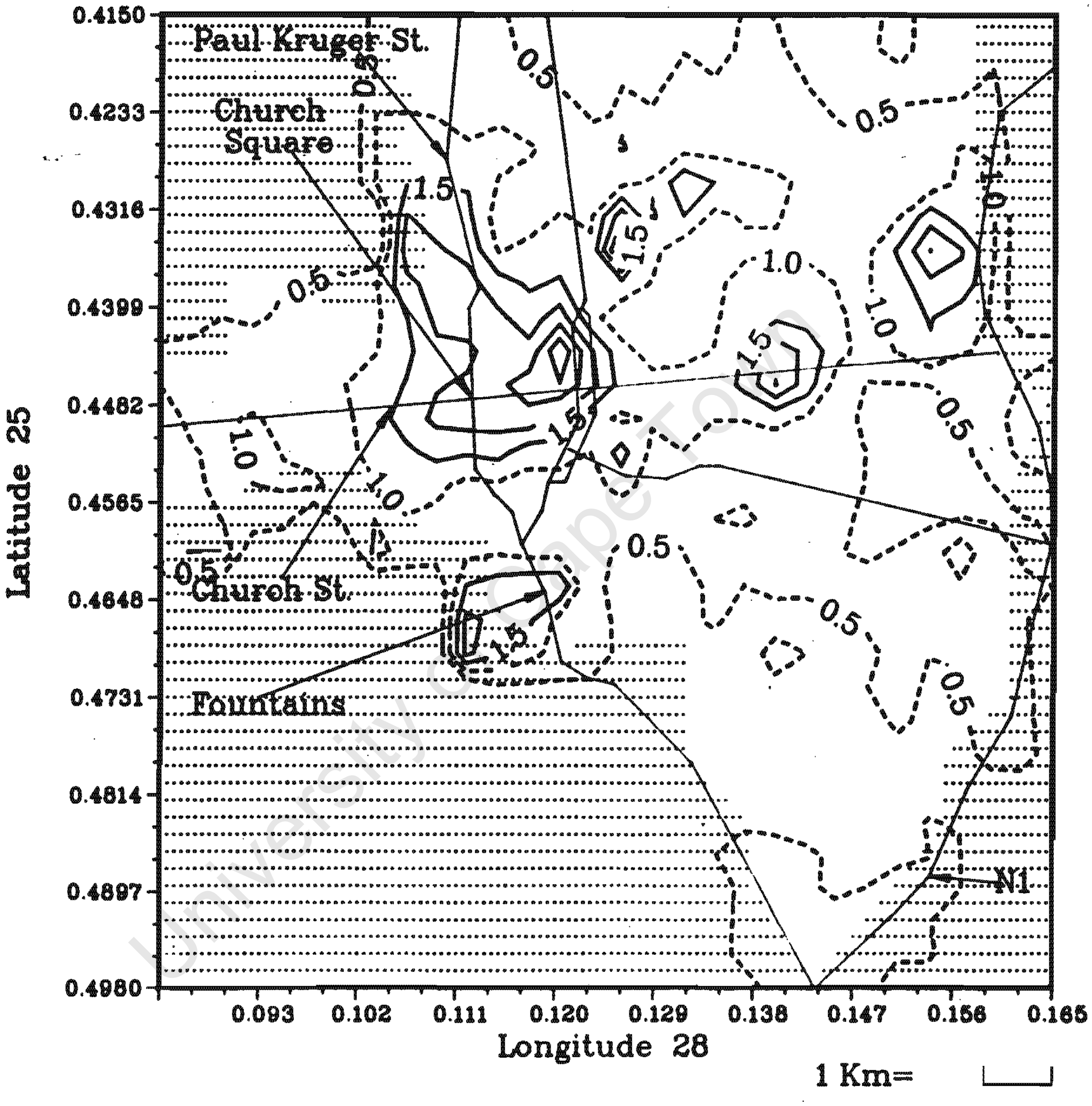


Figure 30. Distribution of lead in air simulated from Jacaranda leaf samples : Pretoria 1984 (μg/m³).

The map shows that the only existing atmospheric monitoring site, the location of which are shown in figure 1, which is within an area of enhanced atmospheric lead concentrations is Munitoria, whilst the Arcadia monitoring station is on the boundary of the area. Consequently, the data collected from the Munitoria site can be considered to be representative of the atmospheric lead concentrations, although not necessarily the highest, that occur in the City centre of Pretoria.

The closeness of the intercept value of the equation [2] to zero confirms that the principle source of the leaf lead is from atmospheric deposition. Very little or no lead in the leaf sample is derived from the uptake and subsequent translocation of lead from the soil.

6.2.2 Iron

The map (figure 31) was drawn after the 1984 leaf data for iron concentrations was transformed by the following linear regression equation [3], the figures in brackets indicate the standard errors.

$$\mathrm{Conc}_{air} = 0.5395 + 0.0384*\mathrm{Conc}_{leaf} \qquad [3]$$

$$(0.6365)\ (0.0040) \qquad R^2 = 0.703$$

Where Conc_{air} is atmospheric iron concentration, $\mu g/m^3$

Conc_{leaf} is leaf concentration of iron (ppm), determined by the cold extraction method

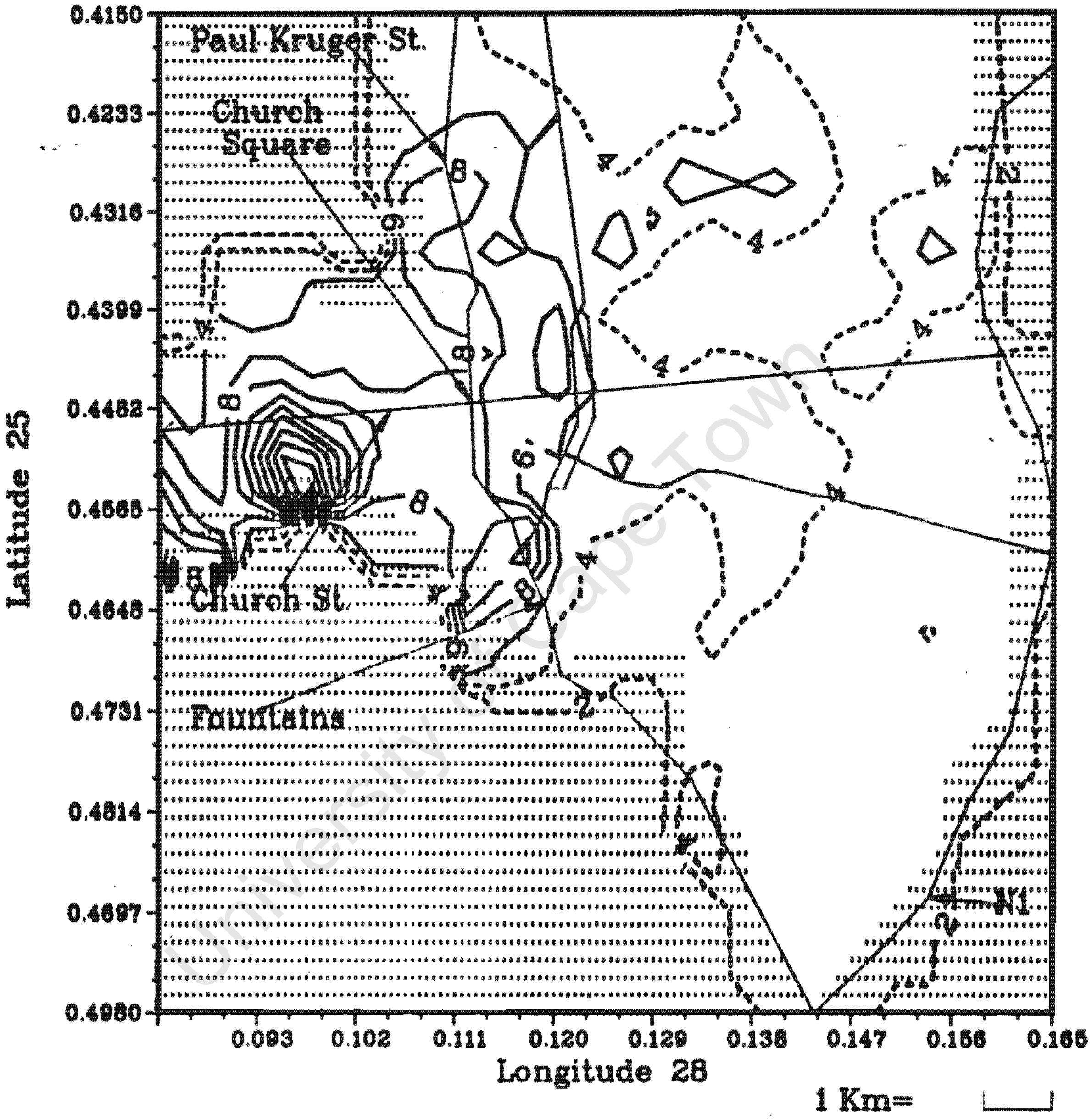


Figure 31. Distribution of iron in air simulated from Jacaranda leaf samples : Pretoria 1984 (μg/m³).

