UNIVERSITY OF
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AN ASSESSMENT OF HEAVY METAL AND PESTICIDE POLLUTION AT A COMMERCIAL AIRPORT

By

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DECLARATION

I hereby declare that this work was carried out in full at the School of Chemical and Physical Sciences, University of KwaZulu-Natal, Pietermaritzburg.

I hereby certify that this investigation, unless otherwise stated, is the result of my own research.

Signed:

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I hereby certify that the above statement is correct.

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DEDICATION

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ABSTRACT

An assessment of heavy metal and pesticide pollution was conducted at a commercial airport in Pietermaritzburg, which is the base for a local crop spraying operation, as well as a small-scale aircraft maintenance centre. The study investigated the presence of heavy metals from the aircraft activities (tyre wear, emission and aircraft body attrition) along the edges of the runway. In addition, the study assessed the pollution of the soil in different parts of the airport (areas adjacent to the crop sprayer hangar and maintenance hangars drainage ditch) caused by organic chemicals (pesticides) originating from the washing and maintenance of the crop spraying aircrafts.

A total of 37 samples were taken from the top soil (0-15 cm) adjacent to both sides of the runway, approximately 100 meters apart, for heavy metal assessment. Total metal concentrations were determined on a 1:1 HNO_3 acid extract analysed using inductively coupled plasma spectroscopy and the results compared with the baseline concentrations of heavy metals in the soils of South Africa. The average levels of the heavy metals in the soils were: Cd - 4.4, Co - 76, Cr - 142, Mn - 6580, Pb - 64 and Zn - 70 mg/kg. The Cd and Co concentrations of all samples and the Pb and Zn concentrations of 86% of the samples were above the South African guidelines for the maximum permissible contents of these metals (2 mg/kg Cd, 20 mg/kg Co, 6.6 mg/kg Pb, 46.5 mg/kg Zn) in soils. In addition, the concentration of Cr was significantly above these guidelines (80 mg/kg Cr) in 51% of the samples. All the metals, except zinc, were highly correlated with one another indicating the source for these heavy metals is the same. In addition the concentration of these metals was high at sampling points adjacent to the runway where pronounced aircraft tyre wear marks were observed, suggesting that the aircraft activities are the sources of these heavy metals.

A total of 13 samples were collected from areas adjacent to the crop sprayer hangar and the drainage ditch (at the maintenance hangars) in order to determine the qualitative presence of organic pollutants. The samples were prepared using soxhlet extraction. Cypermethrin, deltamethrin, azoxystrobin, fusillade and fluazifop-p-butyl as well as fuel oils Jet A1 and Avgas were qualitatively determined using GC/MS. Only fusillade and fluazifop-p-butyl were detected in some of the samples. No quantitative analysis of the organic chemicals was attempted due to time constraints.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
AES	Atomic emission spectrometry
BCF	Bioconcentration factor
BOD	Biological oxygen demand
CEC	Cation exchange capacity
CI	Chemical ionisation
CSIR	Centre for Scientific and Industrial Research
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
dl	Detection limit
EI	Electron ionisation
EPA	Environmental protection agency
EPTC	Ethyl dipropylthiocarbamate
FAS	Iron(II) ammonium sulfate
GC	Gas chromatography
GC-MS	Gas chromatography- mass spectrometry
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
K-D	Kuderna-Danish
K_d	linear distribution coefficient [L kg^{-1}]
K_{ow}	Octanol/water partition coefficient
l.s.d.	Least significant difference
m/z	Mass to charge ratio
MS	Mass spectrometry
NEMP	National Environmental Management Plan
PCE	Polychloroethylene
PMT	Photomultiplier tube
ppm	Parts per million
PVC	Polyvinyl chloride
RF	Radio frequency
s.e.	Standard error
SCOT	Support coated open tubular

TBA	Tetrabutylammonium
TOF	Time-of-flight
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
WCOT	Wall coated open tubular columns

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Industrial growth is the goal of all developing countries. However, with increasing industrialisation comes the inevitable increase in industrial pollution. This is because it requires time to identify and act on pollution problems and political circumstances may slow or halt such action. Governments' concern to create jobs usually means that when investors propose a new factory, little attention is given to the likely environmental impacts. A second reason why pollution can be particularly serious is the concentration of industry in relatively few locations. In most Third World nations, industrial production is heavily concentrated in one or two city regions. For instance Bissau, Nairobi and Port-au-Prince contain a high proportion of their nation's total industrial output.[1] Eritrea, the home-country of the author is no different in this regard.

The manufacturing industrial sector in Eritrea at present consists mainly of light industries producing a variety of goods, including processed food, beverages, textiles, leather goods, chemical products, construction materials, ceramics, and metal products.[2] Eritrea is likely to see an expansion of industrial activities, both public and private, now that the damaging wars with Ethiopia (1960-1991 and 1998-2000) are over.

Eritrea is endowed with commercially significant mineral deposits, including native deposits of gold and silver and minerals containing copper, zinc, lead and iron ore.[2] There are also sizeable deposits of industrially-important minerals such as potash, sulfur, gypsum, feldspar, silica sand, and resources for the construction industry, such as granite, marble and limestone. The government, interested in the potential economic enhancement that mineral production and beneficiation could provide, continues to seek international investment in its mineral industry.

The government of Eritrea realises that development in all sectors has to be planned carefully to ensure the rational use of natural resources and to prevent environmental degradation. Consequently, it has produced and disseminated the National Environmental Management Plan (NEMP)[3] which, it is hoped, will ensure sustainable development of the country's natural resources taking into account social and economic demands. The NEMP includes the application of environmental impact assessment procedures and environmental monitoring.

Although urbanisation in Eritrea remains, as yet, limited, the potential for the deterioration of the environment with increasing urbanisation and industrialisation is a subject of concern to the government. Nearly all the major industries in the country are located in urban areas. According to a 1997 report[4], the distribution of Eritrean factories is uneven, with 55% of private enterprises and about 90% of public enterprises located in the capital city, Asmara. Almost all the waste generated by these industries is either disposed of as liquid wastes, which run untreated into sewers or other nearby water bodies, or dumped on landfill sites. The problem is exacerbated due to the fact that there are limited water resources in the country, and the existing dependable sources are groundwater. Thus, the pollution of groundwater by industrial effluents will have serious consequences.

Industrial pollution is not the only cause of air and water pollution. The high proportion of households and businesses not served by sewers, drains and garbage collection add greatly to land and water pollution problems, while very congested traffic, with inefficient and poorly maintained engines, adds greatly to air pollution.

To determine lines of action to be taken to control and manage natural resources and to minimise or eliminate environmental degradation, the government plans to initiate research through its own institutions, the University of Asmara, non-governmental organizations and the international community in fields embracing natural resources conservation and management. This will require the collection, analysis, dissemination and application of basic data to the conservation and management of soils, forests, wildlife, fisheries and water.

A literature survey into soil and ground water pollution has been undertaken to highlight the possible sources of pollution in Eritrea. The actual project has been designed to train the author in experimental methodology in environmental chemistry, including data collection, analysis of the data and most importantly, forming scientifically-sound conclusions.

As the project area was limited to Pietermaritzburg, a general look at possible sources of pollution was done in the environment of Pietermaritzburg in order to select a study site which may act as a relevant case-study for dealing with environmental pollution applicable to the Eritrean context. Consequently, the commercial airport in Pietermaritzburg was selected as a study site due to the fact that it gives the opportunity to study both organic and inorganic pollutants.

1.2 THE STUDY AREA

Pietermaritzburg is an administrative and industrial city with a population of 457 700.[5] It is located in the midlands of southern KwaZulu-Natal, about 80 kilometres inland of the coastal city of Durban. The city is well served by road and rail network and the busy N3 highway, which links Durban and Johannesburg, passes through the city. The uMsunduzi River flows from the southwest to the northeast across the city. The Baynespruit, Dorpspruit, Chase Valley spruit, Blackburrowspruit, Mkondenispruit and Foxhillspruit are the major tributaries that drain to the uMsunduzi River from the city catchment area.

Manufacturing industry in Pietermaritzburg is focused in six sectors.[6] The leading industrial sector is the metal manufacturing industry in which the Hulett Aluminium factory is having a great economic impact. The other manufacturing sectors are wooden products, shoes, agricultural products, electronics and carpets. Most of these industries are located in four major industrial areas in the city:

- Willowton industrial area, located on the hill slopes to the northeast of the city
- Camps Drift, located in the south of the city
- Mkondeni, located southeast of the city, and
- Victoria road, located in the central part of the city

Another potential pollution source in the city is the local airport, and this was identified as the inspection site for this study. Pietermaritzburg Airport (Oribi Airport) is located south of the city of Pietermaritzburg, nearby Bisley Heights and north of the Ukulinga agricultural research station and Bisley Valley Nature Reserve. The airport is situated between two streams, the Backburrowspruit and Foxhillspruit, located at the east and west side of the airport (runway) respectively.

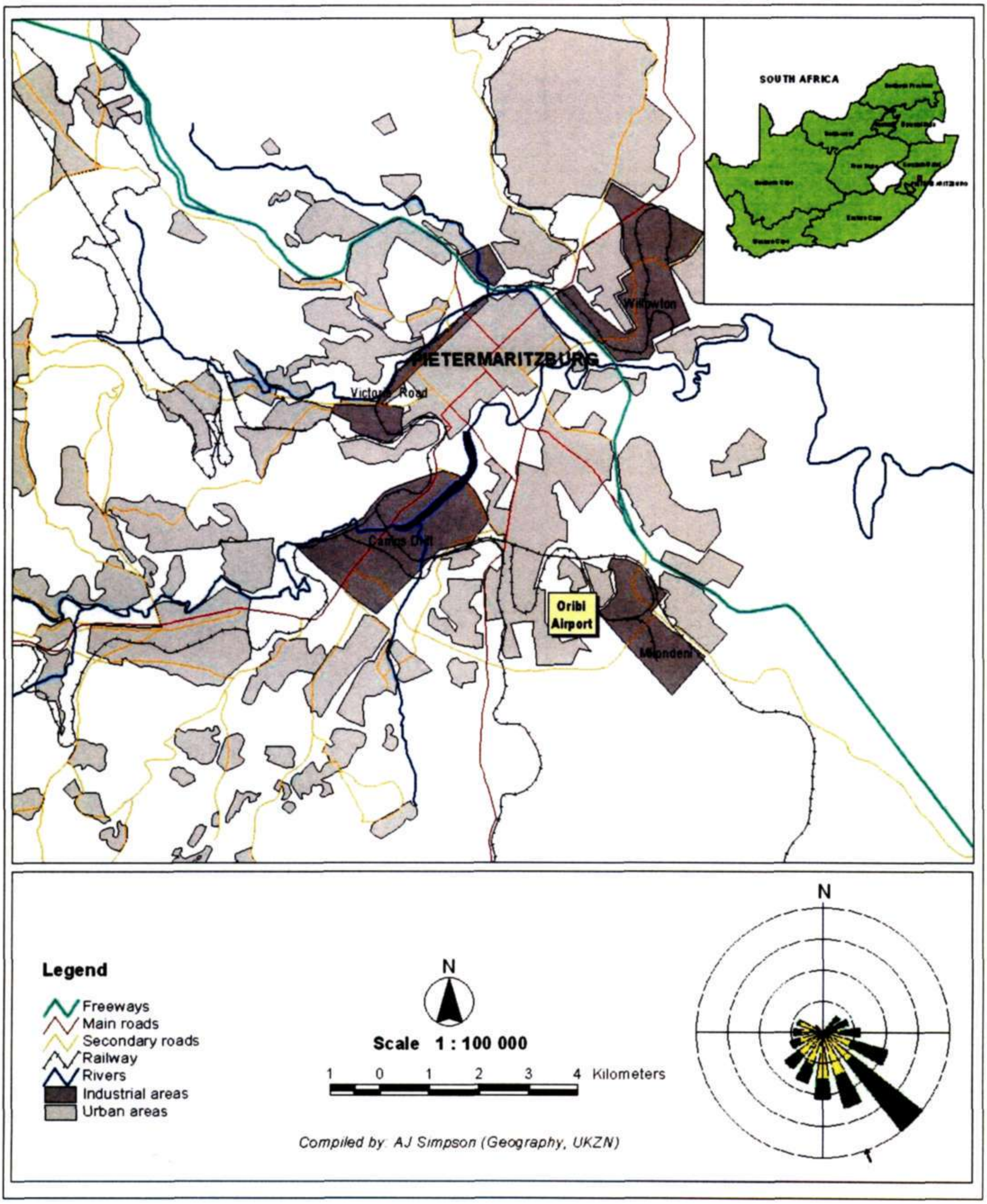


Figure 1.1 Pietermaritzburg study area showing airport, transport infrastructure, rivers, industrial and urban areas. Inset shows location of study area within South Africa.

Turnaround Management on behalf of the Msunduzi City Council of Pietermaritzburg operates the airport. The airport has a runway 1580 meters long and 30 meters wide. There are six tenants in the premises of the airport that are involved in a variety of airport-related businesses.[7] The tenants and services they render include:

- SA Airlink: a scheduled airline that offers passenger services,
- Crop Sprayer Company: involved in agrochemical spraying of crops,
- Pacair and Oribi Flying Services: companies involved in aircraft maintenance operations, and
- Flight Training College and Aero Club: organizations offering flight-training services.

The airfield maintenance involves a fire and rescue vehicle (cat. 4 airport), a maintenance LDV (Nissan Bakkie), and grass cutting equipment (Falcon Shlasher and tractors). The airport gives service to approximately 20000 small passenger (max. 29 passenger), crop spraying and training aircrafts annually.[7] The aircraft maintenance operation organizations provide maintenance and rebuilding (painting, servicing, overhauling) and aircraft washing services to approximately 64 aircraft annually.[8,9]

The Crop Sprayer Company is involved in spraying of pesticides, sugar cane ripening chemicals and fertilizers, as shown in Table 1.1. The crop spraying aircraft, the chemical mixing and refilling equipment are all washed in the crop sprayer hangar. The wastewater from these washing activities goes to a ditch, which flows down approximately 150 meters before it reaches a fence surrounding the airport. During the dry season, the flow of the wastewater does not go far beyond the fence. However, in the rainy season the flow of the water through this ditch can go far beyond the fence, i.e. it drains into the stream in the vicinity (Blackburrowspruit).

Table1.1 Chemicals used by the Crop Sprayer Company.[10]

Type of chemical	Chemical name
Insecticide	∝-Cypermethrins Deltamethrin
Fungicide	Amistar Flutriafol Punch extra
Herbicide	Glyphosate
Cane ripening	Ethephon (Ethrel) Fusilade
Fertilizer	Urea (granular)

Aircraft maintenance and painting in Pacair includes aircraft maintenance and washing.[8] The wastewater from the maintenance is poured into a container that has a water layer (bottom) and a paraffin layer (top). The oil (hydrocarbon) goes to the paraffin and the non-hydrocarbon wastes go to the water. The oil (hydrocarbon) waste is, then, taken by another company for disposal. Aircraft are washed using water and detergents or soap. When painting the aircraft, sawdust is applied to the ground so that the paint spill during painting rests on the sawdust, which then is collected and disposed with the solid wastes. On average two aircraft per month get serviced by this company. The types of aircrafts that get serviced are passenger/spray aircraft below 5000 lb (2268 kg) weight.[8]

Services rendered by Oribi Flying Services include: maintenance rebuilding (painting, servicing overhauling, etc), washing aircraft, painting (acrylic paints) and aircraft washing outside the garage.[9] The methods of waste handling are similar to those used by Pacair. Approximately 40 passenger aircraft below 6000 kg weight per year get major services by this company.

The aircraft use Avgas and Jet A1 fuels stored on site.[7] Lubricating grease and hydraulic fluids used for the aircrafts and support vehicles include Aeroshel and synthetic hydraulic fluids (for brakes).[8,9] In addition polyurethane paints, licathenes, paint thinners and other organic solvents are used in the garage for different activities (washing, painting, etc).

The objective of this study is, therefore, to assess the pollution levels of the soil in different parts of the airport area caused by:

- organic chemicals (pesticides) from the washing and maintenance of the crop spraying aircrafts (area adjacent to the crop sprayer hangar and the drainage ditch)
- heavy metals from the body of the aircraft, the landing gear and tyre wear of the aircraft (along the edges of the runway).

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Though pollution is strictly defined as any departure from purity, environmental pollution means realistically a departure from a norm rather than a pure state. In the context of water pollution, for instance, pure water will mean a state of water in which no substance is present in sufficient concentration to prevent the water from being used for purposes thought of as normal. Some of these uses would be recreation, potable water, agriculture and industry. Hence water suitable for a particular use and therefore considered to be unpolluted, may be considered as polluted when other uses are considered.[11]

Soil and groundwater pollution are not independent phenomena. Groundwater is polluted commonly when liquid or solid wastes are disposed of or stored for a time on land.[12] Soil pollution can also be a hazard to human health when potentially toxic substances move through the food chain or reach the groundwater used for drinking water supplies.[13] The pollutants in soil can further pollute groundwater if the condition of the soil above the groundwater favours the mobility of the pollutants laterally. Hence, the pollution of soil or groundwater has a potential pollution impact on the other.

Freshwater is fundamental to the survival of humans and most other land-based life forms. About 96.5% of the earth's water is the salt water of the oceans and seas. Most of the remaining 3.5% is in polar ice caps, glaciers, the atmosphere or underground and hard to reach. Only 0.4% is available for use. Groundwater amounts to 1.7% of global water reserves, and the freshwater from groundwater resources contains 30.1% of the total global freshwater reserves.[14] According to Alcock[15] groundwater accounted approximately 15% of the total water consumed in South Africa in 1980. Groundwater supply is maintained by water evaporating from oceans and lakes and then falling to the earth as rain in a process called the hydrological cycle.

Population growth, especially in the last 100 years, has increased economic and industrial activity which, in turn, has increased the demand for freshwater. In addition, rapid urbanisation is changing the patterns of consumption of water, and the pressure to increase the area of productive land means there is greater demand for irrigation.

Groundwater is highly susceptible to contamination. Once contaminated, groundwater is difficult to clean, requiring great expense and, in fact is sometimes impossible.[17] Thus, protecting groundwater from possible pollution sources makes sense economically. Some groundwater is more susceptible to contamination because of the kind of soils and rocks above it. In some cases the groundwater is so close to the surface that pollutants do not have far to travel. In other cases, soils above the groundwater are porous and pollutants can move quickly. Groundwater in karst areas (i.e. topography with sinkholes, caves, and underground drainage that is formed in limestone, gypsum, or other rocks by dissolution) becomes polluted more easily and in shorter time periods than water in non-karistic areas.[18] On the other hand, poorly drained soils make it difficult for septic systems to perform well, which may result in groundwater contamination. Hence it is important to know the fates of pollutants in soil to determine their impact on the environment.

2.2 SOIL AND GROUNDWATER POLLUTION

2.2.1 Types of Soil and Groundwater Pollution

Water can be polluted in many different ways, and it is even possible that the same aquatic system can be affected by more than one type of pollution. Depending on the behaviour of the pollutants, water and soil pollution can be classified as arising from physical, chemical and biological sources.[18]

Physical pollution affects the physical properties of groundwater and soil. It is caused by variations in temperature, undissolved solid substances like silt, the colouring or muddiness of the water and as a result of dyes and foam on the water from artificial detergents.[19] The resulting changes in physical properties of groundwater and soil may then affect the biological and chemical processes in the ecosystem.

Biological pollution is caused by the presence of parasites, pathogenic bacteria and viruses. Pollution of this kind comes mainly from infected human and animal wastes. Soils can be contaminated with pathogenic organisms (bacteria, viruses and parasitic worm eggs) from various sources, including the burial of dead animals, manures and sewage.[13]

A large variety of illnesses arise from the microorganisms that pollute water. Some of these microorganisms are parasites, which for part of their life-cycle use man as a host, causing ill health. Water is a potential carrier of pathogenic microorganisms and can endanger health and life. Historically, the prevention of water-borne parasitic diseases, such as cholera, dysentery, typhoid and paratyphoid fever, was the primary reason for water pollution control.[11] Nevertheless, many people and animals, especially in the agricultural sector, depend on drinking water from irrigation canals, often without it having been treated beforehand. Hence, human beings as well as animals are infected by parasitic diseases.

Chemical pollution encompasses a great number of different, naturally occurring and man-made chemicals. Most of the chemicals in commercial use constitute potential toxic hazards. Hence, many of these chemicals can cause pollution of soils as a result of leakage during storage for future use in the environment and from their disposal either directly or through wastes containing them.[13] Chemical pollutants can be classified as biodegradable and nonbiodegradable. Biodegradable pollutants are substances that can be broken down in time by the action of aerobic or anaerobic bacteria. Nonbiodegradable pollutants are materials that are not broken down by biological processes such as plastics, metals and glass. Chemical pollution can be further categorised into two main forms, namely organic and inorganic pollution.

2.2.1.1 Organic pollution

Most forms of organic pollution arise due to the release of human, plant and animal wastes in one form or another, through man's activities in his environment. One of the major sources of organic pollution is the effluent arising from sewage treatment works.[20] Other sources of organic pollution include industries such as breweries, dairies and food-processing plants. Water run-off from hard surfaces and roads in towns, especially during storm conditions can contribute a great deal towards organic pollution. Farm effluents have become a particular problem, with the intensification of livestock rearing and overwintering of animals in confined buildings as well as the increased use of silage to feed them. The biological oxygen demand (BOD) of such silage run-off can be as much as 200 times greater than the normal settled sewage.[20]

Usually organic waste matter ends up in the hydrosphere. Plant and animal remains, which act as nutrients for a large variety of microorganisms and other forms of aquatic life, are the main sources of this organic matter. Much of the oil pollution of water is from petrol and oil washed from roads, together with illegal discharge of engine oil, transport accidents and spillage from storage tanks.[20] In cases where the pollution is limited, the polluted water can be purified effectively using normal purification processes, which include chemical dosing of the polluted water to coagulate the suspended colloidal particles using flocculants, sedimentation of the large particles, filtration of fine particles and disinfection using chlorine, hypochlorites or ozone.[19] However, the decomposition of organic matter utilises the available oxygen in the water. Hence, decomposition of large quantities of organic matter depletes the oxygen content of the water which may become detrimental to aquatic life.

Eutrophication, which is the artificial increase in nutrient levels of lakes or other water bodies, usually causes an increase in the growth of aquatic animal and plant life. Eutrophication sources include agricultural run-off and leaching of fertilizers, manure washes from farms, and acid rain water from fossil fuel burning.[20] According to Mason 50% of the nitrogen applied to crops is lost to water.[20] Septic conditions can develop in water bodies exposed to eutrophication, giving rise to bad smells and tastes in the water. When this water reaches underground sources, it could pollute the drinking water in wells and boreholes.

Many industries contribute towards the pollution of water sources. In fact, industry itself can be its own pollution victim. The purification requirements for water affected with organic salts prior to usage makes it less suitable for many purposes.[19] In this case, the greater any industry's pollution of water, the greater will be the cost to that industry of purifying/treating this resource before it can be used or sent to waste disposal.

2.2.1.2 Inorganic pollution

This category of pollutants includes inorganic salts, mineral acids, and metals or metal compounds. The presence of these pollutants in soil and groundwater may result in an increase in acidity, salinity and toxicity of the soil and groundwater. Sources of acidity are mainly acid mine drainage and industrial effluents. The sources of salinity are varied and include industrial effluents, irrigation, salt brines from mines or oil wells and ocean salts.[11,14]

Industry is creating an enormous range of new chemicals each year, most of which eventually find their way into the aquatic environment. Little is known of their acute, chronic or genetic toxicity to man, plant or animal.[21] Certain inorganic substances are extremely toxic and may destroy aquatic life completely. Compounds containing mercury, lead, arsenic, cadmium, chromium and nickel appear to be the most toxic, persistent, and abundant in the environment.[11] These metals are known to accumulate in the bodies of organisms, remain for long periods of time, and behave as cumulative poisons. For instance, chromium from metal-plating industries is a well-known source of respiratory hazard as an acid Cr(VI) mist and poisons microorganisms used to treat sweage, while mercury discharge also receives a great deal of attention due to its bioaccumulation potential in animal tissues.[11]

Inorganic pollution is much more difficult to control, and potentially more hazardous, than organic pollution because it is more difficult and expensive to treat.[11] Natural purifying processes are often ineffective, and desalination processes are often the only cost effective way to treat this type of water pollution.