Taking into account the standard errors, the expected range of simulated atmospheric concentrations from leaf concentrations of 90 and 180ppm are 3.195 to 4.992 and 6.289 to 8.808 µg/m³ respectively.

In figure 31 the highest atmospheric concentrations of iron are to found in the west, north and centre of the City. This is influenced by Iscor, the iron and steel works situated just to the west of the study area.

Figure 31 clearly shows that the Munitoria monitoring site is located well within the area of enhanced concentrations. The air-filter data from this site is representative of the atmospheric iron concentrations in the central areas of Pretoria, although these are not necessarily the highest in the area.

The source of the pronounced high area of iron concentrations to the west of the City centre is unknown (section 5.3.2). It may be derived from the soil or from local industry. To enable the source to be identified an air-filter unit should be located in the area.

6.2.3 Manganese

The following linear regression equation [4], and standard errors (in brackets), is based on the relationship established between the leaf and air-filter concentrations of manganese at the urban study sites :

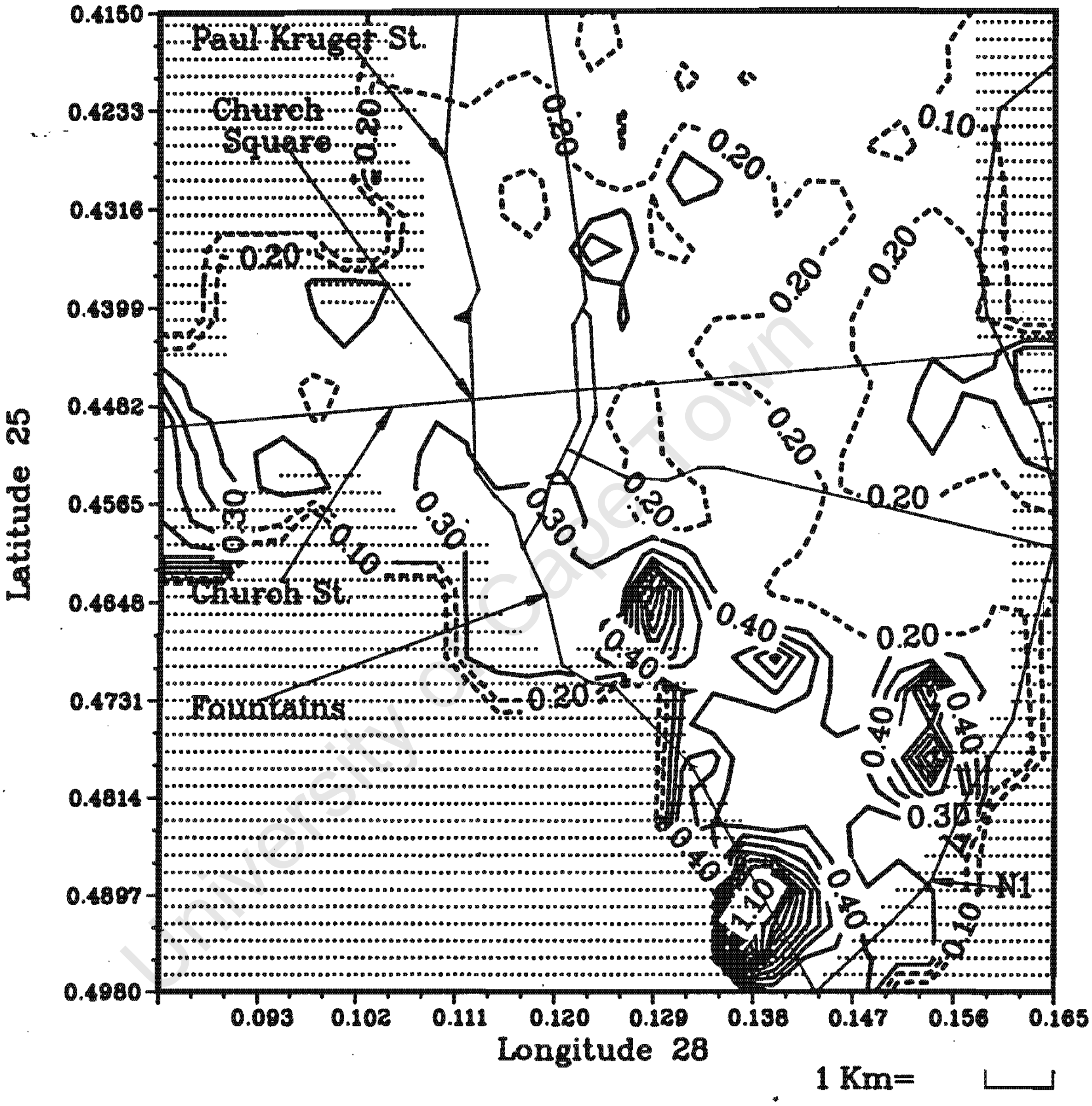


Figure 32. Distribution of manganese in air simulated from Jacaranda leaf samples : Pretoria 1984 (µg/m³).

$$Conc_{air} = -0.0400 + 0.0084{*}Conc_{leaf} \qquad [4]$$

$$(0.0303)\ (0.0009) \qquad R^2 = 0.719$$

Where $Conc_{air}$ is manganese concentration, air, µg/m³
$Conc_{leaf}$ is leaf concentration of manganese (ppm),
determined by the cold extraction method

Leaf concentrations of 30 and 60ppm would correspond to simulated atmospheric concentrations of 0.1547 to 0.2643 and 0.3797 to 0.5483 µg/m³ respectively.

The equation [4] from which the isolines in figure 32 were drawn was derived from data collected only in the central and western parts of the City. In the southern part of the study area where there are no air monitoring stations the leaf concentrations have been shown to be at their highest. The above equation [4] has been applied to the data covering the whole of the study area although in the southern part the input from the soil to the leaf manganese concentrations is possibly greater than the areas from which the equation [4] was derived. This may invalidate the isolines drawn in the southern areas of Pretoria.

The probable negative intersect of this equation, including the standard error, indicates that there is a portion of the leaf manganese that is not derived from atmospheric deposition, but presumably from the soil.

If an assumed value of zero is taken to represent the atmospheric concentration of manganese the equation [4] predicts that 4.75ppm (1.04 to 9.37ppm) of leaf manganese is derived from the soil.

Figure 32 clearly shows that the present distribution of atmospheric monitoring network should be expanded to include stations located in the southern suburbs of Pretoria. The results from these new stations would indicated whether the adnormally high leaf concentrations of manganese were derived from the soil or from the atmosphere. Until such stations are operational it is impossible to eliminate that there exists a major, unknown source of atmospheric manganese to the south of Pretoria.

6.2.4 Zinc

The linear regression equation [5] and standard errors describing the relationship between the concentrations of the leaf zinc and the air filter was derived from the data from the four urban sampling sites.

$$\mathrm{Conc}_{air} = -0.0807 + 0.0181 * \mathrm{Conc}_{leaf} \qquad [5]$$

$$(0.0518) \quad (0.0029) \qquad R^2 = 0.498$$

Where Conc_{air} is zinc concentration in the air, μg/m³

Conc_{leaf} is leaf concentration of zinc (ppm), determined by the cold extraction method

The range of predicted atmospheric concentrations using this equation [5] for leaf concentrations of 8 and 16ppm are -0.0109 to 0.1391 and 0.1107 to 0.3071 μg/m³ respectively.