2.2.2 Sources of Soil and Groundwater Pollution

The sources of groundwater and soil pollution are from natural processes and human (anthropogenic) activities in the environment. Natural pollution has been occurring since the creation of earth and is still continuing. The major contributors to natural pollution are: natural waste, soil erosion, and salts.[19] Natural waste is generated through the decomposition of plant and animal remains in the water sources and the land. The decomposition products are washed from the land down to the water sources usually by rainwater. This leads to a high degree of organic pollution, which gives the water bad odour, colour and taste. Soil erosion, in general, occurs in the mountainous areas and semi-deserts and significantly contributes to the amount of silt present in the water sources. Water acquires its brown muddy colour from the silt, which is finally deposited onto the riverbeds and the impoundments. The salts in the environment are of a geological origin.[19]

Anthropogenic pollution is as old as man himself and gathered momentum through the development of agriculture. The last 200-300 years, during which the industrial revolution was accompanied by major population growth, have led to the greatest problems associated with environmental pollution.[22] With the increase in population, urbanisation and industrialisation the anthropogenic sources of pollution also increased. These pollution sources include municipal and industrial landfill leachate, leakage from septic tanks and petroleum storage tanks, and agricultural (pesticides and fertilizers) leachate.[16]

Anthropogenic pollution of groundwater and soil is classified into two different types, namely pollution originating from point sources and non-point (diffuse) sources. Point sources of pollution are located at a specific point. Hence, it is often easy to control pollution from such sources. Non-point sources, however, are not located at a specific point and as a result pollution occurs over a broad area. Thus it is often not possible to control or even measure pollution from such sources. Pollution arising from non-point sources accounts for a majority of the contaminants in streams and lakes. Every time it rains, the rainwater washes off driveways, roofs, parking lots, roads, agricultural fields, construction sites, forestry operations, and other surfaces carrying with it contaminants to the streams, lakes, oceans and groundwater. Generally, anthropogenic sources contribute by far the largest proportion of pollution into groundwater and soils.[23]

The anthropogenic sources of pollution can also be categorised under the following headings; agricultural, mining, industrial, municipal (urbanisation) and air deposition.[18]

2.2.2.1 Agricultural activities

Malpractices in agriculture, such as extensive grazing and wrong cultivation methods, accelerate natural erosion and the leaching of salts. The storage and movement of agricultural wastes and the application of fertilizers and pesticides also have large negative impacts on groundwater quality.[18]

The application of fertilisers and pesticides generate wastes and salts, which often leach into water environments.[19] Fertilizers contain large amounts of nitrates and phosphates, which when leached into water environments, over stimulate the growth of aquatic plants and algae. Excessive growth of these types of organisms consequently clogs waterways, use up dissolved oxygen as they decompose, and block light to deeper waters. This, in turn, proves very harmful to aquatic organisms as it affects the respiration of fish and invertebrates that reside in water.

Intensive farming practices, such as poultry farming, are also important sources of pollution. Nevertheless, systematic planning practices, such as anaerobic digestion of animal wastes to produce bio-gas, may lead to such wastes being used to great benefit with limited soil and water pollution.[19]

The amount of agricultural wastes produced, in general, is much greater than the municipal-industrial wastes. In the United States, for instance, agricultural waste is produced at a rate of about six and half times that of municipal-industrial waste production.[21] Nevertheless, agricultural pollutants, which originate from agricultural wastes, principally consist of biodegradable materials.

2.2.2.2 Mining

Mining and mineral processing provide the raw materials and energy resources needed to sustain modern civilization. However, it also has an impact on the environment due to the enormous amount of waste generated during the exploration, extraction and smelting of ores.[24]

In non-fuel mining, the valuable portion of the crude ore is a small fraction of the total volume of material that must be handled to obtain it. In copper mining, for instance, over 500 tonnes of solid waste is generated to produce one tonne of copper.[21] However, this enormous quantity of waste generated by mining is not evident as municipal-industrial waste because the mining process takes place in remote areas. It has been estimated that these wastes are generated at a rate of more than four and half times greater than that at which municipal-industrial waste is produced. These types of wastes are largely nonbiodegradable.[21]

Mining involves several stages.[24] Removing the overburden and waste rock exposes the ore. The ores are then extracted (mined) and transported to a nearby mill, where they are beneficiated (concentrated or dressed). Beneficiation processes include physical and chemical techniques such as gravity concentration, magnetic separation, electrostatic separation, floatation, ion exchange, solvent extraction, precipitation, and amalgamation.

Mining and beneficiation processes thus generate four types of large volume waste: mine waste, tailings, dump and heap leach waste, and mine water. Mine wastes are produced in the process of exposing the ore. In dump and heap leaching which often covers hundreds of hectares, different chemicals such as acids and cyanide are added to the ores to dissolve the required minerals.[25] The low-grade ore then becomes a waste. Mine water, the water that infiltrates the mine, must be removed to facilitate mining. This water is mineralised as a result of the oxidation of the ore and rocks, and salt leach-out.[19] Solution mining, whereby water is pumped down an injection well to the deposit where it dissolves the minerals and is then brought back to the surface through extraction wells, is a potential contaminant for groundwater reservoirs.[21] All these wastes produced from the mining process can cause physical and chemical pollution to soils and groundwater.

Ore bodies generally include a range of minerals containing both economically exploitable metals (in ore minerals) and uneconomic elements (in gangue minerals). The uneconomic elements in the ore are left with the tailings since it is not profitable to extract these elements. Though acids are discharged by a large variety of human activities, mining operations and abandoned mines are the largest sources of acids.[26] Coal and ore mines produce acidic drainage, which includes typically 100 to 600 ppm sulfuric acid. Acid mining drainage is produced when the mineral pyrite (FeS_2), commonly found in coal seams, is exposed to air and water resulting in the formation of sulfuric acid and iron hydroxide, as shown in equation 2.1.

$$4\,FeS_2 + 15\,O_2 + 14\,H_2O \rightarrow 4\,Fe(OH)_3 + 8\,H_2SO_4 \qquad (2.1)$$

This is recognised as a serious environmental pollution problem because the mobility of heavy metals such as Mn, Zn, Pb, Cu and Cd in mining effluents, is enhanced by transformation of sulfides and a shift to more acidic conditions.[27] Therefore, metalliferous mining is an important source of contamination by a wide range of metals because most mine sites are contaminated with several metals and accompanying elements such as sulfur. In addition, wind blown tailings and ions in solution from the weathering of ore minerals in tailings from heaps tend to be the major sources of pollution from abandoned metalliferous mine sites.[13] In South Africa gold mining generates much of the wastewater from the mining industry. This water is contaminated with toxic cyanide from the gold leaching operations. Coal mining has also contributed substantially to the pollution of both surface and groundwater resources.[28]

2.2.2.3 Industries

Industries produce a vast variety and large amounts of wastes during their processes. For instance, a 1981 study [29] conducted in the United States showed that the wastes generated by the industrial sector were 264 million tonnes, which was more than one tonne of waste for every person. There has been increasing concern about the dumping of toxic wastes onto landfill sites, particularly the large number of uncontrolled dump sites, and the threat of contamination of groundwater as a consequence of leaching of toxic materials from the soil into water courses.[30]

Rainwater, being the main medium of distribution of pollutants in the tropics, can contain metals like Mn, Fe, Cu, Zn, Hg and Pb in considerable amounts from industrial and fossil fuel combustion emissions.[31] Industrial effluent that is released during production processes can either be reused or discharged into existing water sources after purification. In places where industrial sludge is stored, water pollution could develop due to the leaching of pollutants out of the waste material and subsequent drainage into surface water or groundwater.

Industrial wastes are complex mixtures of biodegradable and nonbiodegradable components.[21] The characteristics of industrial wastewaters can vary considerably. Most of these wastes contain high concentrations of organic substances. The impact of industrial discharges depends not only on their collective characteristics, such as biochemical oxygen demand and the amount of suspended solids, but also on their specific inorganic and organic substance contents. Industries that process basic raw materials are especially responsible for the release of inorganic pollutants such as acids and dissolved mineral salts in the water environment.

The following types of industries are amongst those producing wastes that pollute the water and soil environment.[32]

- Food and related products: these include meat and dairy products, beet sugar refining, brewing, distilling, and canning. Wastes from these industries contain high concentrations of decomposable organic matter.[32]
- Textile products: cooking the fibres and desizing the fabrics produces wastes which have high BOD and are quite alkaline, requiring neutralisation and other treatment. Nemerow, cited by Hodges, reported that the production of 1000 kg of wool leads to 1500 kg of impurities.[32]
- Paper and allied products: the effluent from paper and pulp mills is a complex mixture of chemicals used in the process, stray wood chips, bits of bark, cellulose fibres, and woody tissue carbohydrate (lignin). During the bleaching process of paper strong oxidizing agents are used. The dyes, inorganic salts and chlorinated organic compounds could be dangerous and poisonous to certain water organisms, even in low concentrations, when discharged in the effluent and eventually in water environments.[19]
- Chemical industry: a wide variety of chemicals are produced by chemical plants manufacturing acids, bases, synthetic fabrics, pesticides, fertilizers, detergents and many other organic and inorganic compounds.
- Petroleum industry: oil refineries and petrochemical industries produce great numbers of different pollutants such as hydrocarbons, acids, alkalis, cyanides, phenolic compounds, inorganic and organic sulfur compounds, and halogenated and nitrogenated hydrocarbons.
- Rubber and Plastic industry: wastes from rubber production contain some of all the materials used in the process such as butadiene, styrene, soap solution and acid-brine solution. Wastes from plastic manufacturing include hydrocarbons and other organic compounds, as well as various reagents.
- Metal industries: wastes from steel mills tend to be acidic and contain cyanogen, phenol, ore, coke, limestone, alkali, oils, mill scale and fine suspended solids. Other metal producing and metal finishing industries produce wastes which generally contain the metal being produced or plated such as chromium, lead, nickel, cadmium, zinc, copper and silver as well as acids, alkaline cleaners, grease, and oil.

According to a 1992 Centre for Scientific and Industrial Research (CSIR) report [33] on the industrial waste of South Africa, a total of 418 804 998 tonnes of waste is produced by industry annually, out of which 99% is solid waste and 1% is effluent. Mining waste, most of which is inert tailings, overburden and spoil, accounts for 90% of the total industrial waste. Excluding the mining and power generating wastes, the comparative waste quantities generated by the manufacturing industries are: 1% from chemical products, 11.7% from building materials, 2.3% from food processing, 0.9% from textiles, 2.1% from pulp and paper, 0.2% from metal processing and 81.8% from metallurgical industries such as iron and steel refining mills.

In addition the report showed that 1 892 681 tonnes (0.5%) out of the total bulk waste generated annually is regarded as hazardous. The contribution of each sector to toxic waste is: chemical products 6.7%, electronics 0.1%, textiles 8.7%, building materials 0.1%, metal processing 2.6% and metallurgical 81.8%.

2.2.2.4 Urbanisation

In urban areas, where thousands of people are concentrated, water pollution is expected. Generally the urban areas comprise three main sources of pollution: residential, business and streets. In residential areas pollution occurs as a result of the waste produced by pets, pool backwash, the use of pesticides in and around the house and garden and the use of manure and fertilizers. On business premises, such as garages, light and heavy industries, the spillage of a great variety of pollutants takes place. Spillage and contamination with oil and other pollutants in the streets, where vehicles are constantly moving, on sidewalks and at airports and railway stations is another source of urban pollution. Highway environments are relatively constant sources of anthropogenic organic matter as well as heavy metals.[34]

From studies on the sources of hydrocarbon pollution by Latimer *et al.*[35], it was shown that industrial and highway sources are much greater than commercial and residential sources. In addition, the primary source for the hydrocarbon content in run-off is from used crankcase oil, originating from oil drops on road surfaces and parking areas, as well as illegal dumping of waste crankcase oil.

Waste disposal poses a considerable threat to the environment since the dispersal of the disposed hazardous wastes is a key component in groundwater contamination.[36] Domestic wastes are disposed of mainly in sanitary landfill sites. Many common household products (paint thinners, moth-balls, and drain and oven cleaners, to name few) contain toxic ingredients. Sewage wastes, treated or untreated, are normally released into rivers and are the source of plant nutrients such as phosphorous and nitrogen, which cause excess in aquatic growth. Raw municipal wastewater contains high concentrations of organic material, phosphorous, nitrogen, heavy metals, pathogenic bacteria and viruses.[18]

2.2.2.5 Precipitation of air particles

Air pollutants are emitted both from natural and anthropogenic sources to the atmosphere. The natural emissions include volcanoes, sea spray and dust whilst the anthropogenic sources include emissions from industries, the combustion of fossil fuel for energy and motorised vehicles. These pollutants that are released from the anthropogenic and natural sources are removed from the atmosphere by dry and wet mechanisms and are deposited at the earth's surface (land and water bodies).[37]

Particulate air pollutants includes substances having a very diverse physical and chemical properties, with their diameters ranging from <0.01 to >100 μm. Most of the >2 μm particles consist of pollutants which are natural in origin such as wind-blown soil and marine aerosol. On the other hand, the major part of the aerosol having diameters < 2 μm contain man-made components such as lead from motor exhausts and ammonium sulfate from atmospheric oxidation of sulfur dioxide. But, the major part (by mass) exists in the 0.1–10 μm range. This is because very fine aerosol particles grow rapidly by coagulation, and large particles sediment rapidly under gravitational influence.[37]

Elimination of atmospheric pollutants down to ground level can happen either through dry or wet deposition. Wet deposition can be accomplished by two distinct mechanisms, i.e. rainout and washout.[38] In the rainout mechanism, aerosol particles are incorporated into cloud droplets before the raindrops are formed within the cloud. In the washout mechanism the raindrops falling from higher altitudes scavenge airborne particles at lower altitudes by impaction and coagulation. The overall efficiency of wet deposition is described by the scavenging ratio W, as shown in equation 2.2.[37]

$$W = \frac{\text{Concentration in rainwater (mg kg}^{-1}\text{)}}{\text{Concentration in air (mg kg}^{-1}\text{)}} \tag{2.2}$$

Higher values of W for a pollutant indicate that the efficiency of removal of that pollutant by wet deposition is high. Although fogwater contains moderate volumes of water, the scavenging of particles from the atmosphere by fogwater can be significant as compared with rainwater because pollutant concentrations in fogwater are usually much greater than in rainwater.[37]

Dry deposition involves the transfer and removal of gases and particles at land and sea surfaces without the intervention of rain or snow and accounts for about 20% of the total aerosol deposition.[39] This sedimentation process is governed by Stokes' law (equation 2.3):

$$V = \frac{2}{9}\frac{gr^2}{\eta}(\rho - \rho_a) \tag{2.3}$$

where V is the terminal settling velocity, r is radius of particle, g acceleration due to gravity, ρ and ρ_a density of the particle and air respectively, η is the viscosity coefficient of air.

The law predicts that the terminal settling velocity for particles in the micron and sub-micron range will be less than 0.1 cm s^{-1}, which is much less than the normal eddy velocities associated with turbulence and mixing, and therefore, particles of this size would be expected to remain in suspension.[39] Chamberlain[40], however, reported a greater deposition efficiency for particles of this size on rough surfaces than previously suspected. Hence, even in the absence of precipitation processes there still remains a route whereby particles can be removed from the troposphere.

The overall dry deposition rate of a pollutant is usually expressed in terms of the deposition velocity, V_g, where[11]

$$V_g(\text{cm s}^{-1}) = \frac{\text{Flux to surface (cm}^{-2}\text{ s}^{-1}\text{)}}{\text{Atmospheric concentration (cm}^{-3}\text{)}} \tag{2.4}$$

V_g is influenced by Brownian diffusion for a particle diameter size of less than about 0.1 μm, and gravity settling accelerates V_g for particles with diameters greater than 1.0 μm.

For particles in the diameter range of 0.1 µm to1.0 µm, V_g is nearly constant and only eddy diffusion is regarded as an important deposition process.[41]

In general, dry deposition of atmospheric pollutants is a continuous process, while wet deposition is an irregular process. Hence, only dry deposition may always be relied upon to remove airborne pollutants and is always cleansing the atmosphere.[41]

Industrial emissions and the combustion of fossil fuels for energy emission contribute considerable amounts of pollutants to the environment. Burning of coal for industrial, domestic and power generation purposes is the major source for airborne pollutants such as sulfates, nitrates and chlorides. Sulfur dioxide, one of the airborne pollutants, is set free in the atmosphere where it dissolves in the moisture to form sulfuric acid. This results in acid deposition, both in the form of "wet" precipitation (as acid rain or acid mist) and "dry" deposition, where it is deposited on the surfaces such as the soil, plant leaves and water.[19]

2.2.3 Airport Pollution

Air transport plays an important role in the global economy as the demand for air travel is rising in line with the prevailing global economic growth. Like any other economic activity, air transport has an effect on the environment. This has created concern that the industry's environmental impact is increasing in proportion to its growth.[42]

There are several activities in airports with potential to cause pollution if not controlled. These activities are mainly aircraft servicing and maintenance facilities within the airports.[43] Some soil and groundwater pollution sources from airports are similar to the pollution sources arising from highways. These include: vehicle pollution (e.g. leakage of oil and lubricants, and tyre and brake linings wear), pavement wear (breakdown of asphalt and/or concrete surfaces), maintenance operations (application of de-icing compounds, pesticides, etc), and accidental spills.[44]

Almost all airport maintenance facilities clean and degrease soiled vehicle and aircraft parts in small solvent baths using organic solvents.[45] It is extremely difficult to clean the exterior of aircraft because of their size and the fact that they are built of very sensitive, lightweight, metal-composite materials. Part of the difficulty also comes from the non-uniform shape of the aircraft. Hence aircraft bodies and engine parts that are too large to fit into the parts washers have to be hand cleaned using solvents such as polychloroethylene (PCE).

Many of the service and maintenance vehicles at airports use petroleum-based hydraulic fluid systems, including tractors, heavy trucks for clearing runways of snow and ice, and other equipment. The release of petroleum-based hydraulic fluids can contaminate airport land and the surrounding waterways. According to Hewitt and Candy, cited by Turer *et al.*[36], aircrafts and vehicles used in airports release aerosols from the combustion of lead-containing gasoline.

Lubricating greases are used extensively in airport operations maintenance workshops. The workshop maintains several large trucks used to remove snow and ice from runways and aprons during winter operations. It also maintains several snowploughs and sweepers that are attached to the trucks that use hydraulic systems. In addition, the maintenance workshop is responsible for servicing the grass-cutting tractor and its accessory equipment. Heavy-duty grease is needed to lubricate and protect all moving mechanical parts of this equipment.

Another source of pollution from airport maintenance activities is spills from paints. Vehicle, aircraft, runway and apron-marking paint are mostly oil-based.[46] In addition, aircraft and vehicle tyre wear are sources of pollutants such as Zn and Cd. Lead-acid batteries are used in most vehicles and pump houses at airports. Batteries that sit unused for long periods of time or where vehicles sit idling under a heavy load become flat since crystallised sulfur molecules coat the lead plates. If not handled and recycled properly the lead in the batteries may be washed away by water and find its way into the surrounding soils and groundwater.

In conclusion, different sources from the different activities in the airport contribute to soil and water pollution in the surrounding areas of the airport by heavy metals organic chemicals and pesticides. Pesticides, herbicides, disinfectants applied to the airfield and from the air-spraying activities; oils, paints, wastes from workshops facilities, leakage from pipes and storage tanks, run-off from paved areas, heavy metals from the runway, and aircraft and vehicles maintenance activities all contribute to water and soil pollution near airports.[43]

2.3 FATES OF ORGANIC CHEMICAL (PESTICIDE) AND HEAVY METAL POLLUTANTS IN SOILS

2.3.1 Soil

Soil is made up of solid components, water and dissolved salts, and air.[47] Soil solids have two kinds of components: inorganic clay minerals derived from weathering of rocks and organic mineral matter.[48] The inorganic mineral matter, silicate and nonsilicate clays, is made up mostly oxygen, silicon, aluminium and relatively small quantities of other metals, and accounts, for 50-60% of soils.[47] The organic matter, on the other hand, is derived mostly from plants and microorganisms.[48] The air in soils is composed of gases found in the atmosphere but in different proportions.

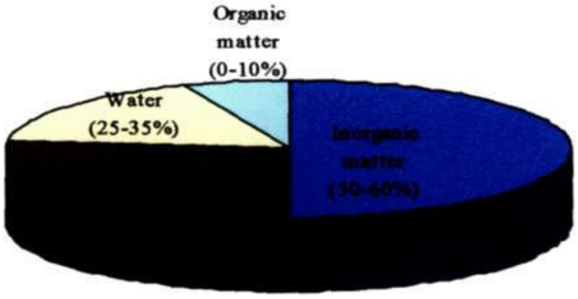


Figure 2.1 Average composition of soil material.[47]

2.3.1.1 The soil horizons

Soils are deposited in or developed into layers, called horizons, which have a distinct structure and composition. The soil nearest the surface contains the most humus (plant and animal materials). The further from the surface (one goes), the less humus and the more rock particles there are. There might be as many as six different soil horizons, in which the thickness of each horizon varies with location.[49]

The top layer is called the 'O' horizon. This layer consists of fresh or decaying organic materials, such as leaves, dead plants and animal remains. The 'O' horizon is usually thick in forest soils as these forest areas produce large amounts of organic waste. Other areas, such as deserts, produce very little organic waste and therefore have very thin or even no 'O' layers. The 'O' horizon has a characteristic dark colour due to the humus formation by decomposition of organic matter. The layer directly below the 'O' horizon is called the topsoil or 'A' horizon. This layer is the top most mineral horizon composed of dark mixture of organic and mineral materials. It is generally darker than the lower horizons because of greater amounts of decomposed organic matter. This layer is mainly mineral material and contains most of the soil animals and plant roots. 'A' horizon is the surface horizon in the absence of 'O' horizon.[50]

The third layer is called the 'E' horizon, a mineral horizon located under the 'A' horizon. It is also known as the zone of eluviation because of the maximum leaching of soil constituents such as humus, Fe and Al compounds occurs in this zone. The fourth layer is the 'B' horizon, or subsoil. This layer is usually lighter coloured, denser, and lower in organic matter than the 'A' horizon. It is commonly the zone where leached materials accumulate (illuviation zone). Hence, it contains silicate clay, iron, aluminum, humus and many of the nutrients that have been washed down by the rain from the 'E' horizon.

Below the 'B' horizon is the 'C' horizon. This layer consists of partially disintegrated rocks and mineral particles, but has no organic material. The lowest horizon, the 'R' horizon, is bedrock. This parent material is the rock from which the minerals in the soil are removed as well as the source of most of the rock particles found in the soil.

2.3.1.2 Clays

Clays are the active mineral portion of soils, mostly newly re-formed from the soluble products of the primary minerals.[51] Most of the clay minerals are aluminosilicates, with oxygen, silicon and aluminium being the major elements in their structure.[48] Clays are divided in two major groups depending on the composition of the atoms, in the main building blocks of the clay structure - silicate and nonsilicate.[50]

Silicate clay minerals consist of Si-O tetrahedron and Al-O octahedron structures, where the Si and Al atoms are surrounded by 4 and 6 atoms of oxygen respectively.[47] The Si-O tetrahedral and Al-O octahedral structures form chains (sheets) by sharing oxygen atoms. The Si-O tetrahedral and Al-O octahedral sheets, in turn, are attached together by sharing oxygen atoms, and form a unit layer which has definite and repeating arrangements of atoms.[51]

Silicate clay minerals can be classified into three groups depending on the ratio of tetrahedral to octahedral sheets arrangement in a unit layer.[47]

- 1:1 clay: clays having one tetrahedral to one octahedral sheet, e.g. kaolin, nicrite.
- 2:1 clay: clay with two tetrahedral to one octahedral sheet, e.g. mica, pyrophylite.
- 2:2 clay: clay having two tetrahedral to two octahedral sheets, e.g. chlorite.

Some soils contain large quantities of clay size nonsilicate minerals which have some similar properties to silicate clays.[48] The nonsilicate clays constitute metal oxides and hydroxides of aluminium, iron and manganese that are commonly found in soils often in large quantities, and are also known as metal oxides.[47,48] Metal oxides occur in soils as free oxides, clay mineral coatings or clay edges.[47]

The charge and large surface area of clays are the two important properties to soil. Substitution of Si and Al by cations of similar size but lower oxidation states, such as Fe^{2+} and $Mg^{2+}$is a common occurrence during re-formation of clays from the soluble products of the primary minerals.[51] Substitution of Al and Si by atoms of lower oxidation state thus gives clays a permanent negative charge.

Another way in which clays obtain charge is protonation and deprotonation of oxygen atoms.[48] The protonation and deprotonation of the oxygen atoms attached to the metal ion renders a positive or negative charge. The charge obtained by protonation and deprotonation of metal oxides depends on the pH of the soil solution.[48] However, the charge on clays obtained by isomorphous substitution is permanent. The protonation and deprotonation reactions at different soil solution pH of Al oxide are shown in equation 2.5. Aluminium oxides have a positive charge at lower pH (acidic solution), are neutral at intermediate pH and have negative charge at higher pH (basic soil solution).

$$\underset{\text{Negative}}{AlO^-} + H^+ \rightleftharpoons \underset{\text{Neutral}}{AlOH} + H^+ \rightleftharpoons \underset{\text{Positive}}{AlOH_2^+} \qquad (2.5)$$

2.3.1.3 Soil organic matter

The major portion of the natural organic matter in soils is the recalcitrant remains of woody terrestrial plants.[52] Humus, the degradation product of these plant residues, consists of 70-80% by weight of the organic matter found in most soils.[53] These altered complex organic substances are referred to as *humic* substances if they are soluble or extractable in aqueous base, and *humin* if they are not.[52] Both humin and humic substances are made up mostly of carbon, oxygen and hydrogen with some nitrogen and sulfur. Humin molecules are larger than humic acid and they contain higher carbon content and lower oxygen content.[54] Humic substances are further subdivided into *fulvic acids* if they are soluble in both acidic and basic solutions and *humic acids* if they are insoluble in acidic conditions but are soluble at high pHs.

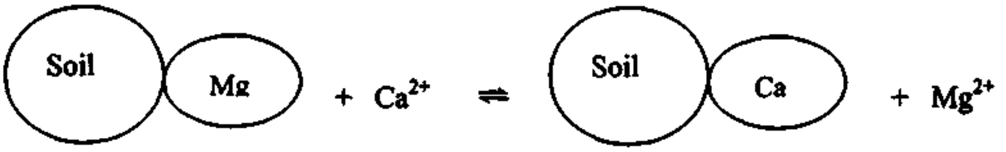
The important features of humic substances is firstly that they contain functional groups, such as carboxyl (COOH), hydroxyl (OH) and carbonyl (C=O), and secondly their large molecular size.[47] Soil organic matter obtains pH dependent charges by protonation and deprotonation of these oxygen-containing functional groups. In addition, humic substances have the potential to form complexes with heavy metals due to the presence of these oxygen containing functional groups in their structure. Moreover humic acids are more polar than humin.[55] This can be attributed to the higher oxygen content in humic acids.

2.3.1.4 Sorption

Different sorptive mechanisms may operate in soils, including ion exchange, cation bridging, charge transfer, hydrogen bonding, and van der Waals interactions.[56] These sorptive mechanisms can be categorised into two broad types: physical and chemical adsorption. Physical or van der Waals adsorption is due to: dipole–dipole, induced dipole (polarisation or dispersion) and ion-dipole interactions. Chemical adsorption is due to coulombic forces and results bond formation between the adsorbent (adsorbing specie) and adsorbate (adsorbed specie). In general, physical adsorption results in a low heat of adsorption (low binding strength), but chemical adsorption results in high heat of adsorption (high binding strength).[57]

Ion-exchange is one form of sorption mechanism in soils. The electrically charged colloidal surface of soils attracts ions of opposite charge in the soil solution.[51] Hence, the negative and sometimes positive charge site in soil clays and organic matter adsorbs ions of opposite charge in an exchangeable and nonexchangable form.

The negatively charged soil colloid surface repels anions in the soil solution away from its surface. This separates cations, which are attracted by the negatively charged surfaces from the anions in the soil solution. However, the exchangeable cations do not stick to the soil colloid surface permanently, but dissociate momentarily from the adsorbing surface due to the heat induced motion.[58] The soluble cation in the soil solution can therefore, replace the exchangeable cation by mass action, i.e. competition for the negative site because of the large number of ions present.[51] This exchange of one cation for another is known as cation exchange, and takes place on the surface of clay and organic matter (humus) colloids (equation 2.6). The amount of available charge sites for cation exchange is termed 'cation exchange capacity' (CEC). The pH dependent sites contribute 10-40% of soil CEC, and most of the CEC of soil organic matter is pH dependent.



(2.6)

Unlike the cation exchange capacity, anion exchange capacity arises mainly from the pH dependent positive charges that develop on soil colloidal surfaces, under strongly acidic conditions.[58] The positive charge on the soil colloids attracts a negatively charged ions from the soil solution, by a mechanism similar to the cation exchange and this processes is known as anion exchange.

Another mechanism of sorption is the complex formation of metal ions and charged surfaces of the clays and organic matter.[47] This reaction involves outer sphere complexation, inner sphere complexation and water bridging. Outer sphere complexation is the electrostatic attraction between metal ions in the soil solution and oxygen in the clay or humic substance. This interaction is relatively weak and the cation can be exchanged by other weakly bonding cations. An inner sphere complexation, on the other hand, is the bond formation between charged surface containing at least two donor atoms and unhydrated cation. This interaction is relatively strong, thus the cation can only be exchanged by cations that are capable of forming inner sphere complexes. In water bridging the metal ions are not directly complexed with the charged surface, but are bridged to the charged surface by water molecules.

Hydrophobic retention need not be regarded as an active adsorption mechanism and is often considered as a partitioning between water and a non-specific organic phase.[59] Partitioning is a processes in which the adsorbate dissolves or is spread into the network of the organic phase. Therefore, partitioning is distinguished from adsorption by homogeneous, non-specific distribution of the sorbed material throughout the entire volume of the organic phase. Hydrophobic retention is related to the water solubility of the adsorbing organic compound and is independent of pH, but does depend on the molecular size of the adsorbing organic compound. In general, the greater the molecular size, the greater the adsorption potential is.[47]

2.3.1.5 Soil pH and oxidation-reduction reactions

Soil solution pH is one of the important properties in soils as it influences the interaction between soil colloids and soil solution components. Ions in the soil solution have the potential to change their oxidation states. According to literature,[47] iron may be present in soil solution as $Fe^{(II)}$ and $Fe^{(III)}$, and manganese as $Mn^{(III)}$ and $Mn^{(IV)}$; and the physical and chemical behavior of these elements depends upon their oxidation state. Moreover, sulfur exists generally as a soluble sulfate (SO_4^{2-}) in its +6 oxidation state, but in its -2 oxidation state it exists as S^{2-}, which is generally insoluble because of its tendency to form insoluble covalent metal sulfides. Hence oxidation-reduction reactions affect the interactions of elements with variable oxidation states as they change their oxidation state from a higher to lower or vice versa.[47]

Soil-water pH is one of the soil properties affected by redox reactions. Reducing conditions increase soil pH by deprotonation of soil water (equation 2.7), while oxidizing conditions release H^+ ions from soil water and decrease soil pH (equation 2.8).[47] For these redox reactions to proceed, there should be a source and a sink for the electrons involved in the reaction. In soils, O_2 acts as a sink (electron acceptor) and plant organic residues act as electron donors (source).[47]

1. Reducing conditions

$$2H_2O + MnO_2 + 2e^- \longrightarrow Mn^{2+} + 4OH^- \qquad (2.7)$$

2. Oxidizing conditions

$$H_2O + S + 3/2\,O_2 \longrightarrow SO_4^{2-} + 2H^+ \qquad (2.8)$$

The hydrolysis reactions in soils tend to increase either the acidity or the basicity of the soil solution depending on the kinds of hydrolysable materials in the soil.[55] For instance Al^{3+} hydrolysis increases the acidity of the soil solution, but $CaCO_3$ hydrolysis increases basicity of the soil solution.

$$Al^{+} + H_2O \rightleftharpoons AlOH + H^{+} \tag{2.9}$$

$$CaCO_3 + H_2O \rightleftharpoons Ca^{2+} + OH^{-} + HCO_3^{-} \tag{2.10}$$

In general, soils are complex mixtures of mineral particles of various shapes and sizes; living and non-living organic materials including microorganisms, roots, and plant and animal residues; air; and water. Soil is dynamic in nature, where closely interrelated physical, chemical and biological reactions occur constantly. The physical and chemical forms of the soil play an important role in influencing the nature of biological and chemical reactions.

2.3.2 Fate of Organic Chemicals in Soil

Soil can receive a substantial quantity of organic pollutants that are either applied on purpose or incidentally deposited from a variety of sources. These organic pollutants may be agricultural chemicals, mainly pesticides, and industrial organics, mostly petroleum by-products, plastics and resins.[47] Following release into the soil surface, the parent organic chemicals and their degradation products may be subjected to various fates. They can enter into the soil or be transported to the aquatic environment by run-off into surface waters and by erosion of contaminated soils into streams. When in the soil, the organic pollutant can percolate through the top layer, then penetrate through the unsaturated zone, and eventually reach groundwater in its original form or as a breakdown product.

The environmental fate-processes of organic pollutants in soil is governed by a variety of complex and dynamic physical, chemical and biological processes.[57] These include: sorption-desorption, biological and chemical transformation, and movement, all of which depend on the physical and chemical properties of both the soil and organic pollutant.

Sorption is a process of accumulation of a substance (organic pollutant) by adsorption, surface precipitation and co-precipitation, and diffusion into the adsorbent.[60] However, since sorption processes are reversible, the sorbed organic pollutant can be released back into the solution by desorption. The sorption-desorption process largely influences the other fate processes of the organic pollutant by controlling its availability in the soil solution.

Although this subject has been studied intensively, sorption processes are still not yet fully understood.[60] However, the available information provides some understanding of the factors affecting adsorption and its mechanisms, and lays the basis for assessing the behaviour of pesticides in soil and in the environment. For instance, it is now evident that soil chemical properties, which increase the sorption of organic pollutants, consequently reduce their transport and therefore protect groundwater contamination.[61]

Organic pollutant transport processes determine their redistribution within the soil and eventually into the environment, i.e. into the atmosphere, surface waters and living organisms. Movement of pesticides within soils can occur by diffusion and mass flow, as adsorbed on soil particles or by volatilisation. The movement of organic chemicals from the soil to other parts of the environment (the atmosphere, biosphere and hydrosphere) occurs by volatilisation, run-off, leaching, absorption and physical removal.

Biotic degradation is the most common process contributing to the disappearance of organic chemicals from soils.[57] The persistence of organic chemicals in the environment has been shown to be directly related to the rate of its degradation processes.[47] Persistence of organic chemicals in the environment is of great concern since pesticide-residues remaining in the soil longer than desired may affect the soil biosphere in several ways. Organisms living in the soil can have their metabolic and reproductive activities affected by the pesticides. The possibility of pesticide-transfer into other parts of the environment will also be enhanced by their persistence.

In summary, fate processes can be divided into three major types: adsorption, which is the binding of pesticides to mineral or organic matter; transfer processes that move pesticides in the environment; and degradation processes that break down pesticides.

2.3.2.1 Adsorption of organic chemicals (pesticides)

Adsorption is the physicochemical process by which an organic chemical present in the soil solution bind to the soil particles.[57] It controls, directly or indirectly, all the other processes in the soil that affect organic chemicals by determining how much of the organic chemical is solubilized and moves to the aqueous and gaseous phase, degrades, or is consumed by organisms.[57] Hence, it represents probably the most important mode of interaction of organic pollutants with soil components.

a) Soil properties and adsorption

Soil solids provide both a sink for the retention of organic chemicals, and sites for a variety of surface reactions as they possess a large and chemically varied surface area.[62] The adsorption behaviour of organic chemicals depends on soil properties such as the soil moisture, organic matter content, clay content and pH.[63] Soil organic matter and clay content play an important role in adsorption of organic chemicals because they provide a large number of sites onto which pesticides and other molecules can bind. Organic matter has an adsorption capacity potential for organic chemicals that may act as cations as well as for non-ionised organic chemicals that can be adsorbed by physical adsorption.[58,64] Studies on the soil adsorption of some pesticides in Australia revealed that adsorption of the pesticides increases with increase in the organic matter content of the soil, indicating that the organic matter content of the soil has an influence on the adsorption of pesticides on soil.[64] It has been reported that organic matter is an important contributor to 2,4,5-T adsorption, and adsorption of the herbicide tended to increase with increase in organic content of the soil.[65]

Organic compound adsorption on soil organic matter can be accomplished in two ways.[47] Ionic (charged) organic compounds adsorb on charged soil colloid surfaces due to electrostatic attraction based on coulomb's law of attraction between unlike charges.[66] The adsorbing organic compound produces a positive charge by protonation and a cation adsorption on soil organic matter occurs. On the other hand, because of the presence of oxygens and nitrogens in its structure, soil organic matter is slightly more polar than hydrocarbons, but not as polar as water. Thus, adsorption can occur by hydrophobic-hydrophobic interactions between soil organic matter and the sorbing organic compound, since soil organic matter offer a relatively nonpolar environment into which a hydrophobic compound may escape without too much competition from water.[47]

Soil pH, or the acid/base balance of the soil solution, has an impact on the chemical's reactivity and certain soil functions such as microbial metabolism. Acidic and basic organic compounds have acid dissociation constants, and thus have pH dependent charges.[47] Acidic organic compounds, such as compounds containing carboxylic acid groups would be fully protonated at pH values approximately two units below their pKa, and have no charges. However, at a pH approximately two units above their pKa, they would be fully deprotonated and would be negatively charged. On the other hand, basic organic compounds, such as amino-group containing pesticides would have no charge when the pH equals their pKa. But when the pH is two units below their pKa, their functional sites would be protonated and they would have a positive charge.

A study on the retention of the pesticides diquat and paraquat in soil show that both the type and the content of clay minerals present in the soil are important for both sorption and subsequent desorption of the pesticides.[67] In addition, the sorption capacity of soils with significant clay contents (>5%) was found to be very high for these pesticides.

The effect of inorganic ions (salts) on sorption of organic chemicals has been noticed in the sorption of diquat and paraquat.[67] The sorption of these two pesticides on bassendean sand decreased significantly with increasing concentration of $CaCl_2$ in the soil solution. This is because the organic (herbicide) and inorganic ($CaCl_2$) cations compete for the sorption sites. In addition, wet soils tend to adsorb less pesticide than dry soils, either because water molecules will compete for the binding sites or some of the pesticide molecules will remain dissolved in the soil water.[68, 69]

Adsorption processes are exothermic and desorption processes are endothermic.[58] Hence, an increase in temperature will reduce adsorption and enhance the desorption processes. A temperature effect was observed for the adsorption of organophosphorous pesticides on clays.[70] This effect of temperature on adsorption was attributed to an increase in the pesticide solubility with increasing temperature, or being an exothermic process, the fact that adsorption will decrease with an increase in temperature.[71] These two factors work together and both lead to decreased adsorption as the temperature increases.[72]

b) Organic chemical (pesticide) properties and adsorption

Had it been only the soil properties that govern the adsorption process, all organic chemicals would have exhibited identical degrees of adsorption on the same type of soil. But in fact, certain pesticides, even within the same family, appear to be more strongly adsorbed than others, regardless of the type of colloid present.[73] The tendency of different organic chemicals to adsorb to soil varies with their chemical and physical characteristics, such as shape, size, polarity and polarisability, acidity and basicity, charge distribution and water solubility.[47]

Bailey *et al.*[74] reported that the major factor that determines the extent of adsorption of acidic and basic compounds on soil is their dissociation constant.[74] In addition, there is some evidence that, within a family of pesticides, there appears to be a relationship between solubility and adsorption.[58,73] Though the relationship between water solubility and adsorption has been the subject of much controversy, it is widely accepted now that water solubility may be related to adsorption only within a specific chemical group of compounds. According to Bailey *et al.*[74] and Leopold *et al.*[75], within a chemical family or an analogous series, the magnitude of adsorption is related to and governed by the degree of solubility.

Nonpolar organic compounds are adsorbed on both soil organic matter and clay. However, the adsorption of nonpolar compounds by organic matter is much greater than their adsorption by clay.[76] Nonpolar (hydrophobic) organic compounds can be sorbed on the hydrophobic surfaces in the soil out of the polar aqueous phase through non-specific, hydrophobic or partitioning processes. Predominant adsorption of nonpolar organic compounds by soil organic matter has been reported in soils that have a clay content to organic content ratio of less than 25.[77] Most often, the pesticide K_d (linear distribution coefficient [L kg^{-1}]) values, which are mostly related to the soil organic content, are used to describe pesticide adsorption capacity of each soil.[47] The adsorption of pesticides by soil increases with an increase in the pesticide's K_d value.

It has been reported that the soil organic matter, as a whole, is about twice as effective as the humic acid at adsorption of relatively nonpolar organic chemicals.[55] This implies that the overall polarity of soil organic matter is lower than that of soil humic acid. Thus this lower polarity and greater sorption capacity for nonpolar organic compounds has been ascribed to humin which constitutes the major part of soil organic matter.[55] Polar organic compounds show marked partition uptake by soil humic acid, while nonpolar compounds show greatly reduced and nearly constant uptake by humic acids.

The organic pollutant may be subject to other processes that can affect retention, after it has been adsorbed. Some chemicals may further react and become covalently and irreversibly bound, while others are only physically trapped into the humic matrix. Although limited evidence is available on their occurrence, van der Waals forces are involved between soil humic substances and non-polar organic pollutants.[78] Hence, hydrophobic sorption processes vary from complete reversibility to total irreversibility.

The sorption of nonpolar organic compounds by soils has been shown to be highly correlated with soil organic matter content, but other soil properties such as the type and amount of clay, soil pH, and hydrous oxide content, have little effect except in low organic matter systems.[76] Because of its polar mineral surface, natural clay is not an effective sorbent for non-ionic contaminants. But in low organic matter soils, the hydrophobic sites associated with mineral surfaces are not covered by natural humus materials and hence contribute to the sorption of nonpolar compounds.[79]

The effect of adsorption on pollutant migration in soil depends on whether the adsorption occurs on insoluble, immobile fraction such as clay, humin and humic acids, or on the dissolved or suspended mobile fraction, such as fulvic acids. Organic pollutant interaction with immobile organic fractions may result in complete immobilisation of the pollutant. Alternatively the pollutant can attach itself reversibly to the mobile organic soil fractions and migrate with them. This constitutes a potential time delayed source of contamination that might affect distant ground.[78]

2.3.2.2 Transfer of organic chemicals (pesticides)

Organic chemical transfer refers to the movement of organic pollutants from their site of application. Once organic pollutants are incorporated into soil, they can move to surface waters through run-off and erosion, to groundwater through leaching and to the atmosphere through volatilisation. Retention, mass flow, biotransformation/degradation and plant uptake are processes which have a great influence on the transfer of organic pollutants to groundwater.[80]

There are five processes that can move organic chemicals in the environment: volatilisation, run-off, leaching, absorption and physical removal.

a) Volatilisation

Volatilisation, the movement of organic chemicals in the vapour phase from the soil to the atmosphere, is an important pathway for the loss of organic pollutants from soil. Once volatilised, a pesticide can move in air currents away from the treated surface, a phenomenon known as vapour drift. Vapour drift differs from dust or spray drift in that it occurs after the organic chemical has settled. The physicochemical properties of the chemical and the soil, along with the prevailing weather conditions would determine the extent of volatilisation.

The potential volatility of an organic chemical is dependant on its inherent vapour pressure.[62] However, the environmental conditions and all other factors that control the behaviour of the organic chemical at the solid-air-water interface influence its actual vaporisation rates. One of these environmental conditions is the type of soil (the soil particle size and the soil porosity). The degree of volatilisation of an organic chemical pesticide can change with a change in the soil composition. Gerritise *et al.*[81] reported that approximately 90-98% of some organochlorine pesticides were lost through volatilisation from a sandy soil within a week, whereas in silt loam soil, the loss ranged from only 9-63%.

Harris and Lichtenstein[82] found that the rate of aldrin volatilisation from the soil rose with an increase in insecticide concentration, soil moisture, and temperature as well as the rate of air movement over the soil surface, but lowered with increase in clay and organic matter content. Similarly, Fang *et al.*[69] observed significant correlation between the loss by evaporation of the pesticide EPTC and soil moisture. The loss of volatile EPTC is prevented by its adsorption by the soil particles, and its adsorption was higher in dry soils than wet soils.[68,69] This is because compounds with a very strong affinity to the soil are strongly bound to soil particles and their concentration in the soil solution will be low, which implies the loss by volatilisation is low. Nevertheless, Spencer *et al.*[83] observed that the moisture content had no effect on the vapour density (volatilisation) of dieldrin, until the soil was dried to a water content corresponding to about a monolayer of water. A decrease below this water content caused a steep drop in the vapour density, which may be attributed to the competition between the water molecules and dieldrin for adsorption sites.

The results of volatilisation tests for 30 pesticides, with and without evaporation, reported by Jury *et al.*[84] showed that volatilisation of the pesticides depends on the evaporation rate of water. In general, the pesticide volatilisation rate is enhanced by evaporation, independent of the chemical properties of the pesticide.

b) Run-off

Strongly adsorbed chemicals on sediments can be transported laterally when the sediments are removed by erosion and run-off water. In addition, downward transport into the lower soil may occur, mainly in aggregated soils characterised by macropores and cracks. The run-off caused by rain or flowing water is an important mode of organic chemical transport from soils to surface waters to another soil location. Thus, the associated movement of the chemical may occur both on the adsorbed solute state or solution form.[85] The ratio of the chemical transported as solution to the amount adsorbed in the suspended particles is dependent on the organic chemical partitioning between the solid and liquid phases. The data on the transport of paraquat, atrazine and diphenamide, reported by Leonard *et al.*[85], showed that transport of atrazine and diphenamide was mainly in solute form whereas that of the strongly adsorbed paraquat was only in the adsorbed form on sediments.

Though the concentrations of pesticides in sediments are often 2-3 orders of magnitude higher than in the associated water, most pesticides are lost mainly in the water phase simply because sediment is usually such a small fraction, by weight or by volume of run-off.[86] In general, organic chemical losses in run-off are most likely when a heavy rainfall occurs or excessive irrigation is applied shortly after a pesticide is applied to the soil surface.

c) Leaching

Leaching is the movement of water and dissolved chemicals through soil. The pesticide leaching process can occur in two main mechanisms, diffusion and mass flow. Diffusion is a process whereby a material moves from a higher concentration to a lower concentration, at a rate proportional to the concentration, as a result of random movement of the molecule. Generally, diffusion of organic chemicals in soils is affected by the diffusion coefficients of the chemical in water and air, adsorption, soil water content, temperature, and some soil physical properties such as porosity and bulk density.[62, 87]

Mass flow is the movement of organic solutes associated with a net movement of water. The mass transport of water in soil, along with the pesticides dissolved and adsorbed to suspended particles, occurs through a network of pores of various forms, sizes and shapes. Organic chemicals flowing through soils are subjected to different interactions such as adsorption, degradation, volatilisation and plant uptake. However, the contact time between solute and soil solid phase is often insufficient to reach equilibrium, and these interactions have almost no effect on organic chemical movement.[62]

Adsorption of organic chemicals by soils and the rate of water flow are the main factors influencing the transport of the chemical through soil by mass flow. The correlation and regression analysis data obtained by Helling,[88] showed that the pesticide mobility was directly related to the water flow. Furthermore, an inverse relationship was observed between the movement of non-ionic compounds and their adsorption.

Organic matter content of the soil affects leaching due to its impact on pesticide adsorption. According to Holstein, cited by Bailey *et al.*,[57] an increase in the organic matter content of the soil results in an increase in adsorption of the organic pollutant to soil colloids and leads to decreased leaching (mobility) of the pollutant to groundwater.

The mobility of dissolved non-aqueous-phase organic compounds in porous media is influenced by non-ionic and anionic surfactants.[89] Large organic macromolecules (e.g. humic and fulvic acids, and commercial surfactants) are capable of increasing water solubility of non-ionic organic compounds, by creating a nonpolar (relative to water), micellar phase in water that is favourable for contaminant uptake by partition.[90] Non-ionic organic compounds partition into this emulsified phase is in inverse proportion to their aqueous (pure water) solubilities. Therefore, the presence of humic and fulvic acids, or commercial surfactants, can increase the apparent water solubility of the solute and thus increase their mobility. Moreover, anionic surfactant solutions can lower the interfacial fluid tensions; as a result their downward mobility by gravity and viscous forces of the organic contaminants increase. However, cationic surfactants are easily exchanged with inorganic ions such as Ca^{2+} or Na^{+} at the mineral-water interface and increase significantly the sorption of non-ionic organic compounds to the soil from water.[89] Thus, the mobility of non-ionic organic compounds is reduced.

In general, the effect of surfactants and humic material on mobility will be greatest for nonpolar compounds since they show the greatest sorption and hence the least movement in the absence of dissolved macromolecules.[91] The solute transport of nonpolar organic compounds is affected by the distribution of organic carbon in a soil-water system. Immobile organic carbon resulting from the sorption of cationic surfactants, or the existence of residual hydrocarbons, will provide a hydrophobic environment that increases the sorption of nonpolar organic compounds from solution and thus decrease their mobility. On the other hand, mobile organic carbon, such as colloidal organic carbon dispersed in the solution, increases the mobility of the nonpolar organic compounds by acting as the carriers of the compounds.[92]

In addition, the movement of organic chemicals in soils depends on the amount of water moving through the soil, the chemical's solubility and its degree of adsorption by the soil. Water flows from higher moisture to points of lower moisture potential, in any direction, i.e. up, down or sideways, depending on the amount and frequency of the water applied and the moisture potential of the soil.[93, 94] Chemicals in the soil solution, thus, move in all directions with the soil solution. Chemicals that readily dissolve in the soil solution, such as organophosphorous pesticides, are more susceptible to movement than the less soluble chemicals in the soil solution such as chlorinated hydrocarbon compounds. The fact that the aqueous solubility of organophosphorous pesticides, generally, is higher than the chlorinated hydrocarbon compounds, would indicate that they are much more susceptible to leaching than the chlorinated compounds.[94]

d) Absorption (uptake) of organic chemicals (pesticides)

Absorption is the movement of organic chemicals into plants and animals. Absorption of organic chemicals by organisms is influenced by species characteristics, environmental conditions, and by the chemical and physical properties of both the organic chemical and the soil. Once absorbed, organic chemicals may be broken down, passed through, or remain inside the organism.