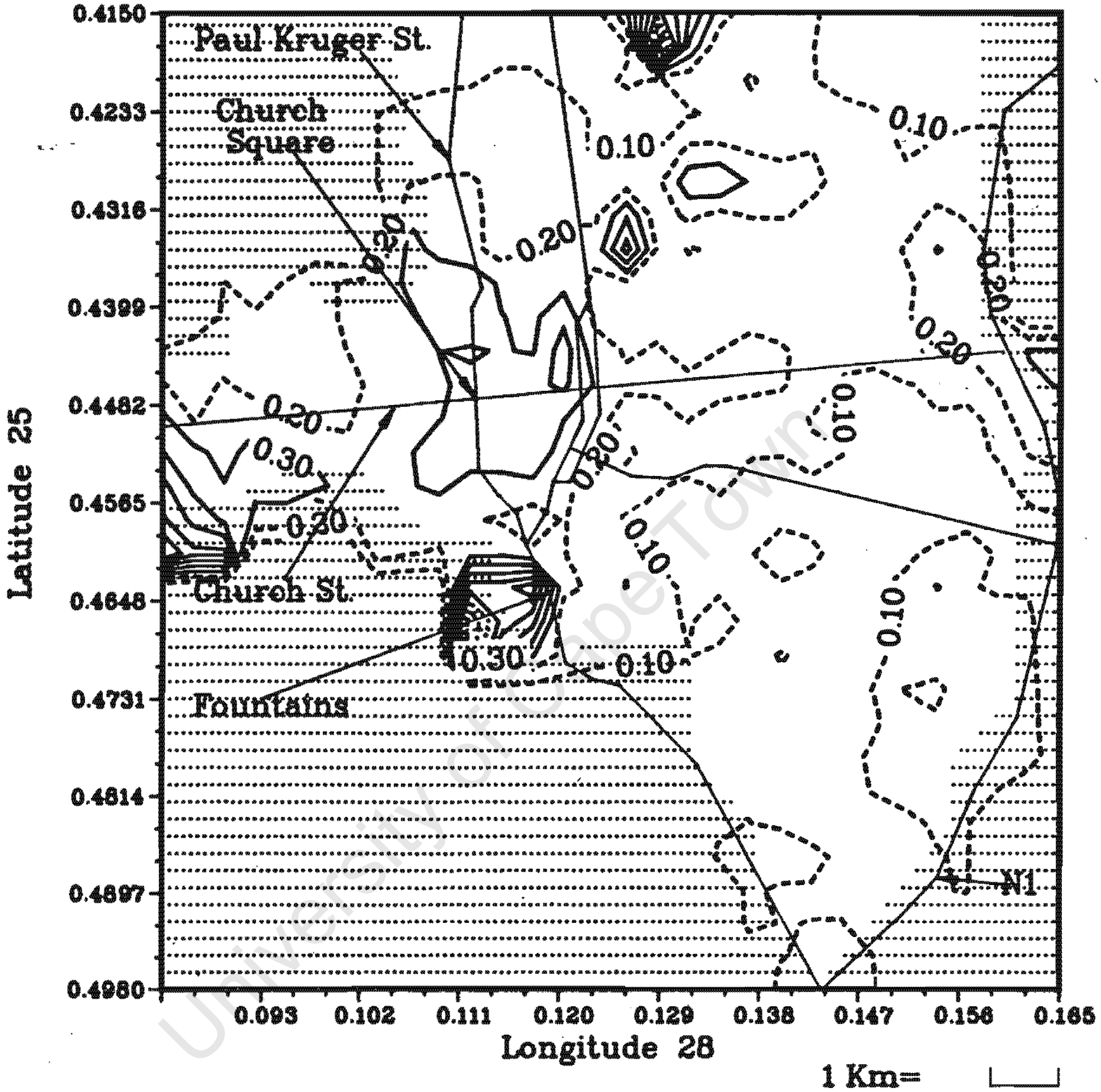


Figure 33. Distribution of zinc in air simulated from Jacaranda leaf samples : Pretoria 1984 (µg/m³).

Figure 33 shows the isolines for the atmospheric zinc concentrations which have been derived from the 1984 leaf data using the above equation [5]. The areas of high predicted zinc concentrations correspond to the predicted areas of high atmospheric lead concentrations (figure 30). The only exception is a high area to the north of the City, in which a single tree exhibited high leaf zinc. None of it's neighbours, nor the corresponding sample in 1983, exhibited a similar concentration. The reason for this could be because of sample contamination from an unknown source. The similarity between the lead and zinc distributions strongly suggests that both are derived from the same source, namely traffic.

Taking into account the standard errors, the negative or near zero intercept of the equation indicates that there is a portion of the leaf zinc which is derived not from the atmosphere but presumably from the soil. This amounts to 4.45ppm (1.38 to 8.72ppm).

Of the existing monitoring stations in Pretoria, the Munitoria site is the best situated to monitor the high, not necessarily the highest, atmospheric zinc concentrations within the City.

6.3 CHAPTER SUMMARY

The maps depicting the distribution of leaf concentrations for the five studied trace elements throughout Pretoria in themselves reveal only relative areas of high and low concentrations, in relation to each other. Although this is useful information, no indication is given to the relative contribution to the total leaf concentration from either the soil or from the atmosphere. It is possible that, except for lead, the majority of the leaf concentration could be derived from uncontaminated soil. A measure of the relative contribution from the atmosphere would therefore allow the data to be interpreted in a manner which would find wider application and provide better understanding.

Throughout 1984 sampling was conducted at four urban sites at which an air filter and/or deposit gauge was in operation next to, but not under, a Jacaranda tree. In this manner an estimate of the contribution from the aerosol to the leaf concentrations could be made, if the correlation between the two sampling mediums is strong.

It was established that although at some sites there was a correlation between the results from the deposit gauge and leaf concentrations, this relationship could not be applied uniformly throughout Pretoria. Therefore no further information can be derived from the collected leaf data to augment the information currently being collected by deposit gauges throughout Pretoria.

The results for the correlation between the air filters and leaf concentrations indicate that there is a strong relationship between these two sampling mediums for lead, iron, manganese and zinc (table 17). The leaf data was transformed using the established linear regresion equations into simulated atmospheric concentrations, and replotted.

In the case of manganese, although the established correlation from the monitoring sites between the atmospheric and leaf concentrations is good, it is questionable whether it should be applied in the southern part of the study area. In this area, there is a strong possibility that the leaf concentrations are being influenced by the uptake and subsequent translocation of soil manganese. Since there are no atmospheric monitoring stations in this area the validity and application of the equation is in doubt.

The existing atmospheric monitoring network in Pretoria should be expanded to include at least one site in the southern most suburbs so as to determine the source of the high leaf manganese in this area. Another additional site needs to be located in an area to the southwest of the City centre in which the leaf concentrations of iron were high in both 1983 and 1984 to enable the source to be identified.

The monitoring site at Munitoria is well situated to representatively measure the high, although not necessarily the highest, concentrations of atmospheric lead, iron and zinc in the City.

CHAPTER 7

SUMMARY CONCLUSIONS

7.1 SUMMARY CONCLUSIONS

The trace element concentrations in Pretoria have been studied since 1974 (Vleggaar et al, 1980), the particle size distributions and sources have been documented by Annegarn and Sellschop (1983). To date the spatial distribution of trace elements in Pretoria has not been addressed.

The aim of this study is to describe the spatial distribution of lead, iron, manganese, zinc and copper throughout Pretoria, (figure 1), by examining the concentrations of these trace elements in Jacaranda leaves.

The easily identified Jacaranda tree has been planted on the pavements throughout Pretoria. The tree leaves act as surrogate sampling surfaces. At the time of sampling the trace element concentrations of the leaf has been derived from a combination of the uptake from the soil and atmospheric deposition.

There are many important factors, both passive and chemical in nature, which control the uptake and subsequent translocation of trace elements by the root to the leaf. The leaf surface deposits continually change due to the difference in the rates of loss and interception.

Relative areas of high and low trace element leaf concentrations are detected by samples taken on a fine grid. From parallel measurements of both leaf and atmospheric trace element concentrations at selected sites an estimate of the contribution from atmospheric deposition to leaf concentrations was obtained.

Two sample preparation techniques were used, cold extraction and hot digestion, the latter indicated total concentrations, the former an approximate surface concentration. The hot digestion method yielded higher concentrations than the cold technique. Varying the concentration of acid in the cold technique, from dilute to concentrated, resulted in only small increases in the extractable portion of trace element deposit (figure 3). The extractable portion varied throughout the year and also between sampling sites (figure 4). The results from both methods were well correlated for all of the elements, except copper (table 17).

No significant difference in the trace element concentrations was established between the tip, middle and base sections of the leaf (section 4.1.1). To ensure a uniform method of preparation and analysis the centre six pairs of pinnae on each leaf were used. From each pinna the pinnules were seperated, and the stems discarded. None of the leaf samples were washed prior to analysis.

It was established that the leaf trace element concentration was influenced by the position of the leaf on a tree. The leaves nearest to the road had higher lead concentrations than those further away (table 4, section 4.1.2). To minimise the positional effect, a composite sample representing a tree consisted of two leaves from each of four positions around the tree, at a standard height of between four and five meters.

A variation was established in the leaf concentrations of trace elements over a period of twelve days (table 10). This was statistically significant normally after three or four days. Consequently the sampling for the annual surveys was conducted as quickly as possible, the 1984 survey was completed in four and a half days (table 12).

The Jacaranda trees in Pretoria are planted within three meters of the kerbside. The close proximity of the road had a dominant effect on the leaf concentrations of lead. It was established (section 4.2), that the concentrations of leaf lead increased at points of traffic congestion (bus stops, stop streets). The leaf lead concentrations along a road was reasonably uniform, but significant differences occurred between trees on major and minor roads (figure 6).

Enhanced trace element concentrations arise by virtue of the retention of the deposit exceeding the loss. The loss from the leaf surface is influenced by rainfall (section 4.4.1.1). The attempt to measure this effect was unsuccessful because either no rain fell, or insignificant falls were recorded. In the latter case any possible effect was masked by the natural variations that occurred in the leaf concentrations (section 4.1.2).

It was established that the wind direction partially influenced the daily leaf concentrations of the five elements (table 11).

It was established that the study tree located within the C.S.I.R., chosen as a background site, was subjected to episodes of zinc pollution (figure 7). The source was established to be a series of burning tests into the properties of various fire retardent chemicals and insulated armoured cables. In one instance the leaf zinc concentrations fell from 120 to 5ppm within thirteen rain-free days.

it could be either local industrial activity or derived from the soil. The effect of the dominant west and northwest winds in winter, in conjunction with the unfavourable dispersion meteorology, results in increased leaf iron concentrations after April in the central Pretoria area.

The distribution of leaf manganese is dominated by high concentrations in the southern residential suburbs (figures 20 and 21). The source, unlikely to be industrial activity, is probably high soil concentrations. The contact between the Karoo and Transvaal geological sequences is within the area, at which points percolating water forms wad, a hydrated manganese oxide.

The distribution of the leaf concentrations of zinc and copper (figures 22 to 25), show little variation throughout Pretoria. Both elements had slightly higher concentrations in the central City area. The distribution of zinc is similar to that of lead.

The leaf concentrations of the five studied elements were higher in 1984, than in 1983. The variance for each element was the same, except for iron which was higher in 1984 than in 1983 (table 14). There is no evidence to suggest that the cause of the increased concentrations was due to the earlier sampling dates in 1984 than in 1983.

None of the elements correlated with each other for either the 1983 or 1984 survey data (table 15). However, at individual sampling sites the concentrations of leaf iron and manganese was correlated. This confirmed the visual similarity between the plots for the leaf concentrations of the two elements at the study sites (figure 11). The trace element aerosol in Pretoria varies considerably, at specific localities a correlation between leaf elements may exist, but this will be dependant upon the source, the distance from that source, and the influence of other sources. These combined factors alter the local aerosol characteristics and the composition of the leaf deposits.

An estimate of the relative contribution to the leaf concentrations from atmospheric deposition was obtained at four specific urban sampling sites, at which an air-filter and/or deposit gauge operated.

The relationship between the deposit gauge results and those for adjacent leaf concentrations was dominated by the results from the Afrox sampling site, because of the close proximity of Iscor (figures 26 and 27; table 17). At this site a very strong local correlation between the element concentrations as determined by the two sampling techniques was shown to exist. However, the relationship could not be applied to the Visagie Street sampling site, only six kilometers away, or any other site. All the other sites exhibited poor relationships between these two sampling techniques.

It was concluded that the data collected from leaf sampling cannot be used to augment or substitute data collected by the present deposit gauge network in Pretoria.

The relationship between the leaf concentrations and the air-filter results for lead, iron, manganese, zinc and copper was measured at three specific sampling sites (figures 28 and 29). The correlation statistics confirmed the visual indication of the relationship between the two sampling techniques for all of the elements, except copper (table 17). The linear regression equation for each correlation was used to predict the atmospheric concentration from the leaf data. The simulated atmospheric trace element concentration data for lead, iron, manganese and zinc was then subsequently replotted.

The advantage of presenting the leaf data in this form was that it could be compared with known emission data. The maps may be used to identify areas of past contamination, and to identify the optimum locations for atmospheric particulate monitors. It was not appropriate to use the estimated concentrations for comparison with health or control criteria because of the indirect method of determination.

The simulated atmospheric lead concentrations (figure 30) highlighted known high density traffic areas, either along traffic routes or in the City centre. The map of the simulated atmospheric zinc (figure 33) is very similar to that for lead, strongly suggesting that both are derived from traffic. The source of lead being the petrol additives and for zinc the tyres and oil.

The influence of Iscor, the iron and steel works, as the dominant source of atmospheric iron in Pretoria is reflected by the high concentrations in the west, northwest and central areas of the City.

The areas of high leaf manganese in the southern suburbs are likely to be derived from the soil. This possibility of a greater contribution from soil uptake to the leaf manganese concentrations may invalidate the use of the regression equation (derived from data collected only in the central Pretoria area) to these suburbs.

Very little or no leaf lead was derived from the soil. The linear equations for manganese and zinc predict that at least 4.75ppm (1.04 to 9.37ppm) and 4.45ppm (1.38 to 8.72ppm) respectively was derived from the soil.

The Munitoria atmospheric monitoring site is the most representative of the current operational sites in Pretoria for the high, although not necessarily the highest, concentrations of lead, iron and zinc.

Two additional atmospheric monitoring sites are required to be operated to investigate and establish the sources of the area of high iron concentrations to the west of the City centre and the high manganese in the southern suburbs. Until such stations are installed the sources of these two anomalies will remain unknown and their influence on the local air quality questionable.

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APPENDIX

Data for 1983 and 1984 Pretoria studies.

Cold Extractions - ppm.