The terrestrial and aquatic organisms' uptake of organic chemicals can be higher especially for hydrophobic or lipophilic organic chemicals. Such chemicals can bioaccumulate in the food chain. The increase in concentration of a chemical in an organism resulting from tissue absorption levels exceeding the rate of metabolism and excretion is known as bioconcentration. The bioconcentration factor (BCF), the ratio of chemical concentration in the organism to that in surrounding water, is often used to quantify the potential of this phenomenon. The octanol/water partition coefficient (K_{ow}), which quantifies the lipophilicity or hydrophobicity of a chemical, is a good indication of the BCF.[57] K_{ow} can be used as a measure of the chemical's affinity to the biota or an index of the ability of a chemical to pass through the biological membrane of living organisms. Hence, chemicals with high K_{ow} values can pass through the biological membrane; as a result they can accumulate in the biota. In general, chemicals with log K_{ow}<3 are accepted as non-bioaccumulating, whereas those with log K_{ow}>3.5 are high-bioaccumulating substances.[95]

e) Physical Removal of organic chemicals (pesticides)

When pesticide-treated plants or animals are removed from an area, any pesticide residues they contain are removed with them. The ultimate fate of those residues is a function of how the plant or animal is handled. Most harvested food commodities are subjected to washing and processing that removes or degrades much of the remaining pesticide residue.[96] Plant materials such as turf grass clippings and tree or shrub prunings also may contain detectable pesticide residues.[97] However, composting and decomposition provide an excellent environment for the degradation of these residues.

2.3.2.3 Degradation of organic chemicals (pesticides)

Degradation of organic chemicals from soil can take place in a number of processes such as chemical reaction, volatilisation, leaching, photodecomposition and uptake by plants.[98] Chemical and biological degradation of organic compounds usually involves reactions such as hydrolysis, oxidation, reduction, alkylation, dealkylation, dehalogenation, dehydrogenation, hydroxylation, ring cleavage, ether cleavage, condensation, conjugation and isomerisation.[62] Chemical reactions, which include biochemical reactions, however, are the dominant processes of disappearance of organic chemicals from soil. The chemical degradation of an organic compound can be either through non-biological or biological transformation.

Organic chemicals are microbially transformed either directly through metabolic processes or indirectly through secondary effects of microbial activity that alter soil pH and redox conditions. The rate of degradation of an organic chemical depends on its chemical properties, the soil environmental conditions and the microbial activity in the system.[57] Organic matter, temperature, moisture and pH generally vary significantly with soil profile and so does the associated microbial activity. Microbial activity in soils decreases with depth in soil profile due to the decrease in the organic matter content.[99]

Soil properties can affect the biological decomposition of organic compounds in many ways.[98] For instance, soil organic matter can affect degradation rates of organic compounds in two opposing ways. On one hand, high organic matter supports the soil microbial population so that it is accompanied by high degradation rates of organic compounds. But on the other hand, organic compounds have high adsorptive affinity towards organic matter, thus high amounts of organic matter in soil may make the organic compounds unavailable for degradation processes and will lower their decomposition. Hence the overall pattern of behaviour and the balance of factors will mainly depend on the individual organic compound.

Depending upon the availability of a sorbed chemical, adsorption may either enhance or decrease microbial degradation rates in soils.[100] Organic chemicals, which are irreversibly bound to soil organic matter, are isolated from the degrading organisms and thereby protected from intracellular degradation. On the other hand, organic chemical degradation by microorganisms can be facilitated since the microorganisms themselves may be sorbed on locations adjacent to the organic compound in the soil surface.[62]

Soil moisture content, pH and temperature can affect pesticide degradation because these factors have a direct influence on the microbial activity and pesticide availability (adsorption) for enzymatic and chemical attack. Guenzi and Beard[101] reported that both temperature and moisture content influenced the chemical conversion of DDT to DDE. In addition, the solubilities of certain elements found in soil systems are known to be pH dependent. This may also be very important in determining the extent of biological availability of pesticides.[58] Furthermore, the degradation pathways of pesticides in soil depend on the soil pH. This influence of soil pH on pesticide degradation pathways is illustrated by sulfonylurea pesticides; whereby chemical hydrolysis dominates in acidic conditions, but microbial degradation prevail in alkaline conditions.[102]

In general hydrolytic reactions, which can be mediated biologically and chemically, can occur in the presence of H_2O, H_3O^+ and OH^-, and are termed neutral, acid or base hydrolysis respectively. Therefore, the rate of hydrolysis is strongly pH-dependant and hydrolysis can be the substantial transformation pathway in soil and water.

Hydrolysis can be a significant factor in the breakdown of certain organic compounds, particularly below the surface zone where biological processes are often dominant. The rate of a hydrolysis reaction depends strongly on pH and temperature.[103] Humic substances can catalyse some chemical degradation reactions including hydrolysis. This leads to the formation of reaction intermediates and products having physical and chemical properties different from the parent compound and behaving differently with respect to migration in soil. However, though certain compounds are quite susceptible to hydrolysis, many experience negligible breakdown by this reaction compared to microbiological degradation.[103]

The rate of applications of pesticides to the environment also has an influence on its degradation rate. Enhanced degradation of certain pesticides with their repeated use has been observed frequently.[104] This is because frequent use of some pesticides may result in a build-up of a select group of microorganisms in soil, capable of degrading these pesticides rapidly.[57]

Soil organic carbon not only has a strong affinity for most non-ionic organic compounds but it can also promote abiotic transformation.[105] Clays with their large specific surface areas can make equally important contributions. Catalytic effects of clay surfaces in abiotic transformation of organic compounds (hydrolysis) have been observed on the degradation of parathion on clays.[106] These transformations are also affected by other soil conditions such as pH, moisture content, exchangeable cations. Similarly, redox reactions can also be biological or abiotic in nature. Oxidation is likely to be the more important pathway for the soils in the well-aerated upper vadose zone, whereas in water, especially in groundwater where oxygen is excluded, reduction is likely.[47]

Photolysis is another abiotic degradation pathway, in which pesticides are transformed due to their exposure to radiation.[57] Sunlight-induced photochemical transformations are important pathways in the abiotic degradation of organic pollutants in the top layer of the soil and waters.[103] Photochemical transformations can be direct photolysis processes, which are initiated by light directly absorbed by the organic pollutant or indirect (sensitised) photolysis, which involve sunlight absorption by natural photosensitisers or producers of photoreactants. Humic substances can strongly absorb sunlight and may behave as initiators of photoreactions.[78] Some of them involve secondary reaction products that have important implications in accelerating, increasing or even determining light induced transformation of non-absorbing, photochemically stable organic pollutants.

2.3.3 Fate of Heavy Metals in Soils

It is important to learn how the metals are distributed in the soil in order to understand and predict the fate of these species in soil. The distribution of heavy metals released in soil from different sources depends on the types and strengths of metal interaction with individual soil components.[107] These interactions of heavy metals with soil components depend on the heavy metal, its speciation and concentration, as well as upon a range of soil properties and conditions, including soil pH, redox potential, organic matter content and composition, clay content and Fe, Mn, and Al oxide content.[108]

The occurrence of metals in soil can be classified into five physico-chemical forms: exchangeable (adsorbed by clay minerals); bound to carbonates; bound to iron and manganese oxides; strongly adsorbed/complexed by soil organic matter and residual (inorganic hydroxide and sulphide precipitates).[109] Water soluble and exchangeable phases are regarded as mobile and readily phytoavailable, whereas other forms are regarded as relatively immobile.[109,110]

The secreted metabolic products of plant roots, such as CO_2 and organic acids, can lower the pH of the soil.[111] In turn, the low pH of the soils can promote the release of metals from their carbonate forms, as shown for the example in equation 2.11. Hence, the carbonate fraction can be seen as a reservoir of potentially phytoavailable (mobile) metals.

$$CdCO_3 + 2H^+ \longrightarrow Cd^{2+} + CO_2 + H_2O \qquad (2.11)$$

The fate processes of heavy metals in soil, in general, can be categorised into the following: retention by soil components, transport (leaching) and plant (animal) uptake.

2.3.3.1 Heavy metal retention in soils

There is much concern that heavy metals will enter the food chain via plant uptake or contaminate groundwater supplies by leaching through the soil. Whether this happens depends to a large degree on the ability of the soil to retain the metals. Metal retention mechanisms by soils include the following:[108]

a. Adsorption on the ion exchange sites of clay and organic matter,
b. Specific adsorption on oxides and hydroxides of iron (Fe), aluminium (Al) and magnesium (Mg),
c. Chelation and complexation by different fractions of soil organic matter, and
d. Precipitation and co-precipitation as carbonates and sulfides.

a) Adsorption

Heavy metals generally have high affinities for the negatively charged adsorption sites associated with organic matter and oxide surfaces.[66] This is because organic matter and hydrated oxides of Fe, Mn, Al and Si, retain metal cations by non-specific electrostatic attraction. Nevertheless, the influence of clays on the total adsorption capacity of a natural soil for metals is negligible compared to the contribution of organic matter.[112]

In addition to the non-specific electrostatic attraction by silicate clay minerals, organic matter and hydrated oxides of Fe, Mn, Al and Si, cation exchange reactions are important modes of metal adsorption.[108] Generally, specific adsorption of heavy metals by soil minerals is related to metal ion hydrolysis and the probability of specific adsorption of heavy metals increases with an increase in the ability of metals to form hydroxyl-complexes. Brummer[113] lists the order of heavy metal hydrolysis as Cd<Ni<Co<Zn<<Cu<Pb<Hg and proposes that specific adsorption increases in the same order. Similarly, Merrington and Alloway[114] reported similar results on the flux of Cd, Cu, Pb and Zn in mining-polluted soils. In addition, Kuo and Baker[115] reported that Cu and Pb have been preferentially sorbed over Cd and Zn.

The rates of adsorption/desorption process are strongly influenced by acidity (pH) and redox potential. This is because of the influence of pH and redox potential on the amount of charged sites available on clay and soil organic matter surfaces and the metal speciation. Wilkens and Loch[116] noted that decreasing the pH of soils decreased the retention of metals by the oxide (aluminium, iron and manganese oxides) fraction. In addition, field studies have shown that Zn is more available to plants under acid soil conditions than under basic soil conditions.[117] Hickey and Kittrick[118], and Chlopecka[109] reported that Cd, Cu, Pb and Zn in natural soils are mainly bound to residual and oxide fractions. Under reducing soil conditions, however, considerable amounts of metals from this stable fraction can be released into solution.[111,119]

b) Complexation

Soil retention capacity is a complex function of soil system parameters and the chemistries of the metals under existing conditions. One factor that complicates the interactions of heavy metals in the soil environment is the presence of organic substances capable of combining with the metals to form soluble complexes and chelates. Organometallic complexes, which are formed by the interaction of metal ions and negatively charged organic groups, have great stability.[120] Even naturally occurring organic matter in some soils is capable of complexing a substantial fraction of heavy metals, like Cu, which binds strongly to organic ligands.[121]

Within the soil profile, heavy metals tend to be concentrated in the humus-rich topsoil due to the strong adsorptive capacity of humic compounds. The average stability of heavy metals complexed with humic ligands decreases with the relative electronegativity of the metal, i.e. Pb>Cu>Zn>Cd.[122]

c) Precipitation

Precipitation is another mechanism of heavy metal retention by soils. At high metal loadings of alkaline and calcareous soils, precipitation of metal hydroxides or carbonates may begin, which is unlikely in acid mineral soils and in organic soils. Under waterlogged and reducing soil conditions, insoluble sulfides and carbonates, metal oxides, and hydroxides of low solubility are formed. Thus, the mobility and possibly the availability of heavy metals, is lowered.[108]

Precipitation of divalent heavy metals is not expected to be an important retention mechanism, since most aqueous solutions are undersaturated with respect to the solubility products involving this metals.[66] However, heavy metals may precipitate when fertilizers are added to soils containing heavy metals, and locally high concentrations of phosphates or other salts are present. However, these precipitates would dissolve again upon uptake of the nutrients from solution by plant roots.

It is difficult to distinguish whether metals are retained by adsorption or precipitation on soil mineral surfaces, since both retention mechanisms may occur at the soil mineral surfaces. Harter[123] reported that adsorption and precipitation of Pb was pH related. Adsorption occurred at pH<6, while the precipitation of lead carbonates occurring at pH>6.

2.3.3.2 Heavy metal movement in soils

Transport of heavy metals in soils may occur:

- in dissolved or suspended form,
- through plant roots, or
- associated with soil (micro-)organisms.

The movement of the dissolved or suspended heavy metals may take place through the soil solution (diffusion) or the moving soil solution (mass flow). In diffusion, the heavy metals move from a higher concentration gradient to a lower concentration gradient in the soil solution. The movement of heavy metals in mass flow, on the other hand, is along with the soil water in any direction due to either capillary flow or gravity. Moreover, leaching of clay and organic matter results in the migration of the metals that are associated with these particles.[66]

Physico-chemical processes, mainly precipitation/dissolution, control the concentration of metal species in the soil solution.[108] Precipitation-dissolution processes depend on the solubility of definite compounds in relation to chemical reactions taking place in soils. However, it is more likely that adsorption-desorption processes which determine the concentration of an element in the soil solution in conditions where the trace element content of a soil is lower and there are more sites available for high affinity adsorption.[124]

The mobility of heavy metals is usually governed by precipitation and organo-metallic complex formation.[125] Chloro-complexes may also have a great influence in determining the heavy metal distribution in the environment since heavy metals can form chloride complexes under certain conditions. Organo-metal ion complexes, which differ in their degree of mobility, are formed in areas where organic matter accumulation takes place in soluble or colloidal form. Organic ligands play a major role in soil water, and generally in natural waters, because organic ligands may form stable soluble complexes with metal ions. There are indications that dissolved heavy metal cations in soil solutions are often to a large extent associated with organic ligands.[121] Soluble organic compounds, found in soils, that may coordinate with metal ions can be divided into:[66]

- low molecular organic substances, which include: polysaccharides, proteins, peptides, amino acids, polyphenols and organic acids. These low molecular organic substances comprise many ligands, such as citric acid and oxalic acid, which are known to form stable chelates with metal cations,
- fulvic acids, and
- humic acids.

Leaching is more pronounced in areas with high rainfall. In the absence of large limestone deposits, these areas will have a low pH value, which promote solubility of heavy metal compounds.[125] However, in areas where high salinity and high pH values prevail, formation of insoluble compounds is usually expected.

Though the relative mobilities of heavy metals through soils is quite variable, it should be possible to qualitatively predict the migration of an element through soil on the basis of the soil's effectiveness for heavy metal retention, which, in turn, is influenced by the physical and chemical properties of the soil.[126] These soil properties are: soil texture, surface area, the content of hydrous oxides, organic matter and clay mineral content, pH and redox potential.

Soil acidity and the redox potential have strong influences on the retention and mobility of heavy metals in soils. According to Plant and Raiswell,[127] many metals are relatively more mobile under acid, oxidising conditions and are retained very strongly under alkaline and reducing conditions. Acid precipitation, organic matter decomposition and plant root uptake contribute to the soil acidification.[108]

Microorganisms may contribute to the transport of these species since heavy metals may become incorporated in, or sorbed on, them. Earth-worm and other soil microorganisms may help to translocate heavy metals by mechanical mixing of the soil or by incorporating metals in their tissues. Although transport through plant roots and transport associated with micro-organisms may be important under certain conditions, transport of heavy metals through the liquid phase is the major way.[66] This is because the majority of the heavy metals enter the soil in dissolved or suspended form and virtually all interactions between heavy metals and solid constituents of soil occur at the solid liquid interface.

Heavy metal deposition from anthropogenic inputs in soils occurs on the top layer of the soil profile. Miller *et al.*[119] investigated the mobility and retention of heavy metals (Cd, Cu, Zn and Pb) in sandy soils. The results revealed that all metals showed somewhat higher concentration in the top 2.5 cm soil, indicating enrichment of metal in this layer. Acid treatments of these soils did not cause significant metal translocation to lower horizons. However, it is proposed that in urbanised areas, the long-term effects of land clearing, profile disruption, and acid rainfall may increase mobilisation of metals present in these soils. Boswell[128] reported that little movement of any element was found beyond the 30 cm depth even with high rates of element additions to the soil through sewage sludge.

However, there is evidence that heavy metals are transported down the soil profile far beyond 30 cm depth. Lund *et al.*[129], for instance, reported heavy metal enrichment to depths as great as 3 m on soils below sewage disposal ponds.

2.3.3.3 Plant Uptake

The chemical forms of heavy metals influence their fate in terms of plant uptake or soil profile migration. The movement and plant availability of several heavy metals was observed to be greater from inorganic than organic sources such as sewage sludge.[130] This is because most of the metals, which were in a relatively less stable organically bound, carbonate, and residual forms in the sewage sludge, shifted towards the most stable residual form, when added to the soil.[131]

Bioavailability of heavy metals in soil is strongly affected by the pH of the soil solution. Van der Watt *et al.*[132] found that heavy metal plant uptake in poultry waste-amended soils was negatively correlated with soil pH. In highly alkaline soils, leaching of heavy metals from the surface soil is negligible and their availability to plants is low.[133] In general, the absorption of a heavy metal cation is promoted as pH increases, and is inhibited by some alkali and alkaline earth cations and by other heavy metals. Liming of the soil reduces the plant uptake of heavy metal cations largely due to retention of the heavy metals by the soil colloids.[134]

In conclusion, soil pollution by organic chemicals (pesticides) and heavy metals is influenced by various physico-chemical interactions of the pollutant with the soil. The forms and extent of these physico-chemical interactions largely depend on the nature and composition of the soil, the physical and chemical properties of the pollutant, and environmental factors such as climate.

CHAPTER 3

MATERIALS AND METHODS

3.1 INTRODUCTION

A number of analytical methods are available for testing soils. The quality of these soil chemical analysis methods is, however, affected by several factors which include: the quality of field sampling, pre-treatment and preservation of samples, and choice and application of analytical methods.[135] In general, selection of consistent and reliable analytical methods should be done depending on ease of duplication, availability of materials, and their facility for accuracy and speed. In this chapter the sampling and assay methods used during the study will be discussed.

3.2 GENERAL

3.2.1 Sampling and Sample Preservation

Generally a chemical analysis is done on a small fraction of the material of interest, known as a sample. Sampling is basically a process of acquiring a small fraction of the material of interest, in which the composition of the small fraction is representative of the whole material of interest.[136] Since the quality of any analytical measurement result depends on the sample analysed, the composition of the sample should be as close as possible to the average composition of the material to be sampled.[137]

Materials that are homogeneous and quite stable in composition may be well represented by a single sample. However, for inhomogeneous materials, such as ores and soils, which have variable composition, composite samples obtained by mixing of a series of smaller samples may average the variation in composition and minimise the cost and effort of analysis.[136]

The samples should be stored in appropriate sample containers and suitable preservatives added depending on the analysis sought. Soil samples for heavy metal analysis should be stored in plastic containers whereas samples for organic analysis must be stored in glass containers.[136] This is because glass containers can adsorb some of the heavy metals and samples for organic analysis can be adsorbed onto or contaminated by, the organic constituents of plastic containers.[136]

3.2.2 Sample Drying and Grinding

Most soil samples contain water that is in equilibrium with the atmosphere. As a result, their composition depends on the surrounding temperature and relative humidity at the time it is analysed.[137] To avoid this variation in composition, it is common practice to remove the moisture content of the sample using a suitable method, such as oven drying or air drying. For organic analysis, in order to render a soil matrix permeable to the extracting solvent, the soil is either air-dried to remove water, or it is mixed with a drying agent, such as anhydrous sodium sulfate, to sequester water prior to the placing of the matrix in the extraction thimble since the extraction solvent is immiscible with water.[138]

Samples are ground to decrease their particle size to get a better homogeneity in mixing and to make them suitable for chemical attack by reagents.[137] However, the particles should not be reduced more than required because grinding might cause appreciable changes in the composition of the sample. Some of the factors that cause appreciable change in the composition of the sample during grinding are: loss of volatile components in the sample due to the heat generated during grinding, increased moisture absorption due to enlarged surface area, and contamination of the samples from the wear and abrasion of the grinding materials.[137]

3.2.3 Soil Texture

Soil texture (particle-size distribution) refers to the percentage of sand, silt, and clay particles in a soil. Particle-size distribution is one of the most stable soil characteristics, being little modified by human activities.[139] Particle-size distribution analysis can be done using different methods such as sieving and sedimentation procedures.

The sedimentation procedure, which includes the pipette and hydrometer method, depends fundamentally on Stokes' law, which states that particles will fall out of suspension at different rates over time, based on the particle size.

The Stoke's law is expressed as: [140]

$$V = \frac{2g\,(p_s - p_r)r^2}{9\eta} \qquad (3.1)$$

where V = velocity of fall (m s^{-1})

g = acceleration due to gravity (9.81 m s^{-2})

p_s = particle density (often assumed to be 2650 kg m^{-3})

p_r = liquid density (1000 kg m^{-3})

r = particle radius (m)

η = viscosity of the liquid (pa s)

The hydrometer method is the most widely used and sufficient for many purposes, but less accurate than the pipette method.[140] The method is based on the fact that larger particles fall more rapidly through a column of water than smaller particles, when a soil/water slurry is placed in a graduated cylinder. The density of water is measured at different time intervals to determine how much soil is remaining in suspension. Since sand particles will fall out of suspension first, followed later by silt particles, the relative amounts of sand, silt, and clay can be determined and the textural class calculated.

The usual methods of fractionation and particle-size analysis require that the particles be dispersed in an aqueous solution, i.e. that they be detached from one another and suspended in the liquid. Dispersion of the particles in an aqueous solution, except the finest colloidal aggregates, can be sufficiently accomplished by shaking the soil in a dilute alkaline solution of sodium metaphosphate. The adsorption of sodium found in the dispersing agents in exchange for other cations causes strong electrical repulsive forces to develop between the soil particles.[140] In addition, shearing action or turbulent mixing, using such devices as mechanical shakers or electric mixers, facilitates the separation of the particles. However, the mixing should not be so vigorous that individual particles are broken down in size.

3.2.4 Soil Organic Matter

Organic matter may be estimated from the more reliable determination of organic carbon. The "organic matter" content is found by multiplying the "organic carbon" content by a factor of 1.724; which is based on the assumption that soil organic matter contains

58% carbon.[140] However, carbon may be present in soils as organic and inorganic compounds, or elemental carbon (as in charcoal), and, when high temperature combustion is used to determine the carbon content of soils, all these forms may contribute to the measurement, resulting in a positive bias. To avoid the need for a preliminary separation of non-organic forms of carbon, a wet oxidation method such as the Walkely-Black method using dichromate as an oxidant is commonly used.[141]

The Walkley-Black procedure is used for the determination of soil organic carbon since plant residues and humus are oxidized but carbon present as graphite or charcoal is not. Although between 90-95% of the total organic carbon in soil may be oxidized and measured by the Walkley-Black method, commonly the amount is much less.

The Walkley-Black method involves the oxidation of organic matter with excess potassium dichromate ($K_2Cr_2O_7$) in the presence of acid and reduction of the unreacted $K_2Cr_2O_7$ by a standard iron(II) ammonium sulfate solution.
The oxidation reaction may be represented by:

$$C_6H_{12}O_6 + 4K_2Cr_2O_7 + 32H^+ \longrightarrow 6CO_2 + 22H_2O + 8Cr^{3+} + 8K^+ \qquad (3.2)$$

In this reaction, soil organic matter is represented by $C_6H_{12}O_6$ and the oxidation number of C changes from 0 to +4 during oxidation. The reduction reaction back-titration between unreacted $K_2Cr_2O_7$ and iron(II) ammonium sulfate in the presence of acid may be represented by:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \qquad (3.3)$$

From the oxidation and reduction reactions, the number of moles of unreacted $K_2Cr_2O_7$ *(Y)* can be calculated by:

$$Y \text{ mol } K_2Cr_2O_7 = \frac{V_{FAS} \times C_{FAS}}{6} \qquad (3.4)$$

where, V_{FAS} and C_{FAS} are the volume (dm^3) and concentration (M) of iron(II) ammonium sulfate consumed respectively. The number of moles of $K_2Cr_2O_7$ consumed to oxidize the soil organic matter (X) is then,

$$X \text{ mol } K_2Cr_2O_7 = \left[\left(V_{K_2Cr_2O_7} \text{ x } C_{K_2Cr_2O_7}\right) - Y \text{ mol } K_2Cr_2O_7\right] \qquad (3.5)$$

where, $V_{K_2Cr_2O_7}$ and $C_{K_2Cr_2O_7}$ are the total volume and concentration of $K_2Cr_2O_7$ used in the determination. Since 1 mol $K_2Cr_2O_7$ reacts with 1.5 mol carbon, the amount of organic carbon oxidized is 1.5(X mol $K_2Cr_2O_7$). As, 1mol C = 12.01 g, then

$$\text{C (mg) oxidized} = (\text{X mol } K_2Cr_2O_7)(1.5 \times 12.01 \times 1000)(1.33) \quad (3.6)$$

where 1.33 is a correction factor since the method only recovers a proportion of the soil organic carbon. The organic carbon content can then be converted to organic matter content by multiplying it by the van Bemmlen factor (1.724). Therefore,

$$\text{Organic matter (mg)} = (\text{X mol } K_2Cr_2O_7)(1.5 \times 12.01 \times 1000)(1.33)(1.724) \quad (3.7)$$

$$\text{\% Organic matter} = \frac{(\text{X mol } K_2Cr_2O_7)(1.5 \times 12.01 \times 1000)(1.33)(1.724)100}{\text{mass of soil (mg)}} \quad (3.8)$$

3.3 HEAVY METALS

3.3.1 Acid Digestion

A number of analytical techniques, such as atomic absorption and atomic emission spectrometry (AAS and AES), require dissolved samples when determining the concentration of an element in an environmental sample.[142] Acid digestion is the most commonly used method for dissolution of the pollutants from the adsorbents especially in cases where the pollutants are adsorbed on the various soil components.[143]

Many acid digestion and extraction methods, which make use of a variety of acid mixtures, have been used for dissolution of metals. However, the ideal method of choice is one having the combined features of accuracy, reproducibility, simplicity, speed and safety.[144] Nitric and nitric/perchloric acid digestion are the most commonly used methods for the extraction of mineral components of organic and geochemical materials. However care must be taken with perchloric acid, $HClO_4$, as solid perchlorates have explosive characteristics. Kovács *et al.*[142] studied soil sample preparation methods for ICP-AES analysis and reported that HNO_3–H_2O_2 and HCl-H_2O_2 acid mixtures are the best reagents for dissolution of total concentrations of heavy metals in soils.