REFERENCE	LEAD		IRON		MANGANESE		ZINC		COPPER	
	1983	1984	1983	1984	1983	1984	1983	1984	1983	1984
1110 43962	71.30	103.00	153.80	252.50	27.00	51.25	4.60	30.25	12.40	9.75
1170 43962	41.30	47.25	78.80	166.25	19.80	40.00	12.40	19.25	4.30	8.50
1200 43962	51.30	64.00	137.50	267.50	19.40	37.00	14.50	28.00	6.30	12.00
1230 43962	15.00	14.00	40.00	57.50	27.30	32.50	7.50	11.25	3.30	3.75
1260 43962	9.00	9.80	41.30	55.00	29.30	44.90	6.90	11.42	4.50	7.00
1080 44240	61.80	83.30	162.50	187.50	27.30	41.67	21.80	25.52	7.50	10.16
1110 44240	54.30	55.00	167.50	155.00	35.30	34.25	15.30	18.25	6.90	7.75
1140 44240	95.50	87.50	218.80	205.00	26.00	28.75	18.10	20.75	9.10	11.75
1170 44240	28.00	43.80	115.00	159.79	27.30	36.60	10.40	13.92	5.00	7.99
1200 44240	188.80	143.00	217.50	220.43	33.50	43.55	27.80	33.33	11.30	18.82
1230 44240	30.80	44.25	61.30	73.50	19.80	21.75	9.30	10.50	5.30	7.75
1260 44240	15.50	22.50	65.00	114.25	32.80	48.75	5.50	10.00	4.50	6.00
1080 44518	41.80	53.75	137.50	180.00	20.00	35.00	12.50	18.00	5.60	7.75
1110 44518	46.80	41.67	157.50	171.88	22.00	32.56	27.00	20.31	17.30	8.07
1200 44518	130.00	160.33	198.80	339.67	25.80	40.76	15.90	37.50	11.30	23.09
1230 44518	41.30	123.00	51.30	180.00	10.00	31.25	4.00	25.25	4.60	15.50
1260 44518	38.00	63.75	68.80	130.00	17.40	35.00	9.30	22.75	5.00	11.75
1080 44796	46.80	89.25	135.00	222.50	26.50	46.25	14.10	22.75	6.90	11.75
1110 44796	76.30	97.66	200.00	307.29	26.30	53.38	17.00	26.56	5.60	16.15
1140 44796	51.80	81.89	188.80	149.43	20.00	36.21	9.00	21.55	7.90	8.91
1170 44796	95.00	102.15	163.80	166.67	22.00	37.63	14.80	26.34	9.30	10.48
1200 44796	59.30	55.92	167.50	139.80	36.30	39.47	20.10	23.02	8.50	10.20
1230 44796	23.80	30.00	85.00	122.00	18.50	35.50	7.60	15.50	4.50	7.75
1260 44796	16.80	16.25	51.30	57.50	17.00	18.00	6.80	8.50	4.00	4.00
1080 45074	77.50	80.00	312.50	200.00	44.80	36.25	17.50	15.25	9.80	10.75
1110 45074	66.80	70.50	233.00	205.00	17.40	30.50	11.70	19.75	9.70	15.50
1140 45074	50.50	70.00	102.50	180.00	14.50	27.50	6.80	19.00	5.00	11.00
1200 45074	171.80	70.00	196.30	151.25	29.00	33.00	16.40	19.00	12.00	9.00
1230 45074	21.30	23.53	128.80	99.42	15.00	34.25	4.00	18.12	38.80	2.64
1260 45074	23.80	22.50	57.50	86.25	13.80	22.50	6.90	13.50	9.80	6.50
1080 45352	26.80	47.50	100.00	233.75	25.00	60.50	8.80	34.00	5.00	9.00
1110 45352	20.00	22.50	325.00	333.75	20.00	52.50	9.80	28.50	4.50	9.00
1170 45352	25.50	28.75	92.50	108.75	15.00	30.00	7.50	36.00	4.50	5.25
1200 45352	34.30	35.00	18.50	167.50	20.80	33.75	4.00	15.50	6.30	7.00
1230 45352	15.00	25.00	81.30	92.50	10.00	23.00	5.50	10.25	4.50	7.00
1260 45352	80.00	123.75	212.50	283.75	24.30	39.25	11.00	25.75	13.10	19.50
1110 43684	82.50	70.00	182.50	247.50	25.30	34.25	21.00	28.00	5.00	7.75
1110 43406	95.80	81.25	207.50	122.00	26.00	22.50	9.20	13.50	13.40	6.00
1110 43128	54.30	65.43	267.50	253.09	26.30	31.48	24.50	24.69	8.50	7.41
1110 42850	60.00	56.25	387.50	312.50	37.30	33.00	20.50	18.00	5.00	7.75
1080 42572	31.30	32.50	112.50	114.25	22.80	41.25	11.50	10.00	5.90	6.00
1080 41738	11.80	20.50	68.80	106.25	17.00	19.25	6.00	8.50	1.80	4.00
1110 42016	6.30	29.50	57.50	108.00	28.00	23.00	6.80	9.50	5.90	3.75
1110 42572	31.30	23.75	132.50	114.25	29.30	24.25	4.60	9.50	8.80	4.00
1140 42572	28.80	40.50	134.30	180.00	27.30	36.75	6.60	15.25	9.10	11.75
1140 43128	10.00	13.00	151.30	173.75	16.50	27.00	8.30	9.13	2.50	9.25
1140 43406	11.30	15.25	56.30	80.00	32.80	42.50	7.90	9.75	1.80	5.00
1170 41738	12.50	12.25	36.80	57.50	13.00	18.75	2.00	6.75	3.50	3.00

1170	42016	13.00	19.00	48.80	108.75	27.00	32.25	8.50	12.50	.90	5.00
1170	42294	10.00	17.50	50.50	122.50	9.50	27.50	5.90	9.25	4.10	6.50
1170	42572	21.80	38.23	70.00	143.53	18.80	30.88	7.30	11.18	1.80	7.06
1170	43128	15.50	20.50	107.00	125.00	19.50	20.00	-	8.50	2.50	5.25
1170	43684	71.30	42.75	146.30	158.75	31.80	30.50	14.10	18.00	8.50	10.00
1200	41738	11.80	11.50	40.00	72.50	15.60	17.50	7.90	7.25	3.40	6.50
1200	42016	9.30	10.00	43.80	65.00	13.80	21.00	2.50	7.00	3.00	3.00
1200	42294	12.00	25.00	57.20	155.36	35.10	39.29	7.80	16.07	6.00	5.00
1200	43406	88.00	42.50	138.80	122.00	17.30	19.25	15.90	17.50	8.80	11.75
1200	43684	61.30	55.50	101.30	166.25	22.80	31.50	13.30	18.00	11.80	13.75
1230	41738	11.30	11.50	53.80	72.50	23.80	37.00	5.30	8.50	4.20	6.50
1230	42294	8.80	12.25	43.80	58.75	23.10	23.75	6.50	8.00	3.40	1.75
1230	42572	13.80	19.00	62.50	108.00	17.30	22.50	11.90	9.50	3.80	7.25
1230	43128	17.80	20.00	105.00	108.00	16.50	25.50	7.50	11.75	1.50	3.75
1230	43406	15.00	23.40	78.60	147.44	28.60	88.14	7.90	16.99	3.70	4.81
1230	43684	16.80	23.75	60.00	75.00	21.50	30.50	5.00	11.25	7.30	14.25
1260	41738	6.80	8.25	48.80	72.50	17.80	28.50	2.70	7.75	5.30	3.00
1260	42016	18.50	14.76	82.50	96.38	27.00	29.52	8.00	9.94	6.80	7.80
1260	42294	12.80	15.50	66.90	58.75	22.10	14.25	12.20	8.00	3.90	3.50
1260	42572	10.00	12.00	45.50	65.00	14.80	15.00	9.30	9.50	3.00	3.75
1260	42850	16.30	25.50	83.80	92.50	18.90	20.50	10.50	12.50	4.20	5.25
1260	43406	10.50	174.66	37.50	251.71	15.80	58.90	3.80	50.68	2.60	14.73
1260	43684	90.50	56.25	130.00	100.00	5.10	38.00	12.50	13.75	4.50	7.00
1290	41738	10.00	10.13	75.00	86.88	24.30	19.63	2.70	79.00	5.50	2.50
1290	42016	10.50	9.50	65.00	72.50	21.80	16.25	9.50	7.00	3.40	2.00
1290	42294	9.50	15.50	51.30	83.75	16.30	25.00	7.00	9.25	3.40	5.25
1290	42572	17.50	15.00	88.80	86.25	25.50	18.75	10.30	8.50	4.80	2.00
1290	43128	41.80	16.75	98.80	58.75	14.80	23.00	15.90	7.75	5.50	3.50
1290	43406	120.60	22.50	216.20	92.50	43.90	23.00	41.10	11.50	8.40	7.00
1290	43962	14.00	17.00	83.30	67.50	36.30	41.00	14.90	14.00	.00	3.50
1290	44240	10.00	10.50	46.30	65.00	21.50	26.25	6.90	17.50	4.00	6.50
1290	44518	36.30	38.00	66.80	73.50	20.00	25.00	11.90	15.00	4.20	4.00
1320	42016	19.00	23.00	53.80	93.75	25.00	36.00	7.50	11.50	4.80	6.50
1320	42294	8.80	11.50	46.30	58.75	13.50	19.25	7.40	7.50	1.50	3.50
1320	42572	27.80	20.18	163.20	120.48	43.70	39.76	23.60	15.66	13.20	6.33
1320	42850	46.30	80.74	146.30	245.90	45.00	63.52	15.80	30.33	6.00	11.48
1320	43128	26.30	66.48	56.30	119.51	17.00	38.46	8.50	20.05	6.00	7.69
1320	43406	6.30	10.00	41.30	66.25	20.00	21.75	10.50	6.00	2.80	1.75
1320	43962	25.00	40.28	72.50	81.67	25.30	28.33	4.00	12.78	3.90	4.44
1320	44240	13.80	12.25	47.50	41.00	19.30	31.00	6.00	11.25	3.00	6.00
1320	44518	42.50	41.25	72.50	81.75	27.50	27.50	18.50	16.25	5.90	6.00
1350	41738	8.00	6.00	61.30	65.00	22.50	22.00	9.00	10.00	4.60	6.50
1350	42294	8.50	9.00	47.50	50.00	15.50	20.00	6.10	8.25	2.30	5.00
1350	42572	10.00	14.50	62.50	75.00	22.00	26.25	7.40	12.00	3.80	7.00
1350	42850	36.80	65.00	85.00	208.75	20.00	48.75	8.00	37.50	3.30	16.00
1350	43128	14.20	13.75	47.30	66.25	27.70	36.25	6.80	10.75	7.10	5.25
1350	43684	21.30	21.25	67.50	57.50	35.80	40.00	6.80	10.50	4.50	4.00
1350	43962	15.00	35.00	40.00	57.50	21.00	31.50	4.40	13.00	4.00	4.00
1350	44240	9.00	11.75	40.00	81.75	24.50	18.00	6.30	9.75	4.80	2.00
1350	44518	39.30	61.14	65.00	141.30	18.80	28.53	13.30	25.54	6.30	12.77
1380	42016	35.00	35.00	100.00	158.75	27.00	33.50	16.80	20.00	9.00	10.00
1380	42294	23.00	20.50	51.30	80.00	23.50	23.00	11.40	14.75	6.80	12.00
1380	42572	17.30	16.25	57.50	83.75	13.30	15.50	9.90	10.00	4.50	7.00
1380	42850	33.00	45.00	85.00	158.75	18.80	30.00	8.00	20.75	7.30	9.00
1380	43128	40.00	43.13	76.30	117.50	41.00	33.00	14.30	19.00	11.30	10.75