Nitric acid is normally used in the digestion of organic matter since it reacts completely with aromatic and aliphatic organic compounds. Although single acids such as HNO_3 and HCl can be used to extract a high percentage of metals, the addition of H_2O_2 to the samples will greatly enhance the decomposition of organic matter.[144] Hence the EPA recommended method of digestion (EPA method 3050B)[145] with nitric acid and hydrogen peroxide, followed by the dissolution with hydrochloric acid is the preferred method for preparation of environmental soil samples for ICP-OES analysis.

3.3.2 Inductively Coupled Plasma-Optical Emission Spectrometry

3.3.2.1 Principles

Inductively coupled plasma optical emission spectrometry (ICP-OES) is a widely used instrumental technique in the determination of the levels of various metals and non-metals, in a variety of samples that have undergone acid dissolution.[143] The advantage of this technique is not only its capability of simultaneous multielement analysis, but also its high analytical precision and good detection limits due to the emission stability and high plasma temperature.[146] Moreover, it can handle much larger concentration ranges than most techniques which for most elements range from *ca.* 1000 $\mu g\ ml^{-1}$ down to the detection limit in the order of $\eta g\ ml^{-1}$.[144]

The principle of this technique is based on the characteristic emission of energy by atoms or ions.[137] When atoms (ions) are exposed to an appropriate energy, the valence electrons orbiting the nucleus of the atom are excited by absorbing the energy. Once the electron is in the excited state, the atom emits light, which is characteristic of that particular element. The energy emitted by the electron in the emission process is equal to the energy difference between the ground state and the excited state and can be expressed as:[147]

$$\Delta E = h\nu \qquad \text{or} \qquad \Delta E = hc/\lambda \tag{3.9}$$

where h is Planck's constant, ν is the frequency, λ is the wavelength, and c is the speed of light. Every element has a unique electronic configuration, and hence emits energy at particular wavelengths. Moreover, the intensity of the radiation emitted by the atoms of the same element is the sum of the intensities emitted by the individual atoms and hence is proportional to the concentration of the element. Based on these two main principles, ICP-OES is used for qualitative and quantitative determination of elements in a given sample, since it is capable of detecting the intensity and the wavelength of the light emitted from the excited species of an element.

3.3.2.2 Instrumentation

The basic components of the inductively coupled plasma optical emission spectrometer (Figure 3.1) include: a sample introduction system, the ICP torch and radio frequency (RF) generator and the spectrometer.

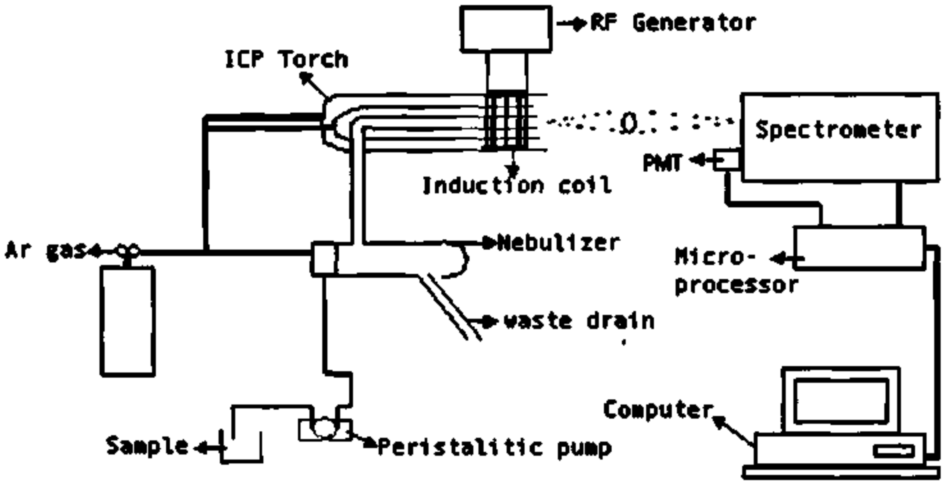


Figure 3.1 Schematic diagram of Axial ICP-OES.

a) Sample Introduction

The sample is introduced to the nebulizer through a peristaltic pump. The nebulizer converts the solution into a fine mist or aerosol, using argon gas. The spray chamber, which is connected to the nebulizer, separates the fine droplets of the aerosol of about 10 µm in diameter from larger droplets and allows only the fine droplets to pass into the plasma.[144] The percentage of the mass reaching the plasma depends on the design of the nebulizer and the spray chamber.[148] Nevertheless, experimental observations have shown that only 0.5 to 2% of the aerosol reaches the plasma and the rest (98-99.5%) of the aerosol in a spray chamber is actually lost to waste.[149]

There are three common types of nebulizers, the concentric (Meinhard), the cross flow and V-groove types of pneumatic nebulizers. All these nebulizers use compressed gas to aspirate the sample.[150] The fine aerosol then emerges from the exit tube of the spray chamber and is transported into the plasma torch via a sample injector.

b) The ICP torch and RF generator

The most commonly used ICP torches consist of three concentric quartz tubes, which are transparent to radio frequency radiation, and are arranged to provide suitable gas flow geometry.[144] The fine aerosol sample is introduced into the plasma through the innermost tube of the torch (the sample injector), while the argon gas that flows through the middle tube (the intermediate gas flow) prevents the plasma from getting too close to the nebulizer flow, and makes nebulizer injection easier. A tangentially flowing argon gas through the outer tube of the torch, the outer flow, provides argon gas for initial plasma ignition, and keeps the load coil cool from the immense heat.

The RF generator produces radio frequency power (an alternating current of 1-3 kW oscillating at 27 or 50 MHz),[137] which is applied to the water-cooled induction coil (load coil) wrapped two or three times around the ICP torch. The argon gas is made conductive by seeding with electrons from a spark produced by a Tesla coil. The RF power is transferred to the conductive plasma through a magnetic field generated by the alternating current passing through the induction coil. The oscillation of the electrons due to the high-frequency-induced alternating current results in an ohmic resistance that produces heat with temperatures as great as 10000 K.[137] The continual transfer of energy from the induction coil to the plasma by the inductively coupled process thus sustains the conductive plasma, which is used as the atomisation and excitation source.

The sample atoms have a 2 ms residence time in the plasma, with temperatures ranging from 6000 to 10000 K.[137] This high temperature ensures that most of the sample in the plasma is completely atomised.

c) The Spectrometer

The atomic/ionic spectrum emitted by the analyte atoms is detected by the spectrometer. The spectrometer constitutes a monochromator for a wavelength selection, a photomultiplier tube (PMT) to enhance the signal and a photodetector to determine the radiation intensity. The spectrometer is attached to a microprocessor and is controlled by a computer. The emitted spectrum by the analyte has two important features; the wavelength of the emitted spectrum helps to determine the elemental composition while the intensity of the detected radiation is employed in determining the concentration of each element in the sample. Attached to the computer is the printer, which prints the results.

3.4 ORGANIC CHEMICALS (PESTICIDES)

3.4.1 Extraction and Cleanup

Organic pollutants in waters, soils, sediments, sludges, solid wastes, and other matrices must be extracted into an appropriate organic solvent for their injection into a gas chromatography (GC) column. Such extraction enables an increase in the concentration of analytes in samples by several orders of magnitude for their detection at ppb level. Depending upon the nature of sample matrices, various extraction techniques, such as Soxhlet, ultrasonic and supercritical fluid extraction, may be effectively applied for accurate and low level detection of organics in soil.[138]

Both the Soxhlet and ultrasonic extraction methods are intended for the complete extraction of specified analytes or group of analytes from solvent-accessible solid matrices.[150] Soxhlet extraction involves the removal and recovery of organic analytes from a permeable solid matrix by means of a solvent which is continually evaporated from a still pot and condensed in such a manner that it falls into and permeates through the matrix which itself is held in a permeable container in a siphonable chamber. In Soxhlet extraction, the solvent is continuously purified and recycled and the extracted material is concentrated in the still-pot.[150] This method is applicable to the extraction and concentration of thermally-stable, water-insoluble and slightly water soluble organics, which subsequently are usually identified and quantified by chromatographic techniques.

Extraction solvents used for Soxhlet extraction need to be of sufficient purity that the extract is able to be concentrated for subsequent steps without the impurities interfering with the analysis.[151] Hence environmental matrices require the use of high-grade purity solvents. Usually Soxhlet extraction methods of analysis for organic analytes use acetone-hexane (1:1) or dichloromethane-acetone (1:1) for soil/sediment matrices, and dichloromethane or toluene-methanol (10:1) for other environmental matrices.[150]

Sulfur is found in many industrial wastes, marine algae, and sediment samples.[138] Sulfur may mask the region of the chromatogram of interest. Sulfur has solubility characteristics similar to that of organochlorine and organophosphorous pesticides and its removal is achieved by treating the extract with one of the following three substances: copper, mercury, or a tetrabutyl ammonium-sodium sulfite reagent.[138]

3.4.2 Gas Chromatograph-Mass Spectrometer (GC/MS)

3.4.2.1 Introduction

Gas chromatography-mass spectrometry (GC-MS) is a very powerful tool for qualitative and quantitative analysis of complex mixtures of organic compounds.[152] It combines the high-performance separation method of gas chromatography with the high-performance mass spectrometric detection technique. GC separates mixtures of organic compounds on the basis of their affinities for the stationary phase and MS detects and identifies the separated components from the mixture of organic compounds based on three-dimensional information: time, mass to charge ratio (*m/z*) and intensity.[136]

GC and MS are highly compatible techniques since both techniques handle the sample in vapour phase and both deal with about the same sample size (typically less than 1 ng). When a packed column is used, however, there is a major incompatibility between the two techniques in the pressure of the carrier gas they handle.[153] This incompatibility is solved by using interfacing devices that reduce the pressure of the carrier gas coming out of the GC before entering the MS. In capillary column GC, on the other hand, the much lower capillary flow rates (1-2 ml/min) mean that no special interfacing device is required to get the pressure down to the MS operating range (approximately 10^{-6} torr).[153]

GC/MS can handle a wide variety of samples, including gas samples, biological samples and soil samples.[152] These samples may require sample preparation processes to make the samples convenient to be handled by GC/MS, such as liquid-liquid and solid-liquid extractions. Most of the results of these sample workup procedures, i.e. gas samples, biological extract or soil sample extract can be directly injected into the head of the column for subsequent GC/MS analysis. However, some samples require special treatment or derivatization prior to injection to the head of the column.

3.4.2.2 Principles

The gas chromatography-mass spectrometry (GC/MS) technique is based on the principles of chromatographic separation of the components of the mixture and mass spectrometric identification and quantitation of the separated components. Chromatographic separation is a dynamic process in which each solute component in a mixture spends part of the time in the mobile phase and part of the time in the stationary phase.[147] The process is a continuous repetition of concentration equilibration caused by adsorption and partitioning between a stationary phase and a mobile phase. For each solute in the mixture, this equilibration can be quantitatively expressed by the partition coefficient K:[154]

$$K = \frac{C_s}{C_m} \tag{3.10}$$

where C_s and C_m are the solute concentrations in the stationary and mobile phases, respectively.[147] The proportion of each molecular species that is in the mobile phase at any given time is a function of its vapour pressure, i.e. the molecules of the components that exhibit higher vapour pressure remain largely in the mobile phase.[154] But the molecules of the components that exhibit lower vapour pressure remain largely in the stationary phase. Hence the magnitude of K is governed by the compound, the nature of the stationary phase and by the temperature. A high degree of interaction of the compound with the stationary phase effectively reduces the vapour pressure of the solute and increases K. Similarly, an increase in temperature increases the vapour pressure of solutes and decreases K.

The sample mixture is injected and instantaneously vapourised at the column inlet and is then carried through the column by the carrier gas. While passing through the column, each component in the sample is adsorbed or is partitioned to the stationary phase according to its characteristic partition coefficient (K). As a result, the difference in the partitioning coefficient of the sample components causes differences in the rate of movement for each component within the column. The components therefore elute separately from the column outlet and are separated in time and space.

The components of a sample mixture are effectively separated when there is a difference in their partition coefficient. The degree of separation is expressed in the relative retention α;[154]

$$\alpha = \frac{K_2}{K_1} \tag{3.11}$$

where K_2 is the partition coefficient of the more retained compound.

The mass spectrometric identification of the separated components of a sample mixture is done by ionisation of the sample components and analysis of the mass spectrum produced. Identification of a compound based on its mass spectrum relies on the fact that every compound has a unique fragmentation pattern, caused by the bombardment of the molecule with electrons or reagent gas ions.[152] The ionised sample components are accelerated to the mass analyser, which separates the particles according to mass to charge ratio. The pattern of the mass spectrum acquired is then used as a fingerprint for identification and the intensity for quantification of the compound.

3.4.2.3 Instrumentation

The main components of a GC/MS instrument are: the carrier gas, injector, column, mass spectrometer and control computer,[152] and are shown in Figure 3.2.

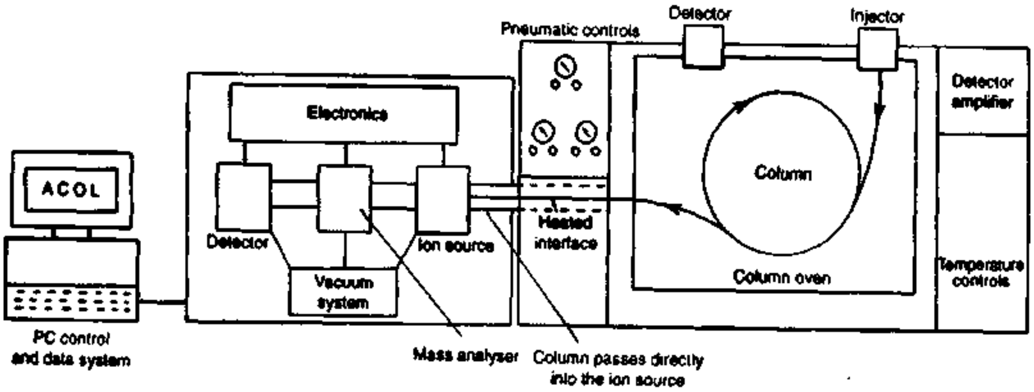


Figure 3.2 Schematic diagram of a GC/MS.[155]

a) Carrier gas

The carrier gas is a gas constituting the mobile phase and most commonly consists of argon, helium, hydrogen or nitrogen.[147] The purpose of the carrier gas is to transport the sample through the column to the detector, hence it must be inert and should not react with either the sample or the column.[156] Impurities in the carrier gas, such as air or water may cause sample decomposition and deterioration of both the column and the detector.[147] Therefore, the purity of the carrier gas should be at least 99.995%.[156]

b) Injector

The function of the sample injection system is to receive the sample, vaporise it instantaneously and deliver the vapourised material to the head of the analytical column with minimum initial band width.[155,156] To accomplish this, the injector has small inlet volume and is equipped with heating system for adequate vaporisation of the sample.[156] The injector system maintains the pressure and the flow through the analytical column during the injection process and prevents air from entering into the column.[155]

The injection of liquid samples into GC is usually done by means of a microliter syringe through a self sealing silicone septum.[156] There are three major GC injection techniques: split, splitless, and on-column. The most common type of GC injector is a combined split/splitless, which can be used in two modes; splitless mode for trace analysis (very low concentration of analyte) but split mode for major component analysis (high concentration of analyte).[156] In the splitless mode the sample injected is vaporised in a heated chamber and passes directly into the capillary column, after a pre-determined time the split vent is opened to allow excess solvent vapour to escape thus preventing column overload by the solvent.[155] When used in the split mode, however, the carrier gas enters the chamber and can leave by three different routes, the column, split vent and septum purge.[155] The septum purge flow prevents septum bleed components entering the column system. The injected sample vaporises rapidly to form a mixture of carrier gas, solvent vapour and vaporised solutes, a portion of which passes onto the column while the greater volume leaves through the split vent. The ratio of the split flow to column flow rate is called the split ratio. Split ratios vary from 10 to 1000:1.[157]

The split injection mode is the best way for dealing with samples containing high concentrations of analyte since it prevents column overloading. Splitting, however can be the source of two major problems, poor detection limits due to small sample size and non-representative samples due to discrimination at the time of injection.[156]

c) Column

Open tubular capillary columns can be divided into two classes: wall coated open tubular columns (WCOT) and support coated open tubular (SCOT) columns. The wall coated open tubular columns are by far the most common, comprising a silica, (or sometimes glass or stainless steel) tube with an internal diameter in the range 0.1-0.5mm and a length of 15-30m.[156] Fused silica columns, coated with a polyamide to protect them from atmospheric oxidation, are flexible and easy to install and to handle compared with glass and steel tubes. The bonded phase silica column, in which the stationary phase is chemically bonded onto the silica column, is the most common high-resolution column,[155] and has a considerably higher maximum operating temperature, low bleed and a much longer life compared with film coated columns.[156]

The column in GC/MS is heated by an accurately temperature-controlled fan blown oven with adequate space to accommodate several columns and with an even temperature distribution throughout the oven.[155] Therefore, chromatograms can be performed under isothermal or temperature programmed conditions. Limitations of isothermal GC/MS analysis are that compounds with a high boiling point temperature in unknown samples may go undetected or will give very low, broad peaks that are difficult to accurately quantify.[156]

Programmed-temperature GC is therefore preferred for its improved detection limits and precision of peak measurement, and reduced analysis time.[156] Moreover, chemical transformations of unstable sample materials are minimised and the required speed of injection is not as fast as for isothermal methods. Care must be taken that the initial temperature in programmed temperature GC/MS should be lower than the boiling point temperature of the lowest-boiling components in the sample.

d) Mass Spectrometer

The tremendous versatility of MS is in large part due to the wide variety of mass analysers that are available.[152] The different types of mass spectrometers are usually characterised on the basis of the physical property they employ to separate ions of different mass-to-charge ratio (*m/z*).[152]

- In a time-of-flight (TOF) instrument, ions are separated on the basis of their different velocities down a flight tube.
- In a magnetic sector instrument, ions are separated on the basis of their different curvatures through a magnetic field.
- In a quadrupole mass spectrometer and a quadrupole ion trap, ions are separated on the basis of their stability in the presence of a radio frequency (RF) electric field.

According to Story, cited by March,[158] quadrupole and ion trap mass spectrometers comprise more than 75% of all mass spectrometers; most likely because these particular mass analysers provide the best combination of sensitivity, performance, size, ease of use and cost. With respect to sensitivity there are minor differences between the detection limits of various mass spectrometers used in GC/MS instruments. Selectivity can be enhanced through the use of selective ionisation techniques and/or more specific MS scan modes.[152]

The MS consists of an ionising source, an accelerating system, an analyser with an ion collector, a vacuum system and computer controlled data management system.[156] Chemical alteration of the analyte occurs in the ionisation chamber by various means, including electron ionisation (EI) and chemical ionisation (CI).[156] EI is the most generally used ionisation source, consisting of tungsten or rhenium filament heated by electric current to a temperature at which electrons are emitted.[156] The electrons are accelerated in a potential field of 5-100 V and attain energies in the 50-100 eV range, but most instruments have standardised on 70 eV electrons, so that spectra can be compared with computerised libraries of spectra.[156] High vacuum is maintained in the ion source to minimise reaction between the ions formed and other ions or radicals.[156]

EI is the most common ionisation mode, typically employing 70 eV electrons to "knock" an electron off a sample molecule and produces a positively charged ion by the following reactions:[152]

$$M + e^- \rightarrow M^{\cdot+\bullet} + 2e^- \qquad (3.12)$$

$$M^{\cdot+\bullet} \rightarrow M^{\cdot+} \qquad (3.13)$$

$$M^{\cdot+\bullet} \rightarrow A^+ + B^\cdot \qquad (3.14)$$

$$M^{\cdot+\bullet} \rightarrow C^{\cdot+} + D \qquad (3.15)$$

This process results in an ion population with a distribution of energies which can subsequently undergo collisional or vibrational deactivation to form the molecular ion $M^{\cdot+}$, fragmentation to form the ion A^+ and radical $B^\cdot$, or rearrangement to form the ion $C^{\cdot+}$ with a loss of neutral molecule D. The result is a mass spectrum that includes a wide range of fragment ions that can serve as a fingerprint for that compound.

CI is the next most common ionisation technique. It is typically employed to provide an increased molecular ion signal from which a compound's molecular weight can be deduced. The major reactions associated with CI are illustrated below, when methane is used as a CI reagent gas.[152]

$$CH_4 + e^- \rightarrow CH_4^{\cdot+} + 2e^- \qquad (3.16)$$

$$CH_4^{\cdot+} + CH_4 \rightarrow CH_5^+ + CH_3^\cdot \qquad (3.17)$$

$$M + CH_5^+ \rightarrow MH^+ + CH_4 \qquad (3.18)$$

Methane is preferentially ionised by an EI process to form the ion $CH_4^{\cdot+}$, when the pressure of the methane reagent is significantly greater than that of the sample molecule M. This cation then undergoes a proton transfer reaction with neutral methane molecule to produce the reagent ion CH_5^+, which in turn undergoes another proton transfer reaction with the sample molecule M to form a protonated molecule MH^+.

Most of the positive ions formed will carry a single charge since it is much more difficult to remove further electrons from an already positive ion. These positive ions are persuaded out into the mass analyser by the ion repeller, another metal plate carrying a slight positive charge, and the ions are accelerated into a finely focused beam.

The quadrupole ion trap mass analyser (Figure 3.3) consists of three hyperbolic electrodes: the ring electrode, the entrance endcap electrode and the exit endcap electrode.[158] These electrodes, when held at appropriate potentials, cause the formation of a pseudo potential cavity in which it is possible to trap (confine) ions for a long period of time. Both endcap electrodes have a small hole in their centres through which the ions can travel.

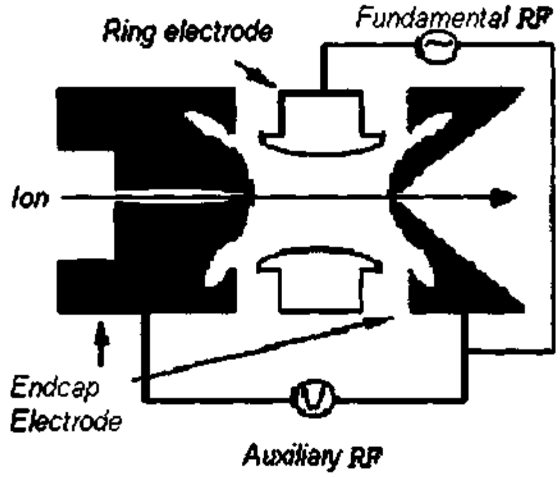


Figure 3.3 Schematic diagram of quadrupole ion trap.

Ions produced from the ion source enter the trap through the inlet focussing system and the entrance endcap electrode. Various voltages are applied to the electrodes to trap and eject ions according to their mass-to-charge ratios. The ring electrode RF potential, an a.c. potential of constant frequency and variable amplitude, is applied to the ring electrode to produce a 3-dimensional quadrupolar potential field within the trapping cell.[158] This will trap ions in a stable oscillating trajectory confined within the trapping cell.

When the amplitude of the RF potential applied to one of the ion trap electrodes is changed, it produces instabilities in the ion trajectories and thus ejects ions of a particular mass-to-charge ratio in the axial direction.[158] Hence, mass selective ejection of ions is done by changing the amplitude of the RF potential in a linear fashion. The ions ejected in order of increasing mass-to-charge ratio are focused by the exit lens and detected by the ion detector system.