REFERENCE	LEAD		IRON		MANGANESE		ZINC		COPPER	
	1983	1984	1983	1984	1983	1984	1983	1984	1983	1984
1380 43406	7.00	7.75	40.00	66.25	16.50	13.00	4.50	5.50	3.40	3.50
1380 43684	41.80	65.00	57.50	106.25	34.30	52.50	6.80	16.00	4.50	6.00
1380 44240	45.00	35.00	55.00	73.50	11.00	21.75	7.50	14.50	4.00	7.75
1380 44518	82.50	90.50	66.80	98.00	18.10	31.75	15.90	23.25	7.50	9.75
1410 41738	11.80	12.25	61.30	72.50	20.80	21.00	8.50	12.75	3.90	5.00
1410 42016	31.80	23.00	45.50	116.25	22.30	26.50	11.90	12.25	3.40	6.50
1410 42294	18.90	13.00	85.20	93.75	34.50	31.50	11.40	8.75	14.20	8.50
1410 42572	22.00	17.50	51.30	117.50	16.80	20.50	9.00	9.75	4.50	9.00
1410 42850	112.80	40.50	328.50	217.50	49.70	27.50	29.70	20.50	18.30	10.75
1410 43128	34.80	42.50	92.50	150.00	16.30	22.50	15.50	20.00	6.00	5.25
1410 43406	11.30	10.00	68.80	66.25	26.30	29.25	6.80	8.00	3.80	7.00
1410 43684	53.80	68.75	78.80	106.25	32.00	48.75	4.90	16.75	3.90	9.75
1410 44240	9.50	12.25	53.80	49.25	21.80	20.00	5.50	8.25	4.50	6.00
1410 44518	188.00	258.62	65.00	131.32	19.40	24.71	15.90	27.87	5.90	13.51
1440 41738	8.80	7.50	38.80	57.50	15.00	19.25	5.00	8.00	1.50	3.75
1440 42016	6.30	7.50	48.80	65.00	19.50	21.75	5.50	7.50	2.30	6.50
1440 42572	19.00	19.00	68.80	92.50	21.30	24.25	11.30	19.00	4.80	3.50
1440 43128	13.80	16.00	45.00	80.00	41.50	45.50	8.80	14.00	7.50	8.50
1440 43406	9.00	8.25	40.00	50.00	26.00	31.00	6.80	10.25	2.30	5.00
1440 43684	50.50	54.25	57.50	81.75	14.80	19.25	8.50	13.50	3.90	4.00
1440 43962	9.30	9.00	42.50	65.00	16.50	21.50	5.00	8.25	3.30	5.00
1440 44240	75.50	70.50	96.30	90.00	24.00	38.75	11.10	18.50	6.90	7.75
1440 44518	14.30	13.00	71.30	50.00	19.00	20.50	8.00	7.50	3.90	3.75
1470 42016	8.00	7.00	43.80	50.00	17.00	15.00	4.90	5.00	2.30	2.00
1470 42294	13.30	11.50	68.80	80.00	32.50	31.00	8.00	10.75	5.30	8.50
1470 42572	12.30	12.25	71.30	66.25	21.00	13.00	9.80	13.25	4.80	3.50
1470 43406	16.50	23.00	57.50	85.00	18.50	20.00	6.30	12.00	2.80	6.00
1470 43684	38.80	33.00	193.80	65.50	16.50	23.75	7.50	9.50	4.50	6.00
1470 43962	21.50	12.25	48.80	72.50	25.00	27.50	10.30	11.25	3.80	5.00
1470 44240	22.50	38.25	86.30	108.75	21.50	31.50	7.00	15.00	5.30	5.00
1470 44518	13.80	10.50	52.50	180.00	17.80	23.75	5.50	7.25	3.30	6.50
1500 41738	14.30	20.75	38.80	65.00	15.30	20.00	6.10	8.50	2.30	3.75
1500 42016	9.50	11.25	65.00	80.00	17.30	18.75	6.00	8.50	2.30	3.75
1500 42572	35.00	22.00	102.50	24.00	27.00	13.00	10.50	8.75	3.00	17.50
1500 43128	12.50	13.00	92.50	87.50	20.50	17.50	7.00	9.50	4.00	5.00
1500 43684	38.80	30.50	70.00	73.50	16.00	36.25	4.00	12.25	4.00	6.00
1530 42016	7.30	7.50	60.00	57.50	16.30	21.25	5.40	7.00	1.50	2.00
1530 42850	15.00	13.83	41.80	69.15	15.60	18.62	9.30	9.57	3.40	5.32
1530 43406	67.50	109.25	131.30	197.25	29.50	43.00	13.30	24.75	4.80	11.75
1530 43684	74.30	64.25	103.80	106.25	22.50	33.00	11.50	18.25	4.50	9.75
1530 44240	46.30	60.00	66.80	90.00	45.40	43.00	18.40	19.00	6.30	7.75
1560 42016	8.80	9.50	55.00	50.00	17.50	15.00	7.00	6.25	1.50	2.00
1560 42294	13.80	16.75	57.50	66.25	12.00	8.00	7.80	8.50	2.30	1.75
1560 42572	30.50	35.75	30.00	93.75	13.90	23.00	9.30	12.00	2.50	5.00
1560 43128	39.30	35.00	86.30	108.75	20.80	22.50	9.30	14.00	3.00	6.50
1560 44240	53.80	31.25	68.80	73.50	27.50	26.75	15.90	15.50	4.20	6.00
0870 45352	37.50	37.65	285.00	174.70	42.50	51.20	21.00	23.49	7.50	9.34
0870 44796	21.30	21.25	105.00	90.00	22.00	30.50	9.30	10.50	4.30	11.75
0900 45352	12.50	22.22	102.50	144.44	19.50	30.56	10.50	18.61	6.90	8.61
0900 45074	15.00	23.00	100.00	114.25	17.90	42.50	8.50	15.75	6.30	9.75
0900 44796	18.00	34.54	92.80	160.53	11.80	35.20	5.70	18.09	3.70	10.20
0930 45074	34.30	61.08	565.00	507.73	27.30	43.81	13.40	31.44	10.00	12.11
0930 44796	12.50	18.61	155.00	183.33	13.10	23.61	6.60	10.56	4.30	8.61

REFERENCE	LEAD		IRON		MANGANESE		ZINC		COPPER	
	1983	1984	1983	1984	1983	1984	1983	1984	1983	1984
0930 44518	13.00	16.25	265.00	295.00	14.50	26.25	7.50	10.50	3.60	6.00
0930 44240	11.90	15.50	95.20	130.00	19.20	45.00	7.10	15.00	4.30	6.00
0930 43962	8.80	12.50	70.00	98.00	17.90	27.50	4.40	7.75	1.80	4.00
0960 45074	19.50	25.50	915.00	817.50	24.10	51.25	10.60	23.50	10.60	9.75
0960 44796	14.30	23.77	130.00	253.09	16.10	32.41	6.10	11.11	4.30	4.94
0990 44796	10.50	16.25	55.00	130.00	47.30	13.00	13.50	10.75	3.90	4.00
0990 44518	11.80	20.50	80.00	155.00	12.30	21.50	4.90	10.25	3.00	6.00
0990 44240	16.30	19.44	90.00	135.56	31.00	41.67	8.40	14.44	3.00	4.44
1020 45074	17.50	29.41	185.00	441.18	13.50	36.76	7.00	16.18	4.30	11.47
1020 44518	33.80	55.00	107.50	197.50	16.10	33.00	7.40	17.25	5.00	7.75
1020 44240	19.50	20.50	215.00	252.50	27.80	60.00	12.10	19.00	4.30	7.75
1050 45074	50.00	43.50	170.00	267.50	16.60	28.00	14.00	21.25	5.00	11.00
1050 44796	48.80	52.00	120.00	130.00	11.10	21.00	10.60	18.25	5.00	6.00
1050 44518	13.00	15.50	75.00	197.50	10.10	39.25	6.00	12.75	5.60	7.75
1050 44240	11.30	20.00	72.50	106.25	17.50	25.00	9.80	14.75	4.30	7.75
1050 45352	19.30	19.75	117.50	145.00	20.50	30.50	9.10	14.00	4.60	8.50
1080 45630	41.00	36.50	132.50	152.50	27.30	33.25	17.30	18.25	4.80	8.50
1110 45630	8.80	13.00	107.50	173.75	19.50	36.50	8.80	11.25	2.30	6.50
1170 45630	22.50	18.75	90.20	103.75	26.30	47.33	4.90	11.50	4.00	6.00
1170 45908	16.30	15.25	65.00	487.50	35.30	48.50	6.10	9.25	3.90	6.50
1170 46464	35.70	72.55	125.00	199.73	27.70	40.76	16.80	59.24	4.60	15.49
1200 45630	8.80	12.25	46.30	93.75	21.30	60.50	5.00	21.25	5.00	11.00
1200 46464	12.80	85.49	77.80	114.20	48.90	51.54	16.40	15.43	3.30	6.48
1200 46742	17.30	11.50	45.00	66.25	31.00	38.00	7.30	7.75	2.30	1.75
1230 45630	4.00	9.00	22.50	108.75	14.80	38.00	3.00	8.25	20.00	5.00
1230 45908	12.50	13.75	62.50	101.25	52.00	41.50	6.00	11.25	5.60	8.50
1230 46186	12.50	16.75	46.30	50.00	17.80	28.00	6.80	10.75	2.30	3.50
1230 46464	7.80	13.75	47.50	83.75	35.30	62.50	7.30	16.50	3.00	5.25
1260 45630	4.30	9.00	25.00	72.50	10.50	20.00	2.50	6.25	12.50	3.00
1260 45908	18.00	15.25	96.30	87.50	53.50	36.00	8.00	10.00	5.00	6.50
1260 46464	5.00	10.00	40.00	75.00	15.30	30.00	5.30	8.75	2.80	1.75
1290 44796	46.30	46.50	90.00	166.25	17.00	31.00	10.00	20.00	6.90	10.00
1290 45074	12.50	13.75	42.50	57.50	9.00	13.50	4.30	7.25	2.60	3.00
1290 45352	20.00	24.50	75.00	130.00	11.00	25.50	5.50	13.75	20.00	8.50
1290 45630	10.00	9.00	42.50	65.00	16.80	24.75	4.10	7.00	1.60	5.00
1290 46464	3.80	10.00	40.00	66.25	35.50	161.75	4.00	13.75	2.80	5.25
1320 44796	113.00	52.50	172.50	144.40	32.00	31.67	23.30	18.06	35.30	9.44
1320 45074	63.80	40.50	137.50	187.50	20.80	60.75	11.00	15.00	8.50	10.00
1320 45630	12.50	10.00	40.00	65.00	14.50	14.50	5.60	6.00	1.80	3.00
1320 46464	8.80	7.75	55.00	58.75	31.50	67.50	3.60	7.00	2.80	3.50
1350 44796	15.00	13.75	52.50	87.50	19.50	27.50	4.40	10.00	4.00	6.50
1350 45074	60.00	42.00	97.50	130.00	17.30	27.50	11.30	15.00	6.30	6.50
1350 45352	5.60	9.00	23.60	80.00	27.80	39.25	12.50	13.75	3.70	5.00
1350 45630	20.50	27.50	31.30	108.75	16.30	29.00	6.50	10.00	3.40	6.50
1350 45908	7.50	7.50	28.80	50.00	24.50	32.00	7.50	7.50	4.30	6.50
1350 46186	27.50	31.25	65.00	83.75	27.50	21.75	6.50	10.75	3.30	5.25
1350 46464	11.30	16.25	30.00	75.00	44.00	35.50	6.90	9.00	4.30	3.50
1350 46742	10.50	18.61	42.50	138.89	15.00	62.50	4.30	13.89	20.00	10.00
1350 47020	7.30	8.50	40.00	75.00	41.50	53.00	6.00	8.25	3.00	5.25
1350 47576	5.80	7.00	33.80	57.50	39.30	43.00	53.80	7.00	3.00	3.75
1350 47854	8.50	12.00	33.80	108.00	44.80	77.50	4.90	9.50	4.50	7.25
1380 44796	37.50	27.50	70.00	108.75	16.00	27.50	4.90	12.00	8.50	6.50
1380 45074	18.80	17.50	52.50	130.00	13.00	30.00	5.50	10.50	20.00	5.00

REFERENCE	LEAD		IRON		MANGANESE		ZINC		COPPER	
	1983	1984	1983	1984	1983	1984	1983	1984	1983	1984
1380 45352	11.80	9.00	38.80	116.25	26.00	39.75	6.50	6.50	1.80	3.00
1380 45630	10.50	10.75	54.30	130.00	21.80	30.50	5.30	7.75	3.90	1.50
1380 45908	17.50	12.25	71.30	242.50	26.00	47.50	7.50	11.25	3.90	8.50
1380 46186	10.00	12.25	60.00	58.75	14.50	18.75	3.90	9.50	3.90	5.25
1380 46464	7.50	10.75	23.80	142.50	45.80	36.75	11.80	9.50	3.40	5.25
1380 46742	10.30	6.25	81.20	50.00	50.00	29.25	8.20	7.00	7.20	7.00
1380 47020	6.80	9.25	78.80	75.00	102.00	90.50	7.10	9.00	7.30	7.00
1380 47298	6.30	10.00	40.00	92.50	23.30	41.25	6.30	10.00	20.00	5.25
1380 47576	9.50	7.50	46.30	43.75	22.50	43.00	5.00	7.50	2.80	3.75
1380 47854	7.50	9.50	52.50	72.50	33.50	34.25	4.00	6.00	3.90	2.00
1380 48132	8.00	14.00	50.00	93.75	35.50	42.50	5.30	10.50	2.30	3.75
1410 44796	28.00	24.50	72.50	87.50	13.80	25.00	5.60	9.00	3.90	6.50
1410 45074	20.00	27.50	55.00	122.50	14.00	36.00	5.00	9.50	5.30	8.50
1410 45352	28.80	38.25	212.50	122.50	27.80	29.50	9.00	12.25	7.90	6.50
1410 45630	11.30	7.50	5.00	65.00	17.30	19.25	10.00	7.25	2.50	5.00
1410 45908	12.50	10.00	38.80	87.50	18.30	45.00	7.50	9.00	4.30	5.00
1410 46186	32.60	46.25	69.40	133.75	11.10	25.00	5.90	16.75	5.60	10.75
1410 46464	10.00	8.50	52.50	66.25	24.50	16.25	6.80	7.00	4.00	3.50
1410 46742	6.80	7.75	71.30	66.25	25.00	26.25	6.80	7.25	2.70	5.25
1410 47020	18.80	33.00	41.80	92.50	56.30	184.25	5.00	13.50	4.60	5.25
1410 47298	5.00	12.25	25.00	58.75	18.00	53.00	3.00	9.75	20.00	16.00
1410 47576	18.00	8.75	43.80	42.50	46.50	29.25	7.00	6.00	1.80	2.00
1410 47854	7.50	8.75	36.80	42.50	43.00	43.75	4.40	7.00	4.60	6.50
1410 48410	9.60	8.75	61.20	72.50	39.90	34.25	7.20	8.25	4.80	2.00
1410 48688	20.40	23.50	67.10	80.00	42.60	90.50	12.00	17.50	5.10	6.50
1410 48966	19.30	24.25	40.00	65.00	108.00	233.75	5.00	7.50	2.60	3.75
1440 44796	17.50	15.25	46.30	72.50	13.80	23.00	6.00	8.25	5.60	5.00
1440 45074	10.60	8.25	42.60	65.00	11.70	18.75	5.30	6.50	5.30	5.00
1440 45630	6.30	7.50	31.30	57.50	27.00	27.75	7.90	7.00	6.80	5.00
1440 45908	26.30	28.25	4.50	93.75	16.50	25.00	9.30	10.00	1.80	6.50
1440 46186	15.00	13.00	56.30	50.00	17.00	25.00	5.80	11.00	4.00	7.00
1440 46464	11.30	13.00	40.00	42.50	34.00	29.25	5.80	6.75	6.60	3.50
1440 46742	5.00	8.50	21.30	58.75	25.30	25.00	6.80	9.00	2.50	3.50
1440 47020	15.00	12.25	61.30	66.25	49.30	31.75	5.60	9.50	5.30	5.25
1440 47298	9.30	7.00	56.30	42.50	46.80	39.25	5.30	7.25	5.30	7.25
1440 47576	5.50	7.50	47.30	80.00	35.00	40.00	4.00	7.00	3.90	6.50
1440 47854	9.50	7.50	47.50	42.50	59.50	55.00	6.60	5.75	2.30	3.75
1440 48410	12.00	6.00	62.50	50.00	62.80	62.50	7.10	6.00	4.50	3.75
1440 48688	14.80	17.50	50.00	86.25	36.50	56.25	7.50	10.00	3.40	3.75
1440 48966	11.80	11.25	61.30	101.25	82.00	58.75	9.80	9.75	2.00	2.00
1440 49522	33.80	26.00	55.00	72.50	36.00	53.75	10.50	11.00	2.60	2.00
1470 44796	8.80	7.50	40.00	57.50	12.30	28.75	4.30	7.25	12.50	3.00
1470 45630	15.00	13.00	37.50	65.00	15.50	26.25	6.30	6.75	2.50	6.50
1470 45908	10.00	10.00	20.00	65.00	10.00	22.50	5.30	7.00	1.80	5.00
1470 46186	10.50	8.50	80.00	66.25	27.00	25.50	7.90	7.00	5.30	3.50
1470 46464	21.30	26.75	63.80	92.50	18.50	18.00	6.80	9.50	3.40	5.25
1470 46742	5.00	8.50	30.00	58.75	42.30	28.00	5.80	8.25	4.60	3.50
1470 47020	11.80	9.25	45.50	66.25	23.50	30.00	12.00	7.25	3.90	1.75
1470 47298	8.80	6.00	28.80	57.50	21.50	18.75	7.50	7.50	1.80	2.00
1470 47576	9.00	6.00	40.00	28.75	26.30	27.50	7.10	5.00	4.50	3.75
1470 48132	23.00	16.58	57.50	89.00	22.80	40.30	12.80	10.50	6.00	12.75
1470 48410	10.00	13.00	40.00	65.00	35.80	25.50	6.10	8.50	3.10	3.75
1470 48688	9.70	7.50	40.30	43.75	17.50	20.50	6.90	8.50	1.60	3.75