The principal difference between a quadrupole and an ion trap ioniser is that ions are filtered in quadrupole analyser in an oscillating electromagnetic path, whereas an ion trap confines the ions with the oscillating electromagnetic field.[159] The ion trap analyser is more sensitive but less precise for quantitative analysis than quadrupole mass analysers.

When an ion hits the metal box in the detector, an electron jumping from the metal onto the ion neutralises its charge. This leaves a space amongst the electrons in the metal, and the electrons in the wire shuffle along to fill it. A flow of electrons in the wire is detected as an electric current, which can be amplified and recorded.

e) Computer

GC/MS instruments have computers equipped with data systems so as to enable both instrument control and to handle the raw data flow, which is hundreds of times more than other detectors in GC. Some major functions of the GC/MS computer include:[156]

- optimisation and controlling the mass-scanning voltages, ionisation source, accelerator and ion collector,
- monitoring the entire system, providing error messages and taking corrective action,
- comparing chosen spectra with tens of thousands of spectra in the library,
- tabulating the relative intensities of the strongest lines in chosen spectra, and
- filing, retrieving, scaling and displaying both chromatograms and spectra.

CHAPTER 4

HEAVY METALS: EXPERIMENTAL, RESULTS AND DISCUSSION

4.1 INTRODUCTION

Soil and ground water heavy metal pollution from activities of aircraft on the runway are generally similar to the pollution on and around highways. Several studies have reported that soils close to a highway are contaminated by heavy metal pollutants, such as cadmium, lead, chromium and zinc, which come mainly from the fuel combustion emissions and tyre and metal platings on car parts.[36,165,161,162] Likewise, soils close to an airport runway can be contaminated by different heavy metal pollutants originating from different aircraft related sources.

A study on the heavy metal levels of soils adjacent to the runway was thus carried out to assess the impact of the aircraft activities on the soils in the vicinity of the runway.

4.2 MATERIALS AND METHODS

4.2.1 Sampling

The runway in the airport was expected to be the point source from which heavy metals, which arise from the tyre wear through friction with the runway asphalt, brake lining wear and aircraft body abrasion can contaminate the surrounding soil. Hence, sampling points for heavy metals on the airport were chosen along the sides of the runway.

The runway extends 1580 meters from south to north and has a 30-meter width. Samples were taken at every 100 meters starting from the south end of the runway, on the east and west side of the runway (Figure 4.1). However, in places where pronounced tyre wear indications (i.e. skid marks) were observed, samples were taken at distances of 50 meters apart. Each sample was taken 2 meters away from the adjacent edge of the runway.

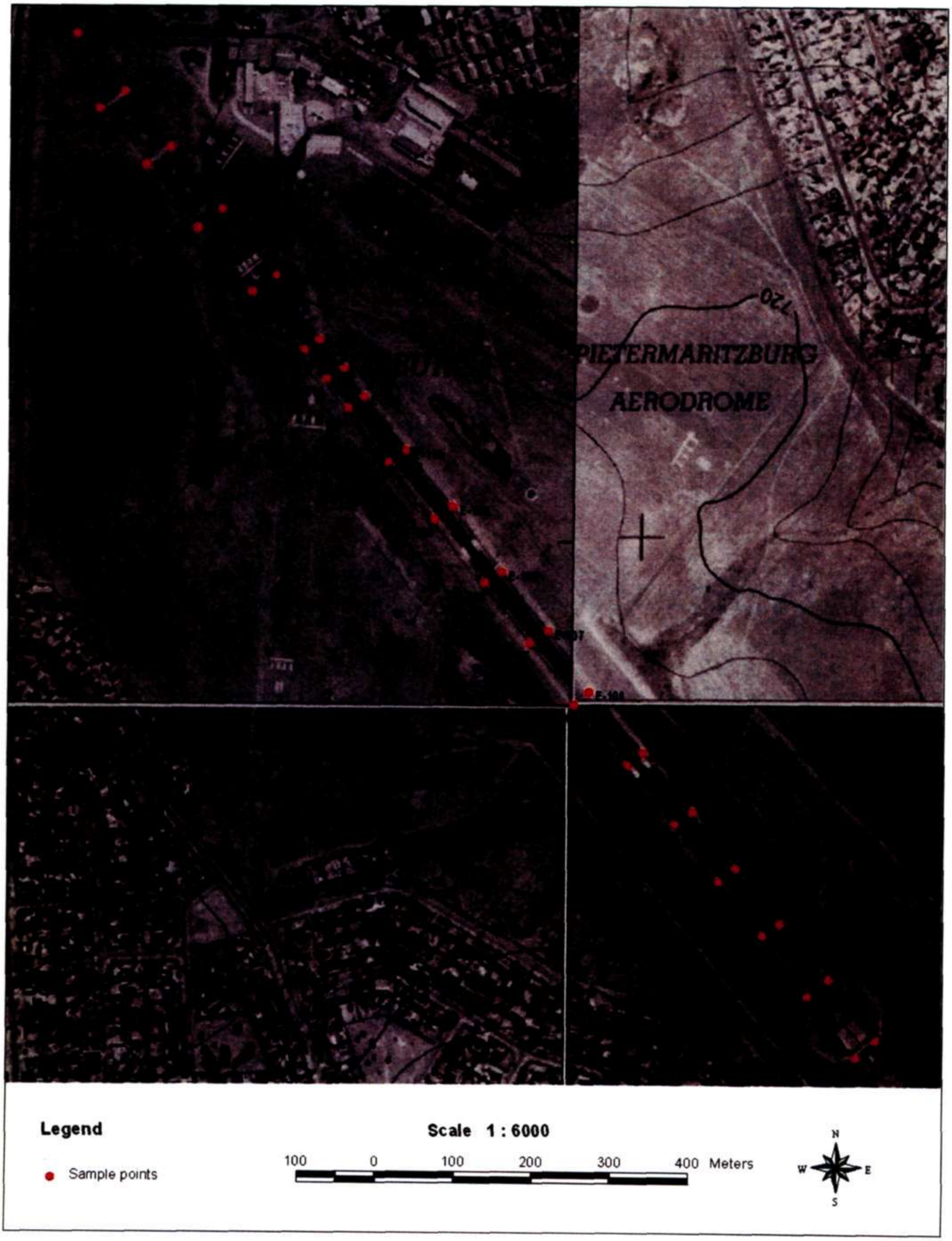


Figure 4.1 Sampling site and sampling points for heavy metal analysis. The map is compiled, georeferenced and mosaiced from four aerial photographs.[163]

The soil samples were taken using a bucket auger from the top 0-15 cm of the soil. Three sub-samples, 1 meter apart, were taken from each sampling point and mixed to get a representative sample of every sampling point. At least 1 kg of the composite sample was taken for each sampling point. The samples were collected in polyethylene bags, the bags were labelled and a site description was also recorded for each sampling point.

4.2.2 Sample Drying and Grinding

The samples were spread over a plastic sheet laid in cardboard boxes and air-dried at room temperature (approximately 25 °C) for 2-3 days. Stones and plant materials were removed from the soil samples and the soil sample was mildly crushed using a mortar and pestle. The soil sample was then divided into three portions and the portions were sieved sequentially using sieves with mesh sizes of 2.0 mm, 1.0 mm and 0.5 mm (Laboratory test sieve BS410/1986, Serial No. 311641, Endecotts, London, England) for analysis of soil texture, heavy metals and organic matter. The soil that passed through the 1.0 mm size sieve was collected in a properly labelled plastic bag and was ready for analysis.

4.2.3 Texture and Colour

The soil samples from the east and west sides of the runway were grouped into three categories, based on their colours as shown in Table 4.1. One representative sample from each category was taken for texture and colour analysis. The colour of the soil was determined by comparing against the colours in the Munsell chart (Munsell Soil Colour Charts, 1992, Macbeth, New York).

Table 4.1 Soil samples grouping according to their colour.

Group	Samples	Soil colour	Representative sample for texture analysis
1	E-102 - E-107, E-111 – E-115, W-102 – W-107, W-111 – W-115	Brown	E-105
2	E-108 – E-110, W-108 – W-110	Yellowish Brown	E-109
3	E-100, E-101, E-116 – E-118, W-100, W-101, W-116, W-117	Dark Brown	E-117

The texture (particle size) of soil samples was determined using the hydrometer method.[139] A 50 ml aliquot of calgon solution (40.0g sodium hexametaphosphate and 9.1 g sodium carbonate dissolved in one litre of hot distilled water) was added to a stirrer cup which contained 50 g of air-dried soil sample, that had passed through a 2.0 mm sieve. About 500 ml of distilled water was added to the stirrer cup and the mixture was stirred for 5 minutes in a stirrer. After allowing the cup to stand for 1 min, the suspension was poured carefully into a 1 litre sedimentation cylinder. The cup was then rinsed with distilled water to ensure that all the soil material was transferred to the sedimentation cylinder. The volume of the suspension was then raised to 1000 ml by adding distilled water. The temperature of the suspension was measured using a thermometer and was used to determine the time required for the sand and silt to settle (R_1 and R_2) from the table given in the method.

After removing the thermometer from the cylinder, the soil suspension was mixed thoroughly and carefully using a plunger. The plunger was then removed and the timing for the first reading was started immediately. At approximately 30 s before the first reading (R_1), the hydrometer was lowered carefully into the suspension, causing as little turbulence as possible. After taking the first reading, the hydrometer was removed from the cylinder and the cylinder was kept covered with a watch glass until the time for the second reading. A second hydrometer reading (R_2) was taken at the corresponding time by lowering the hydrometer in the suspension as described for the first reading. A blank reading (R_b) was taken using the same procedure described for the samples, but with no soil in the cylinder.

The moisture content of the air-dried soil samples was determined by taking about 10 g of the air-dried sample in a pre-weighed 100 ml beaker. The soil was then oven-dried overnight at 105 °C, allowed to cool in a dessicator and weighed. The percentage of moisture content was then calculated using the loss in mass of the soil. The % sand, silt and clay contents of the soil samples were then determined using R_1, R_2, R_b and the moisture content. Finally, the texture of the soil was determined from the texture chart using the % sand, silt and clay contents of the soil samples.

4.2.4 Organic Matter Content and pH

The organic matter content of the soil was determined by the Walkley-Black oxidation procedure[140] using an air-dried soil sample sieved to pass the 0.5 mm sieve. 10 ml of a standard 0.017 M potassium dichromate (Saarchem) solution was added to 0.50 g of the soil sample in a 500 ml Erlenmeyer flask and was mixed by swirling. Then, 20 ml concentrated H_2SO_4 (98% Set Point Instruments) was added carefully, the solution was mixed gently in a fume cupboard for 1 minute, and was left to stand for 20 minutes. A 170 ml aliquot of ultra-pure water, 10 ml of concentrated H_3PO_4 (85 % Saarchem), 0.2 g of NaF (AnalaR 99%, BDH) and 5 drops of ferroin indicator (BDH) were added. A blank sample was run following the same procedure, omitting only the soil.

Iron(II) ammonium sulfate (FAS) (99%, Saarchem) was used as titrating solution for the sample. The blank sample was titrated first to standardize the iron(II) ammonium sulfate and to recognise the titration endpoint more easily when the solution is titrated. The volume of iron(II) ammonium sulfate used to turn the blank sample gradually from golden brown to dark green then to bright green and finally to brownish black was noted and used to determine the concentration of FAS used. The volume of FAS consumed by the soil sample solution to turn to a dark brownish black was also noted. The percentage of organic matter is calculated using equation 3.8, given in chapter 3.

The pH of the soil samples was determined in a 1:2.5 soil:water ratio suspension on a mass basis.[140] A 10 g air-dried soil (that had passed the 2.0 mm sieve) sample was weighed in a 50 ml beaker and 25 ml of distilled water was added. The sample was stirred rapidly for 5 seconds with a glass rod then allowed to stand for 50 minutes. The solution was stirred again and allowed to stand for another ten minutes. The pH of the supernatant liquid was then measured and recorded with a glass electrode and a pH meter (Crison micropH 2000 microprocessor controlled pH meter). The pH meter was calibrated with standard buffer solutions of pH = 4.00 and pH = 7.00 prior to sample pH measurements.

4.2.5 Acid Digestion

Sample preparation of the soil samples from the runway area for heavy metal analysis by ICP-OES was done by an acid digestion method (EPA-3050-B).[145] A 10 ml aliquot of 1:1 HNO_3 (65% pesticide grade, Fluka) was added to 1.00 g of soil sample (that had passed the 1.0 mm sieve) in a 100 ml digestion vessel. The resulting solution was covered with a watch glass and heated in a water bath for 15 min in a fume hood. After allowing the solution to cool, 5 ml of conc. HNO_3 was added and the solution was refluxed for 30 min in a water bath after covering the digestion vessel with a watch glass. This step was repeated until no more brown fumes were given off. Then the solution was heated for 2 h, without boiling, by covering the digestion vessel with a watch glass.

The solution was then allowed to cool, and 2 ml of water (ultra pure) and 3 ml of 30% H_2O_2 (chemically pure, Saarchem) was added. The solution was again heated until the effervescence subsided and then allowed to cool. A 1 ml aliquot of 30% H_2O_2 was continually added with warming until the effervescence was minimal. The total amount of 30% H_2O_2 was limited to about 10 ml. Then the sample was heated for two hours.

After allowing the solution to cool, it was refluxed for 15 min after first adding 10 ml of HCl (30%, Fluka) and covering the digestion vessel with a watch glass. The solution was then diluted to 100 ml with ultra pure water in a volumetric flask. Finally, the solution was filtered using Whatman filter paper No. 41, collected in a polyethylene plastic container and stored in a refrigerator until it was analysed using ICP-OES.

4.2.6 Operating Conditions of ICP-OES

The analytical wavelengths recommended in method 3120-b of the Standard Methods for the Examination of Water and Wastewater[164] were used to select the working wavelength. The instrument detection limit, the wavelength, and the peak search window of each analyte used in the analysis are given in Table 4.2. The selection of the working wavelength from the alternative wavelengths was based on their freedom from spectral interferences from the other elements.

Table 4.2 Wavelength, calculated instrument detection limit (dl) and peak search window used in the ICP-OES analysis of heavy metals.

Element	dl (μg/l)	Wavelength (nm)	Peak Search window (nm)
Cd	1.5	214.438	0.027
Co	5	228.616	0.027
Cr	4	267.716	0.040
Mn	0.3	257.610	0.040
Pb	14	220.353	0.027
Zn	0.9	213.856	0.27

dl : three times the standard deviations of seven replicate results of a blank.

The specifications and operating conditions of the ICP-OES (Figure 4.2) used in the analysis of the total concentration of the heavy metals are given in Table 4.3.

Figure 4.2 Varian Liberty 150 AX Turbo ICP-OES Instrument used in this research.

Table 4.3 ICP-OES Instrument specification and operating conditions used for analysis.

Instrument	Liberty 150 AX Turbo (Ser. 95081574), Varian Australia Pty Ltd.
Integration time	1.00 sec
Replicates	3
Power	1.00 kW
Plasma	15.0 L/min
Auxiliary	1.5 L/min
Sample uptake rate	2.2 ml/min
Nebulizer (Pneumatic)	240 kPa
Stabilisation time	15 s
Rinse time	10 s
Sample delay	30 s
PMT (Photomultiplier)	800 V
Correlation coefficient limit	0.995
Hg line reslope	every 4 hours
Monochromator type	Air
Tubing	Nalgene™ 180 PVC Metric tubing

4.2.7 Calibration Curve

ICP ready-to-use standard solutions (Fluka) were used to prepare the standard solutions for the ICP-OES calibration curves. These solutions contain 1.000 g/l of the respective heavy metal analytes each. From these standard solutions, a mixed stock standard solution (1000 ppm) containing all the target analytes was prepared. The working standards were then prepared by diluting the stock solution. The respective volume of stock solution was pipetted into a 100 ml volumetric flask and made up to the mark using 0.1 M HNO_3 (65% pesticide grade, Fluka) solution. The concentrations of the working standards are given in Table 4.4. A 0.1 M HNO_3 solution was used as a blank.

Table 4.4 Concentration of standard solutions (ppm) used for ICP-OES calibration.

Analyte	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6	Standard 7
Cd	0.005	0.05	0.01	0.25	0.50	1.00	2.00
Co	0.05	0.5	1.0	2.5	5.0	10.0	20.0
Cr	0.05	0.5	1.0	2.5	5.0	10.0	20.0
Mn	0.05	0.5	1.0	2.5	5.0	10.0	20.0
Pb	0.05	0.5	1.0	2.5	5.0	10.0	20.0
Zn	0.05	0.5	1.0	2.5	5.0	10.0	20.0

Initially the instrument was switched on and allowed to warm for at least 30 minutes before starting the analysis. Then it was aspirated for at least 60 seconds with a blank solution to eliminate any carryover from the previous sample (or standard) run. The blank and standard solutions were then run, starting with the blank and followed by the standard with the lowest concentration, in the order of increasing concentrations.

The correlation coefficients of the first order calibration curves obtained from the analysis of the standard solutions were >0.995 for Cd, Co, Cd, and Mn, but were <0.995 for Pb and Zn. Hence, the standards were run in second order calibration curves, in which correlation coefficients >0.995 were obtained. The graphs of calibration curves constructed by plotting concentration versus intensity of the standards are shown in Figure 4.3.

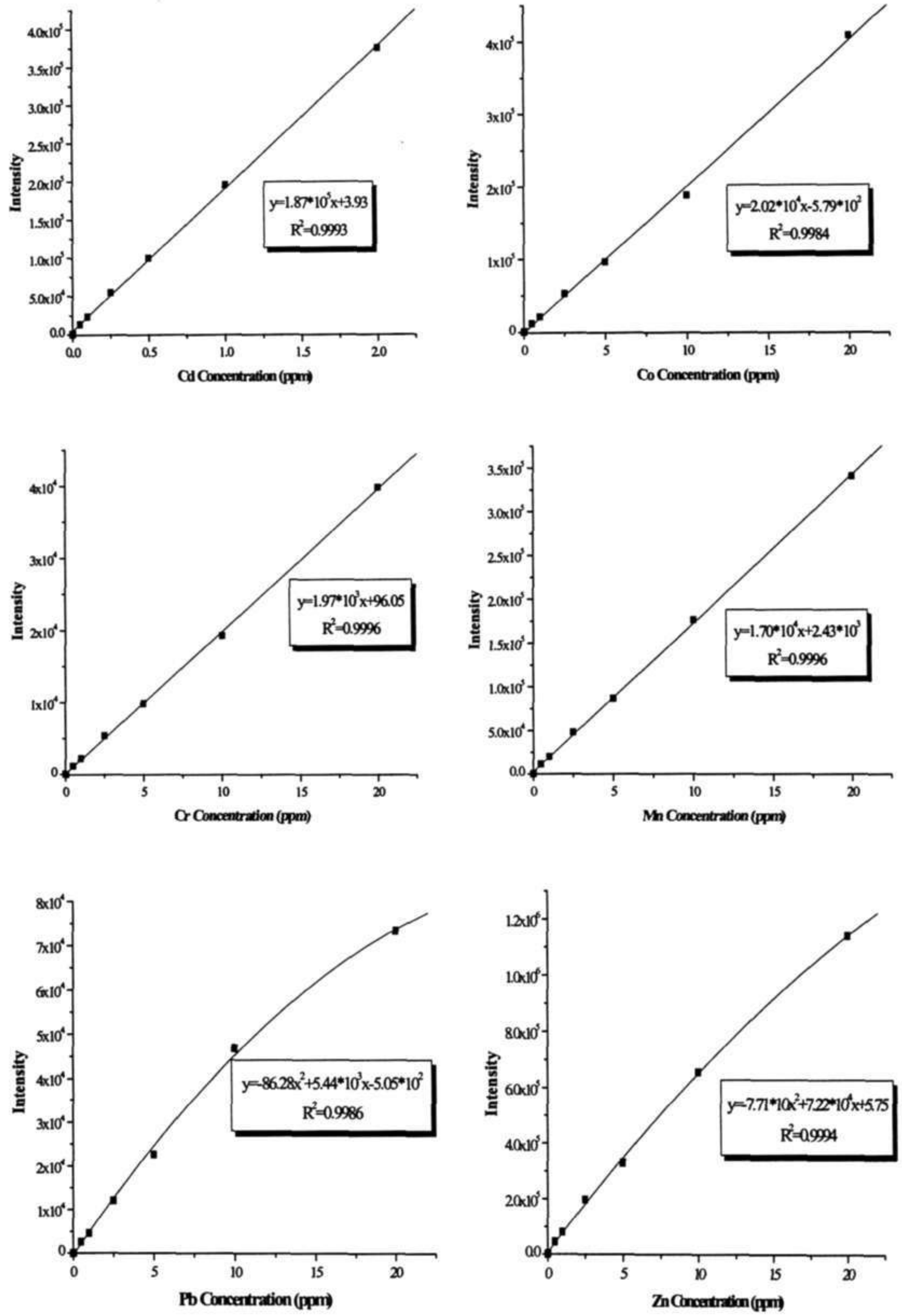


Figure 4.3 Standard calibration curves for cadmium, cobalt, chromium, manganese, lead and zinc.

4.2.8 Statistical Analysis.

Genstat®-Release 4.2[165] was used to run all statistical calculations and the graphs are constructed using the computer statistical package, Microsoft® Excel 2000.

4.3 RESULTS

4.3.1 Texture and Colour

The results of the texture and colour analysis of the representative samples from each group are given in Table 4.5.

Table 4.5 Texture and colour analysis results of the representative samples.

Moisture content	**E-105**	**E-109**	**E-117**
Mass of empty beaker	48.20	50.69	49.24
Mass of beaker + soil	58.32	60.71	59.25
Mass of air dry soil (Ma)	10.12	10.02	10.01
Mass of beaker + soil after oven drying	58.00	60.56	59.05
Mass of oven dry soil (Md)	9.80	9.87	9.81
% Mass moisture content= ((Ma-Md)/Md)*100	3.27	1.52	2.04

Texture Analysis	**E-105**	**E-109**	**E-117**
Mass of air dry soil (g)	50.0	50.0	50.0
Equivalent mass of oven dry soil (Mod) (g)	48.4	49.2	49.0
Temperature for first reading	22.0	22.0	22.0
Hydrometer reading Rb (g/l)	1.0	1.0	1.0
First hydrometer reading R1 (g/l)	19.0	14.0	29.0
R1 corrected for blank = R1 - Rb (g/l)	18.0	13.0	28.0
Temperature for second reading	22.0	22.0	22.0
Second hydrometer reading R2 (g/l)	8.0	6.0	14.5
Silt + Clay = ((R1 - Rb)*100)/ Mod (g/100g soil)	37.2	26.4	57.2
Clay = ((R2 - Rb)*100)/ Mod (g/100g soil)	14.5	10.2	27.6
Silt = (Silt + Clay) - Clay (g/100g soil)	22.7	16.2	29.6
Sand = 100 - (Silt = Clay) (g/100g soil)	62.8	73.6	42.8
Soil Texture from texture triangle	Sandy loam	Sandy loam	Clay loam
Colour	Brown	Yellowish Brown	Dark Brown

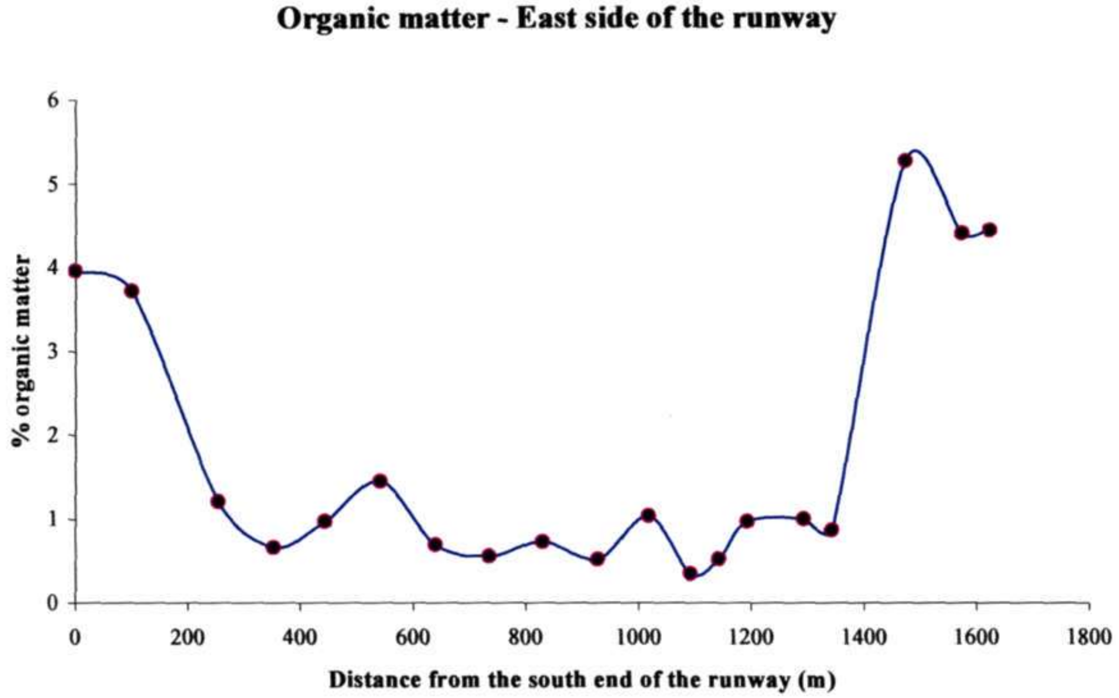
4.3.2 Organic Matter Content and pH

The organic matter content obtained from the analysis of the soil samples collected for heavy metal analysis using the Walkley-Black oxidation procedure (section 4.2.4) are given in Table 4.6.

Table 4.6 Organic matter contents (%) of soil samples from the runway.

Sample No.	Distance from south end of runway (m)	% Organic matter	
		East	West
100	0	4.0	1.5
101	100	3.7	2.0
102	255	1.2	0.86
103	353	0.65	1.1
104	444	0.96	1.2
105	542	1.4	1.2
106	640	0.69	1.4
107	735	0.55	1.1
108	830	0.72	0.90
109	928	0.52	1.1
110	1018	1.0	2.1
111	1093	0.34	1.0
112	1143	0.52	1.6
113	1193	0.96	1.5
114	1293	1.0	0.76
115	1343	0.86	1.0
116	1473	5.3	4.0
117	1573	4.4	3.8
118	1603	4.4	-
	Fpr	<.001	<.001
	l.s.d	0.35	0.15
	s.e	0.12	0.05

Figure 4.4 shows the trends of organic matter contents of soil samples from the east and west sides of the runway. From the table it can be seen that the organic matter of the soil is generally higher for sampling points close to the two ends (south and north) of the runway. In addition, sampling points E-105 and W-110 show relatively higher organic matter contents than the neighbouring sampling points.



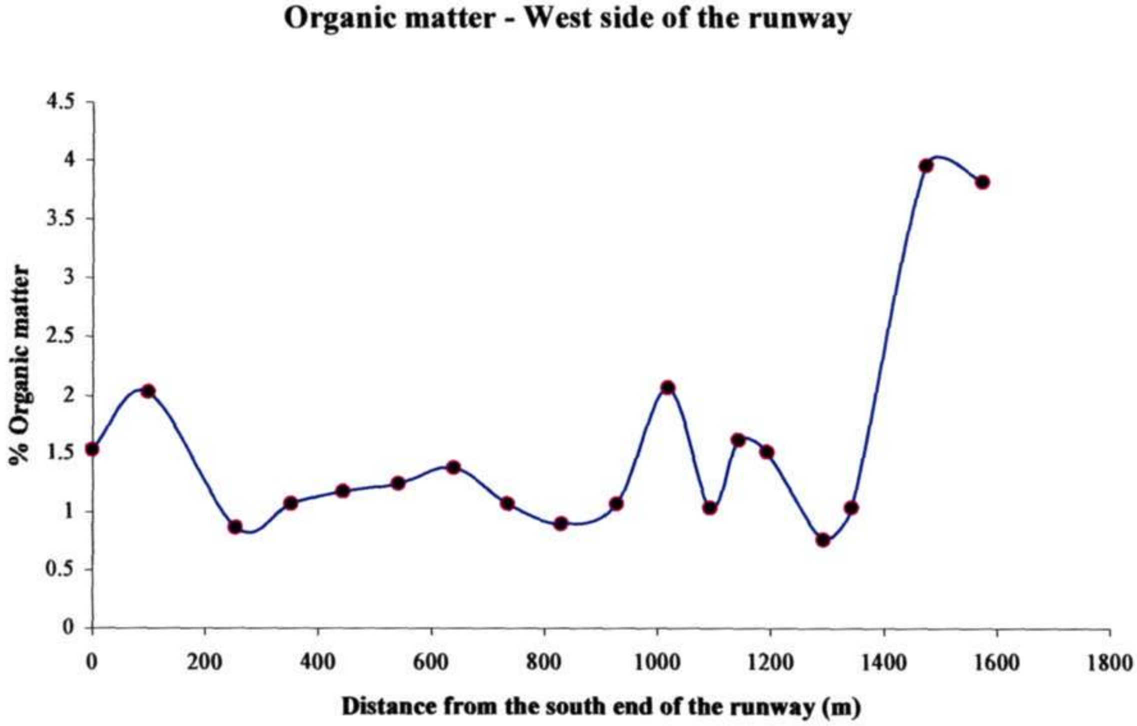


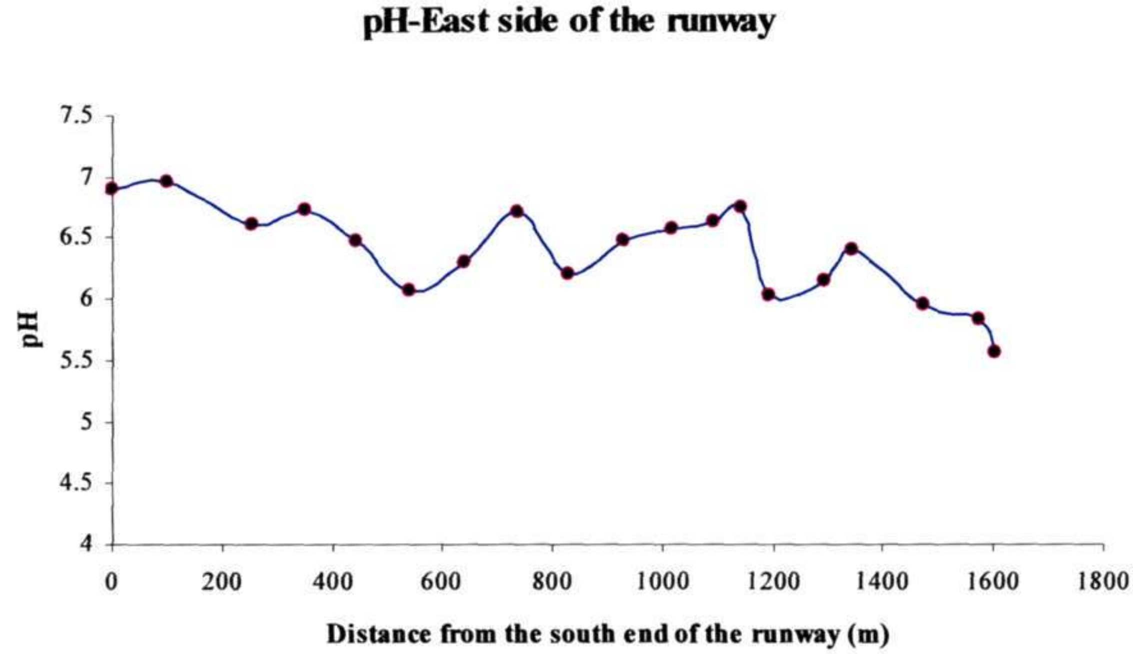
Figure 4.4 Organic matter contents (%) of soil samples from the east and west sides of the runway.

Higher pH ranges were obtained in soils from the east side of the runway than soils from the west side. The pH values of the soils (Table 4.7) varied from 5.55 to 6.95 in the east side and 5.92 - 6.20 in the west side.

Table 4.7 pH analysis results of the soil samples from the runway.

Sample No.	Distance from south end of runway (m)	pH	
		East	West
100	0	6.89	6.10
101	100	6.95	6.10
102	255	6.60	6.34
103	353	6.73	6.51
104	444	6.46	6.52
105	542	6.07	6.41
106	640	6.30	6.21
107	735	6.71	5.92
108	830	6.20	6.29
109	928	6.47	6.25
110	1018	6.57	6.39
111	1093	6.62	6.13
112	1143	6.74	6.13
113	1193	6.03	6.29
114	1293	6.13	6.51
115	1343	6.40	6.51
116	1473	5.95	6.26
117	1573	5.83	6.15
118	1603	5.55	-
	Fpr	<.001	<.001
	l.s.d	0.184	0.153
	s.e	0.062	0.051

The pH values of the soil samples from the east and west side of the runway are graphically shown in Figure 4.5.



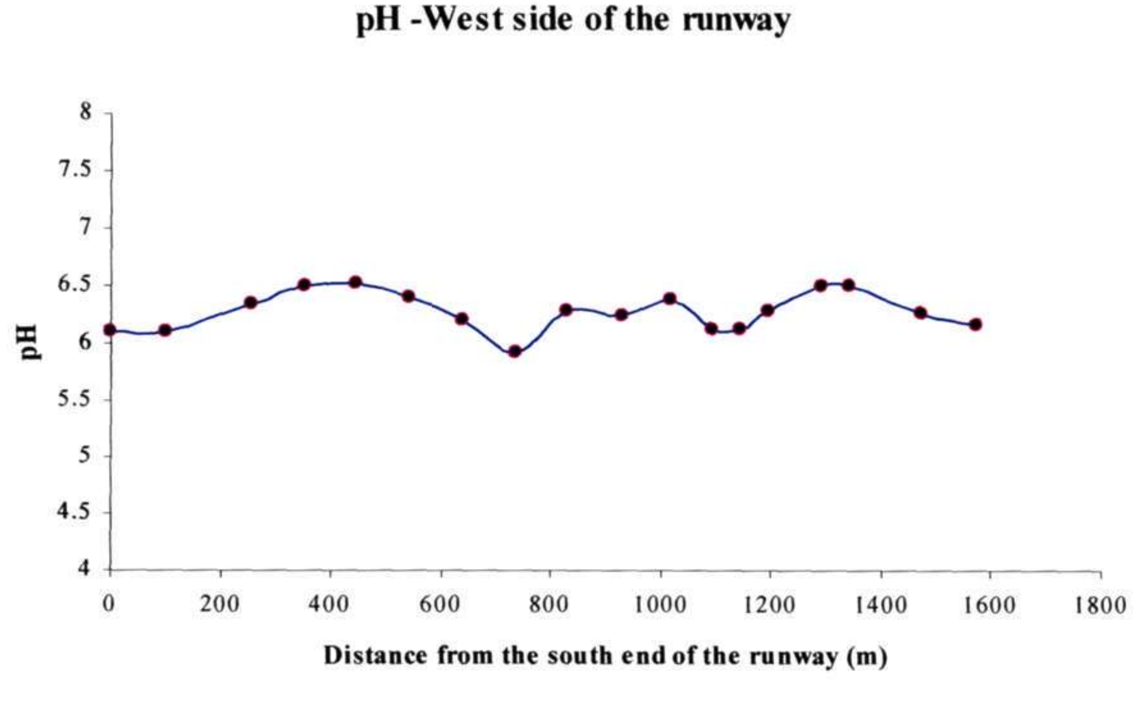


Figure 4.5 pH values of the soil samples from the east and west side of the runway.

4.3.3 ICP-OES Analysis Results of Heavy Metals

The total concentrations of the heavy metals Cd, Co, Cr, Mn, Pb and Zn in the soil samples from the east and west side of the runway, expressed as mg per kilogram of soil, are presented in Tables 4.8 and 4.9. The mean concentrations are calculated from the values obtained from four replicate measurements for every sample.

Variance analysis of the results showed that there is significant difference (P = 0.05) in the results with the given least significant difference (l.s.d.) and standard error (s.e.) values for all the heavy metals of interest.

Table 4.8 Heavy metal concentrations of samples east of the runway.

Sample No.	Distance from south end of runway (m)	Mean concentration (mg/kg) [n* = 4]					
		Mn	**Cr**	**Zn**	**Cd**	Co	**Pb**
E-100	0	4110	126	60	3.6	60	51
E-101	100	6410	114	50	4.2	91	63
E-102	255	4500	103	67	3.6	51	50
E-103	353	4490	82	74	3.4	45	43
E-104	444	7150	155	76	4.4	72	54
E-105	542	5270	100	60	3.3	55	44
E-106	640	4000	83	58	2.9	40	37
E-107	735	2380	66	78	2.8	29	31
E-108	830	4700	58	83	3.2	41	36
E-109	928	2100	49	85	2.7	27	28
E-110	1018	2240	52	77	2.6	23	28
E-111	1093	1140	48	87	2.5	22	24
E-112	1143	4450	76	78	3.9	40	49
E-113	1193	4980	98	76	4.0	53	54
E-114	1293	2960	69	70	3.1	32	34
E-115	1343	2430	56	79	3.0	26	38
E-116	1473	1440	115	57	2.3	23	62
E-117	1573	1950	119	31	2.5	30	35
E-118	1603	2470	136	44	2.6	36	51
	F_{pr}	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
	l.s.d.	522	17	3.8	0.20	3.4	7.8
	s.e	185	6.1	1.4	0.07	1.2	2.75

*: number of replicate samples

Table 4.9 Concentrations of the heavy metals in samples west of the runway.

Sample No.	Distance from south end of runway (m)	Mean concentration (mg/kg) [n* = 4]					
		Mn	**Cr**	**Zn**	**Cd**	**Co**	**Pb**
W-100	0	3860	137	63	3.6	57	58
W-101	100	6490	128	53	4.4	97	69
W-102	255	6920	83	109	3.7	45	37
W-103	353	5860	124	86	4.3	55	50
W-104	444	4480	113	79	3.7	40	41
W-105	542	4670	115	64	3.5	49	41
W-106	640	4420	120	55	3.1	42	38
W-107	735	2470	86	72	2.6	27	30
W-108	830	2410	65	67	2.6	24	24
W-109	928	2740	85	67	2.7	23	34
W-110	1018	3840	143	60	3.2	39	29
W-111	1093	5100	141	61	3.3	43	47
W-112	1143	4000	93	66	3.0	32	39
W-113	1193	4370	112	75	3.4	35	36
W-114	1293	5290	103	71	3.4	41	34
W-115	1343	3900	109	59	2.9	35	37
W-116	1473	2230	91	167	2.1	26	154
W-117	1573	2510	98	38	2.3	28	33
	F_{pr}	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
	l.s.d.	418	17	7.8	0.22	4.5	12
	s.e	170	5.9	2.8	0.08	1.6	4.3

*: number of replicate samples

In Figures 4.6- 4.9, the mean concentrations for each heavy metal in the sample from both the east side and west side of the runway are plotted against distance of the sampling point, by taking the south end of the runway (sampling points E-100 and W-100) as a reference point. Figures 4.6 and 4.7 show that samples E-104 and E-113 have higher Cd, Co, Cr, Mn and Pb concentrations compared to their surrounding sampling points. Similarly, Cd, Co, Mn and Pb show higher concentrations at points E-101 and E-108. In general, Cd, Co and Cr show similar trends in the graphs for samples from the west side of the runway. The "box" in the plots represents the 95% confidence interval for each set of results and the ends of the "whiskers" represent the maximum and minimum values obtained. The mean is given alongside each box.

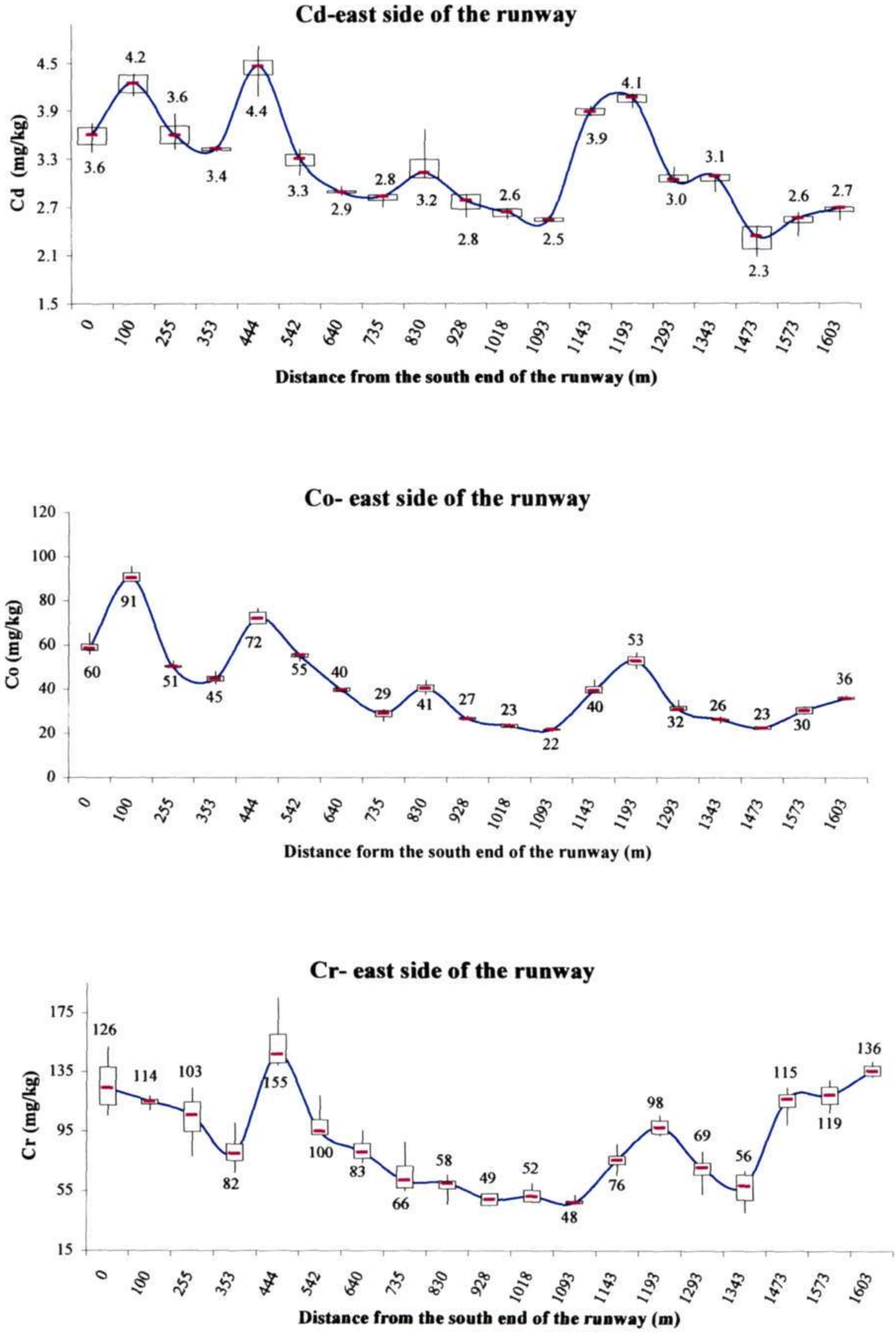


Figure 4.6 Cd, Co and Cr concentrations of soil samples from the east side of the runway.

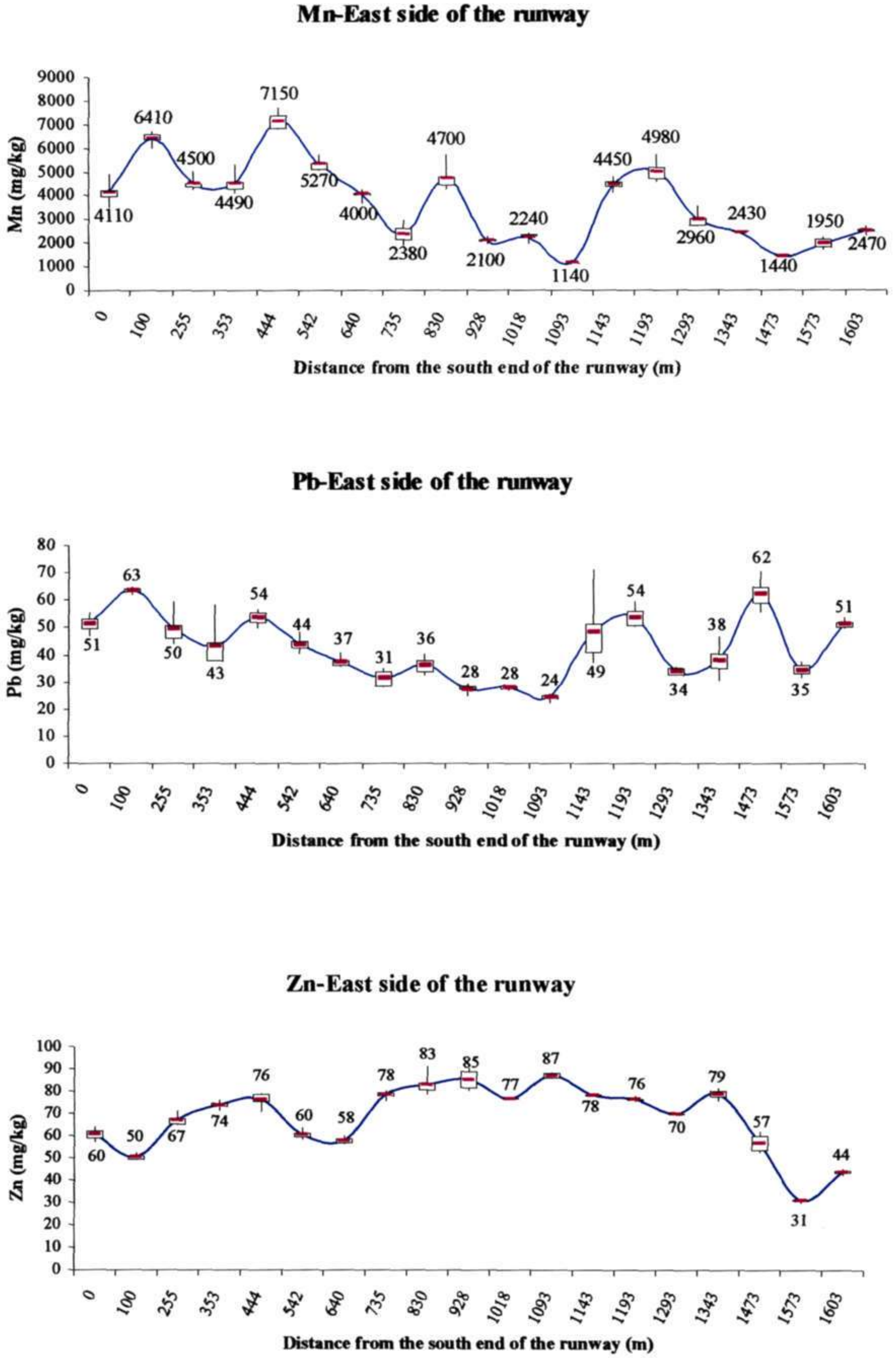


Figure 4.7 Mn, Pb and Zn concentrations of soil samples from the east side of the runway.