REFERENCE	LEAD		IRON		MANGANESE		ZINC		COPPER	
	1983	1984	1983	1984	1983	1984	1983	1984	1983	1984
1500 44796	5.50	7.50	37.50	65.00	17.30	25.00	4.10	8.25	4.00	3.00
1500 45074	6.30	8.25	26.30	80.00	16.00	30.00	6.40	10.75	1.80	3.00
1500 45352	15.50	10.75	48.80	80.00	39.80	49.00	8.30	9.25	2.50	5.00
1500 45630	6.30	7.00	31.30	42.50	18.30	25.50	4.60	5.50	3.30	1.50
1500 45908	6.30	7.50	26.30	35.00	18.00	17.50	5.80	5.00	1.80	1.50
1500 46186	18.80	16.75	56.30	92.50	42.80	31.25	13.90	11.25	3.90	5.25
1500 46464	19.30	27.50	40.00	66.25	17.80	18.75	8.40	12.50	5.00	5.25
1500 47298	18.50	39.00	47.50	93.75	34.30	43.75	9.80	17.50	5.30	9.00
1500 47854	8.10	11.25	75.60	101.25	36.90	66.75	14.00	15.75	2.30	7.25
1500 48410	8.50	8.75	40.00	50.00	18.00	26.25	6.80	8.00	1.50	3.75
1500 48688	10.80	12.00	41.30	65.00	22.00	44.50	6.40	9.75	2.30	3.75
1500 48966	21.50	20.00	53.80	50.00	40.00	48.00	5.00	8.50	3.40	6.50
1530 44796	8.80	9.00	52.50	72.50	23.00	51.00	5.80	9.25	5.00	5.00
1530 45074	8.60	7.50	27.40	50.00	38.50	70.00	9.30	13.00	2.90	6.50
1530 45352	12.50	8.25	56.30	35.00	34.00	29.00	5.30	6.00	4.60	3.00
1530 45630	17.50	7.50	50.00	65.00	20.00	29.00	8.00	8.25	3.40	5.00
1530 45908	6.30	7.50	31.30	50.00	10.30	24.50	5.50	7.25	1.80	5.00
1530 46186	22.50	21.50	56.30	100.00	27.30	26.25	14.00	13.25	5.90	7.00
1530 46464	13.00	15.50	40.00	50.00	17.80	17.50	6.80	7.00	2.30	3.50
1530 46742	14.30	28.50	37.50	122.50	37.00	19.25	6.80	12.00	3.00	9.00
1530 47020	7.50	9.50	43.80	72.50	35.00	48.75	6.30	8.50	2.00	7.25
1530 47298	6.50	7.00	59.90	80.00	55.50	176.25	11.60	23.00	10.10	11.00
1530 47854	12.00	7.50	62.50	57.50	119.80	156.25	12.00	11.25	4.50	6.50
1530 48410	19.20	15.75	37.80	36.25	23.50	33.75	8.70	10.50	2.60	6.50
1560 45074	5.50	7.50	26.30	50.00	47.80	27.50	5.60	5.50	1.80	3.00
1560 45352	13.80	14.50	56.30	122.50	21.80	29.00	6.10	7.50	4.60	5.00
1560 45630	7.50	7.50	21.30	42.50	25.80	27.00	6.00	5.25	1.80	3.00
1560 45908	13.80	14.50	38.80	65.00	23.80	23.00	8.00	9.00	2.50	3.00
1560 46186	45.00	82.95	56.30	123.58	23.80	22.73	6.80	18.47	3.30	5.97
1560 46464	15.30	17.50	43.80	50.00	18.50	15.50	6.30	8.25	4.00	3.50
1560 47298	8.50	8.75	41.30	57.50	40.00	46.25	5.00	10.00	3.80	9.00
1560 47576	9.50	11.25	36.30	57.50	29.80	29.25	7.50	10.25	2.80	2.00
1590 45074	7.40	9.00	30.90	50.00	16.80	32.50	7.10	9.00	1.00	3.00
1590 45908	11.80	11.50	37.50	65.00	18.50	26.25	5.90	9.00	.90	5.00
1590 46464	11.30	13.00	37.50	58.75	29.30	28.75	8.50	8.25	3.80	5.25
1590 46742	17.50	25.00	73.80	100.00	30.30	31.25	8.00	14.00	4.00	9.00
1590 47020	21.10	13.75	44.40	58.75	24.20	27.50	8.10	9.50	3.30	7.00
1590 47298	95.00	31.00	45.00	86.25	2.80	38.75	12.50	14.00	2.60	3.75
1620 44796	56.30	29.75	27.50	108.75	11.00	59.25	6.80	21.25	12.50	10.00
1620 45074	47.50	75.25	42.50	108.75	22.80	41.50	5.50	21.25	4.00	5.00
1620 45352	24.60	16.75	56.80	42.50	50.50	43.00	16.70	12.83	2.70	3.67
1620 45908	17.50	14.50	21.30	42.50	32.00	19.25	7.90	8.25	1.80	3.00
0840 45074	86.30	54.69	165.00	215.63	53.50	95.31	20.00	25.94	4.50	12.19
0840 45630	36.30	19.95	200.00	236.70	22.00	73.14	24.30	27.93	7.30	10.37
0750 45630	55.00	65.00	585.00	395.00	105.00	103.75	90.00	110.00	44.00	42.50
0780 45630	56.30	58.75	225.00	615.00	36.00	88.00	28.00	60.50	10.50	27.00
0750 45908	44.70	34.66	466.00	755.68	77.60	154.83	22.90	67.05	11.10	35.23
0690 45908	19.30	28.33	220.00	383.33	54.50	183.33	16.80	41.67	5.30	13.06
0840 45630	36.30	50.87	200.00	395.35	22.00	79.94	24.30	39.24	7.30	13.66
0810 45074	16.80	23.00	75.00	106.25	19.50	45.00	7.50	13.75	6.50	9.75