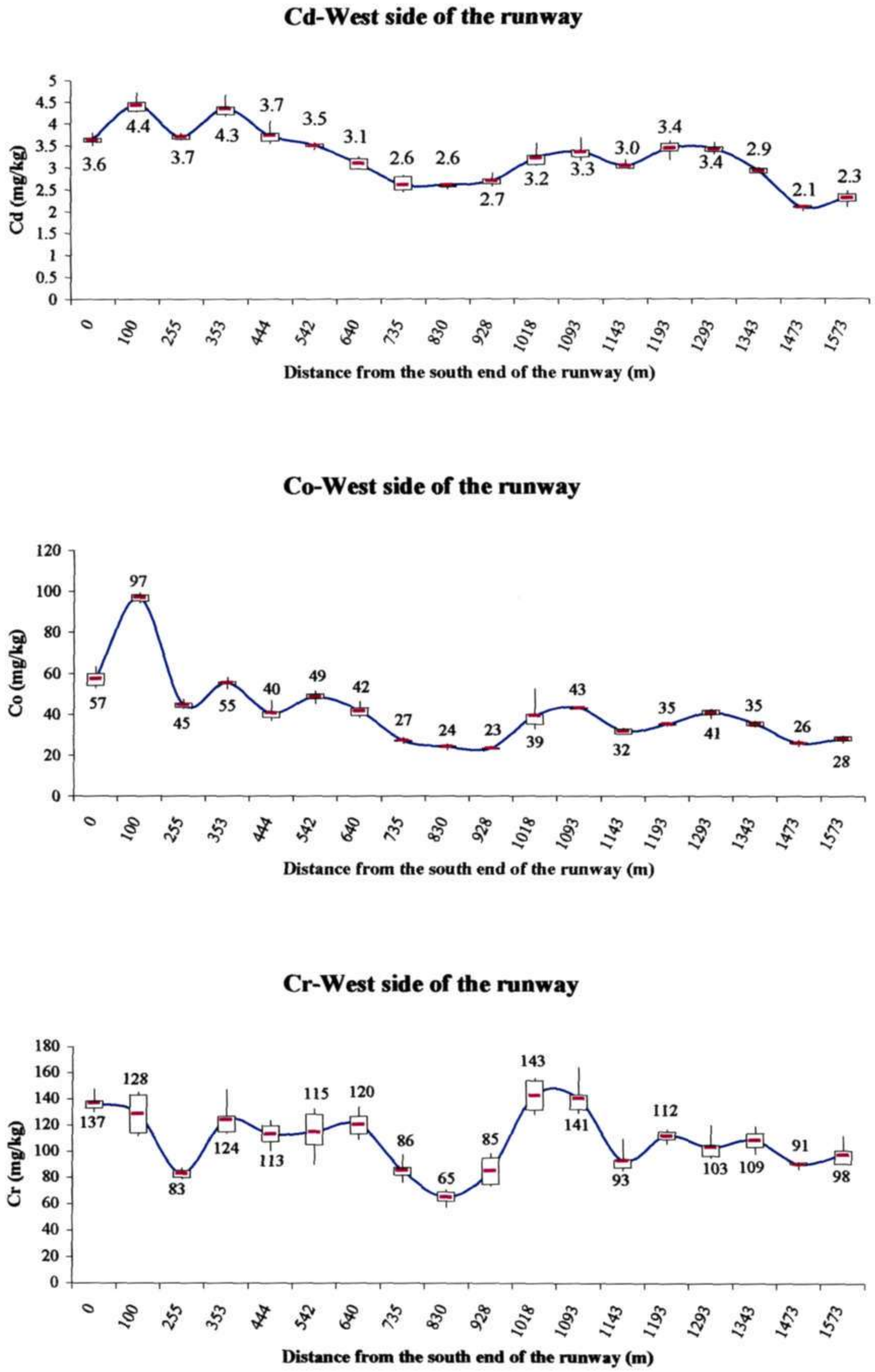
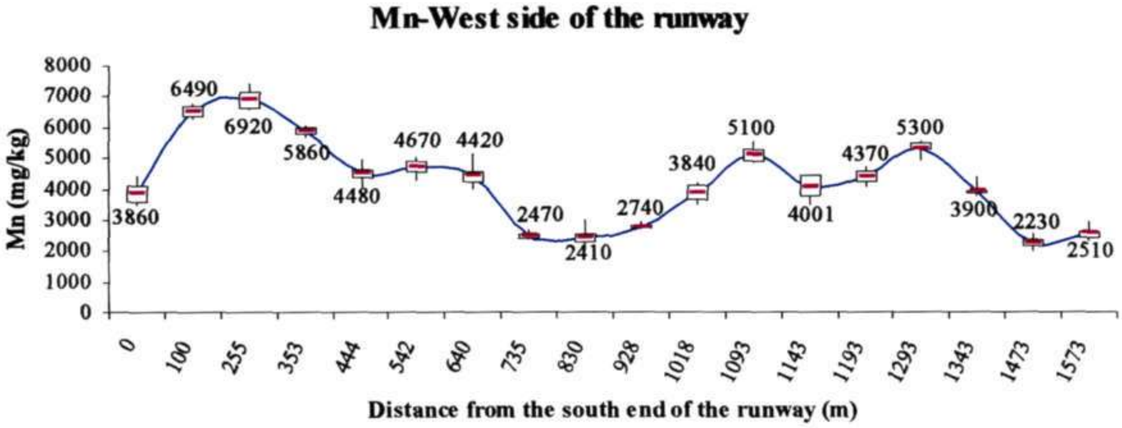
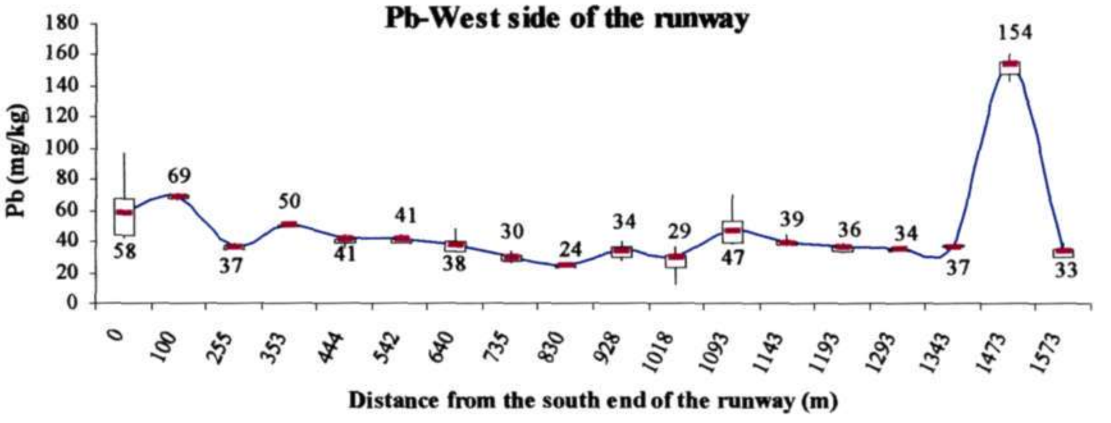


Figure 4.8 Cd, Co and Cr concentrations of soil samples from west side of the runway.





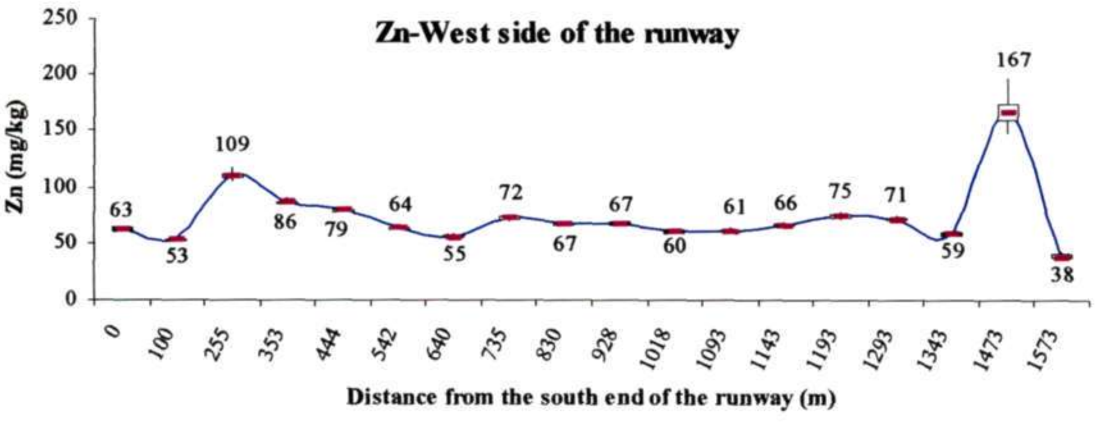


Figure 4.9 Mn, Pb and Zn concentrations of soil samples from west side of the runway.

4.4 DISCUSSION

It is evident that the soil in the runway area had been disturbed during the construction of the runway. It is highly probable that the majority of the soil, close to the runway where samples were taken, is either new to the area or the topsoil has been removed, and therefore is quite different from the soil in the surrounding area. Consequently, it was not practical to take a soil sample to be used as control from the surroundings of the runway, which is not affected by the runway activities.

The soil texture analysis results of the representative samples for the soil samples show that soils at sampling points 100, 101, 116, 117 and 118 on both sides of the runway are clay loam, while soils at sampling points 102-115 are sandy loam. This suggests that the background concentrations of these two groups of soils could be different. In addition, the colour of the clay loam soils, at both the south and north of the runway, is darker than that of the sandy loam soils found in the middle parts of the runway, which indicate that the clay loam soils have higher organic matter contents than the sandy loam soils. This suggestion agrees with the results obtained from the organic matter analysis of the soil samples.

Soils at both south and north ends of the runway showed higher organic matter content and clay contents. The organic matter content of the soils in the east was found to be higher than their corresponding west side samples, for the clay loam type of soils (samples 100, 101, 116 and 117). However, most of the sandy loam type of soils (samples 102-115), exhibited higher organic matter contents in the west side soils than the east side soils. East side samples showed a wide range of pH values (5.55-6.95) as compared to the west side samples (5.92-6.52). Moreover, the samples for east side of the runway exhibited a decreasing trend in pH values from the south end to the north end, but the pH values of the west side samples appear to be less variable.

The results of the analyses carried out on the soil samples and the baseline values on South African soils reported by Herselman *et al.,*[166] for the heavy metals are summarised in Table 4.10 and Figure 4.10 shows a comparison of these summarised results graphically.

Table 4.10 Heavy metal concentration (mg/kg) of the soil samples from the runway and baseline concentration of the South Africa soils.

	Samples					Baseline concentration of the South Africa soils				
Element	N*	95th %tile	Mean	Min	Max	N*	95th %tile	Mean	Min	Max
Mn	37	6580	3910	1140	7150	-	-	-	-	-
Cr	37	142	99	48	155	4351	353	72	nd	1329
Zn	37	70	70	31	167	4322	115	45	nd	1647
Cd	37	4.4	3.2	2.1	4.4	4441	2.7	0.1	nd	5.5
Co	37	76	41	22	97	4321	69	18	nd	286
Pb	37	64	44	24	154	4441	66	21.7	0.02	532

*: number samples analysed.

The concentrations of chromium in the soil samples are all much less than the 95th percentile of the baseline concentrations for South African soils given in Table 4.10. The concentrations range from 48 to 155 mg/kg. There was a wide range of manganese concentrations found in the soil samples (1140 to 7150 mg/kg). Similarly, lead exhibited a wide concentration range with values as high as 154 mg/kg and as low as 24 mg/kg. The 95th percentile concentration, calculated from the results of the lead concentrations in the soil samples from the runway, are no higher than the 95th percentile of the baseline lead concentrations found in South African soils. In addition, zinc also exhibited a wide range of concentrations (31 to 167 mg/kg), with all the concentrations of the soil samples below the maximum baseline concentrations reported[166] for soils of South Africa.

Cobalt concentration results for the soil samples obtained ranged from 22 to 97 mg/kg. These values are all well below the maximum baseline concentration for South African soils reported.[166] However, the 95th percentile concentration of cobalt (76 mg/kg) found in the results of this study is only slightly above the 95th percentile of the baseline concentration (69 mg/kg) of South African soils reported by Herselman *et al.*[166] In this latter study, the concentration range for cobalt in the soil samples was reported as being between 22 and 97 mg/kg.

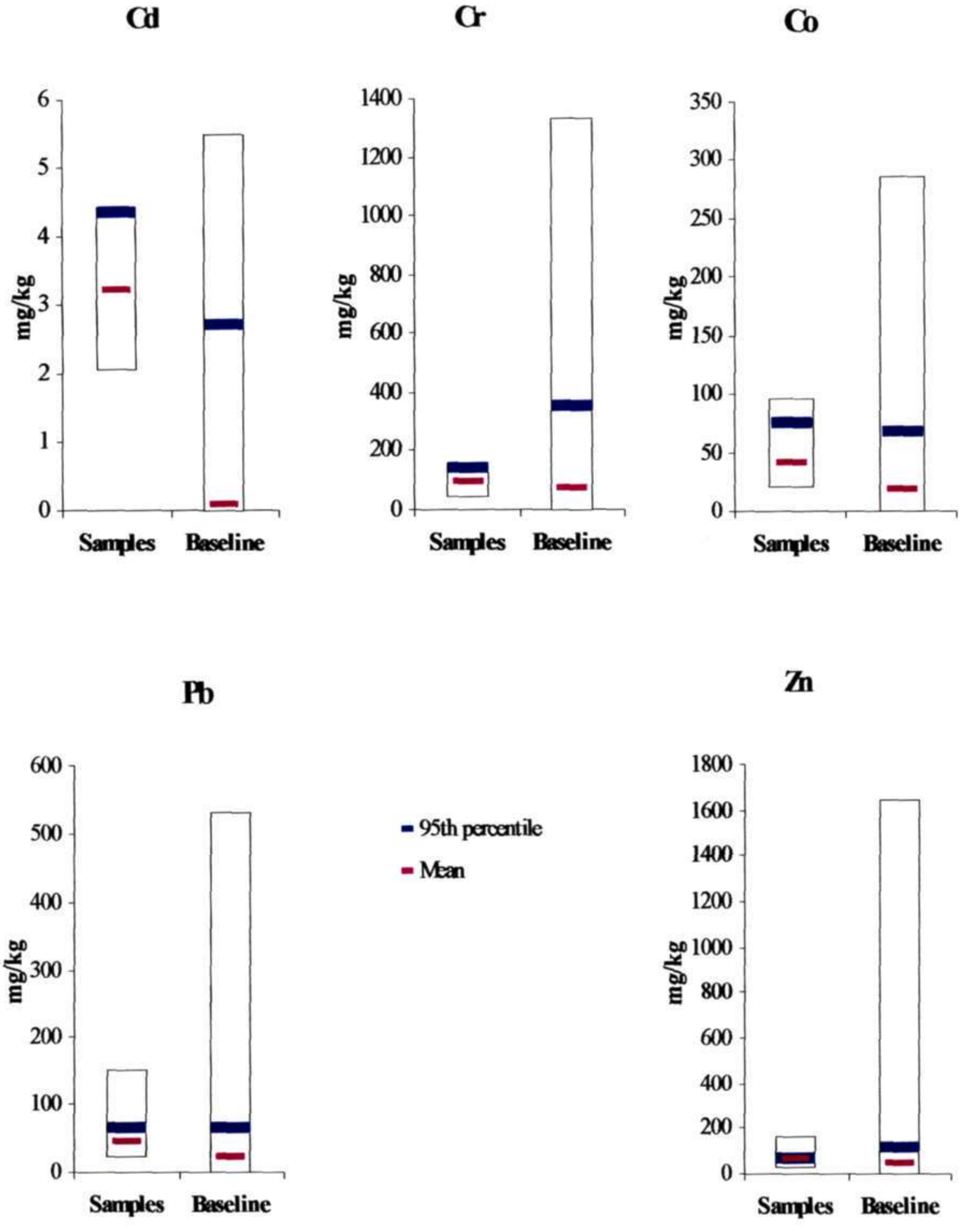


Figure 4.10 Comparison of the heavy metal concentrations of the sample and the baseline concentrations for South African soils.[166] The boxes in the graph represent the range of values.

The results for cadmium concentrations varied from 2.1 to 4.4 mg/kg, with all the samples having concentrations below the maximum of the cadmium baseline concentrations in South African soils (5.5 mg/kg), found by Herselman *et al.*[166] (Table 4.10). Nevertheless, the concentrations for 73% of the soil samples from the runway are above the 95th percentile of the cadmium baseline concentrations reported.[166]

There are some distinct patterns in the concentrations of Cd, Cr, Co, Mn and Pb on the east side of the runway (Figures 4.6 and 4.7). Generally the results of Cr, Cd, Mn and Pb concentrations for the samples on the east side of the runway show a decrease from south to north along the runway up until sampling point E-111. On the other hand Cr concentration increases from south to north for the rest of the sampling points. This increasing and decreasing trend of heavy metals follows the slope of the runway, which slopes down from a point close to the middle to the south and north ends. Hence, the increase in the heavy metal concentration down the slope can be attributed to the transport and deposition of these metals by rainwater. Moreover, the trends are similar to the trends exhibited by the clay and organic matter contents of the soil, on which heavy metals are readily adsorbed. This indicates that the organic matter and clay content have a significant contribution to the accumulation of these heavy metals in the soils.

Similar results have been observed in several studies. Li and Shuman[167] observed the accumulation of Pb and Cd on top soils that have relatively high levels of organic matter, and attributed the accumulation of these metals in the top soils to the binding of the metals to soil organic matter. Miller *et al.*[168] also reported the increase in accumulation of Cd and Pb with the increase in clay and organic matter content of soils. Similarly, Lu *et al.*[169] found significant and positive correlations between organic carbon content of soils and Cr, Pb and Zn concentrations. However, in contrast to the results obtained in this study, they reported that Zn and Pb were inversely correlated to soil clay content.

The trend for zinc on the east side of the runway is different from those of the other metals. It showed low concentrations at both the south and north ends of the runway, where the organic and clay contents of the soil are relatively higher than the rest of the soils close to the runway. It also showed higher but relatively constant levels in the in the sandy loam soils, a trend contrary to that exhibited by the rest of the heavy metals in the east side of the runway.

Three sampling points have noticeably higher concentrations than their neighbouring sampling points and appear to fall out of the general trend in the east side of the runway. These sampling points with highest concentrations of all the heavy metals, except Zn, compared with the rest of the sampling points were found at approximately 400 meters from the south and north ends (sampling point E-104 and E-113) and the central part (sampling point E-108) of the runway. These points correspond to the runway areas where a considerable number of tyre wear marks are observed, which indicates the points where the aircraft tyres make the first contact with the runway during landing.

The trends of the heavy metal concentrations on the west side of the runway are different from the trends observed on the east side of the runway. The concentrations of chromium, cadmium and manganese showed more or less similar trends. Generally, the concentration of these metals decreased from the south end towards the north up to sampling point W-110. The concentrations, then increase up until sampling point W-114 and again decrease towards the north end of the runway. On the other hand, the results showed higher concentrations for Pb at sampling points W-101 and W-116. Similarly Zn showed higher concentrations at sampling points W-102 and W-116. However, relatively constant concentrations were found in the rest of the samples. The unusually high concentrations of both lead and zinc, approximately 4 fold and 2 fold of their mean concentration respectively, suggests that it is highly probable that this was due to the contamination of this particular area from sources other than the routine activities of the runway.

Soil and ground water pollution sources from airports are generally similar to the pollution sources in highways. Several studies have reported that soils close to a highway are contaminated by heavy metal pollutants, such as cadmium, lead, chromium and zinc, which come mainly from the fuel combustion emissions and tyre and metal platings on car parts.[37,160,161,162] Likewise, soils close to a runway can be contaminated by different heavy metal pollutants originating from different aircraft related sources. These sources of pollutants are the fuel combustion products, the tyre wear and other aircraft body abrasion.

Cd, Co, Cr, Mn, Pb and Zn were expected to contaminate the soils around the runway since they are related to the aircraft in one or the other of the following uses:

- Most forms of fuel contain some heavy metals. Hence the combustion produces aerosol emissions that contain heavy metals such as Pb and Zn.

- Tyres, brake linings and lubricant oils are other sources of heavy metal contaminants such as Zn, Cr, Co and Cd.
- Mn is used not only in dry cell batteries, but also as an additive to improve the regeneration of diesel exhaust filters and as an antiknock agent.
- The galvanized metals used in making aircraft are coated with chromium.

In general, fuel combustion, tyre and brake linings wear, lubricant oil spill and other aircraft body abrasion and wear are the possible sources of the heavy metals of interest in the soils close to the runway. Nevertheless, the trends and levels of the heavy metal contaminants are different in the east and west side of the runway. This difference may be due to the effect of the topography and climatic conditions (wind direction) on the movement of the medium of transport, such as water and air, of these heavy metal contaminants on the surface of the soil.[160] Moreover, the percolation of water down the profile is slow since the soils are made compacted for obvious construction reasons. This will facilitate the horizontal transport of heavy metals especially areas where there is significant sloping of the surface of the soil.

Pearson's correlation coefficients[165] were used to examine any relationships between the levels of the heavy metals in the different sampling points to find out if the heavy metals are originating from the same source. The correlations were calculated in two ways:

- including all sampling points and
- excluding sampling points at the south and north ends of the runway (sampling points E-100, E-101, E-116, E-117 and E-118),

The second option was chosen because, as mentioned before, the soil properties (such as texture and organic matter) were different at the extreme ends of the runway. Also, any aircraft activity would be different at the ends of the runway compared to the central part of the runway. The correlation matrixes for the heavy metals calculated using the concentration of these metals obtained from the analysis results are given in Tables 4.11 and 4.12.

The correlation coefficients (Table 4.11) show that Cd, Co and Mn are highly correlated in samples from the east side of the runway ($r > 0.84$). In addition, Pb showed high correlation with Co (r > 0.6) and Cr (r >0.7). These correlations, however, were found to be even higher when sampling points at the south and north ends of the runway (sampling points E-100, E-101, E-116, E-117 and E-118) were excluded. Some correlation graphs of heavy metal concentrations along the east side of the runway are presented in Figure 4.11.

Table 4.11 Correlation matrix for heavy metals at the east side of the runway

Correlation coefficients for all samples in the east side of the runway					
	Cd	Co	Cr	Mn	Pb
Cd	1.00				
Co	0.86	1.00			
Cr	0.39	0.60	1.00		
Mn	0.92	0.90	0.46	1.00	
Pb	0.56	0.66	0.75	0.55	1.00
Zn	0.14	-0.23	-0.66	<0.01	-0.41
Correlation coefficients for sandy loam soil samples east					
	Cd	Co	Cr	Mn	Pb
Cd	1.00				
Co	0.88	1.00			
Cr	0.83	0.95	1.00		
Mn	0.88	0.97	0.88	1.00	
Pb	0.95	0.87	0.83	0.87	1.00
Zn	-0.41	-0.44	-0.42	-0.42	-0.37

On the other hand, Zn showed poor correlations with the Cd and Mn, but a negative and relatively higher correlation with Pb and Cr when all samples in the east side of the runway were considered. It also exhibited a negative and relatively similar correlation with all the heavy metals, in the soils close to the runway that are used by the aircraft during landing and takeoff (the sandy loam soils). This shows that the dominant sources of Zn contamination are different from the sources for the other heavy metals.

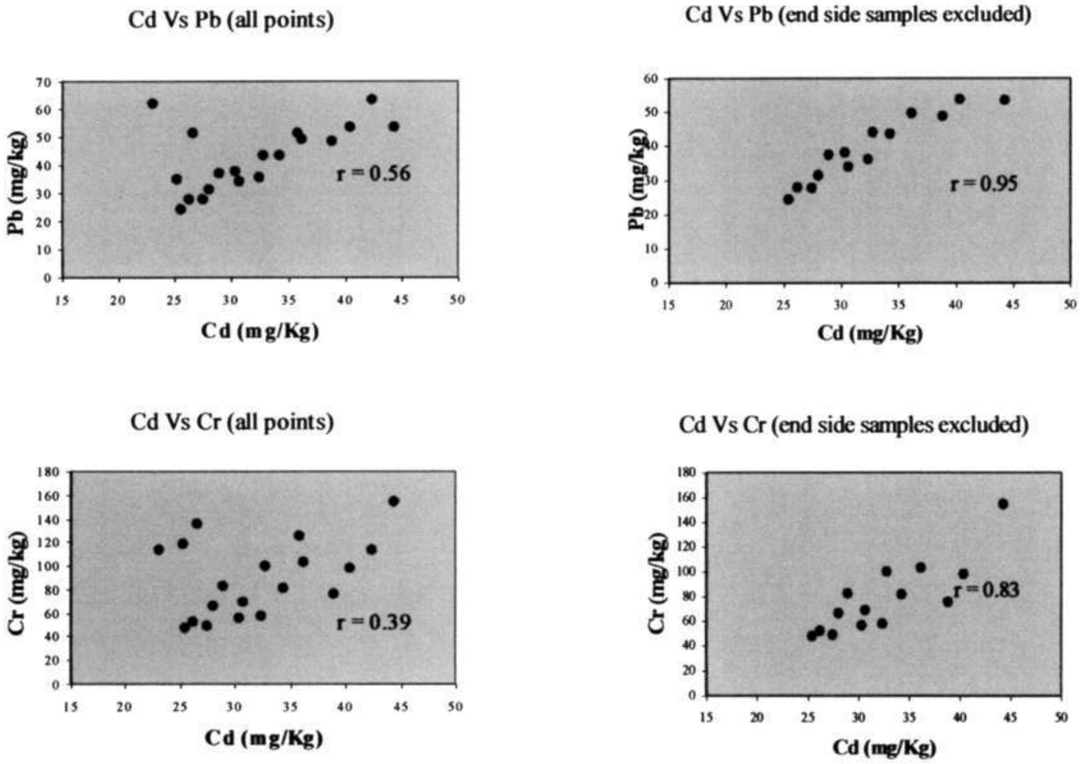


Figure 4.11 Correlations of Cd with Pb and Cr for all sampling points and sandy soil samples from the east side of the runway.

The correlation matrix for heavy metals at the west side of the runway, Table 4.12, reveal that there is significant correlation between Cd, Co and Cr. Similarly, Mn exhibited a good correlation with Cd and Co. However, lead and zinc showed poor correlation with Cd, Co, Cr and Mn, when all sampling points were considered.

Table 4. 12 Correlation matrix for heavy metals at the west side of the runway.

Correlation coefficients for all samples in the west side of the runway					
Cd	Cd	Co	Cr	Mn	Pb
Co	0.83				
Cr	0.56	0.59			
Mn	0.88	0.73	0.42		
Pb	-0.16	0.12	0.03	-0.13	
Zn	-0.19	-0.20	-0.31	-0.6	0.77
Correlation coefficients for sandy loam soil samples West					
Cd	Cd	Co	Cr	Mn	Pb
Co	0.90				
Cr	0.48	0.63			
Mn	0.84	0.84	0.36		
Pb	0.74	0.75	0.55	0.64	
Zn	0.54	0.29	-0.33	0.59	0.17

When sampling points at the south and north end of the runway were excluded, the correlation coefficients increased considerably for all the samples, except for correlations of manganese with Cr and Cd, and the correlation of Cd with Cr that showed a relatively small decrease. Graphical representation (some) of the correlation between the heavy metals in the west side of the runway is given in Figure 4.12.

The correlation between Zn and Pb showed a marked decrease in the sandy soils (when the end side samples are excluded) compared to the correlation of these metals found for the whole sampling area. This suggests that the correlation of these metals is high in the clay loam soils rather than in the sandy loam soils.

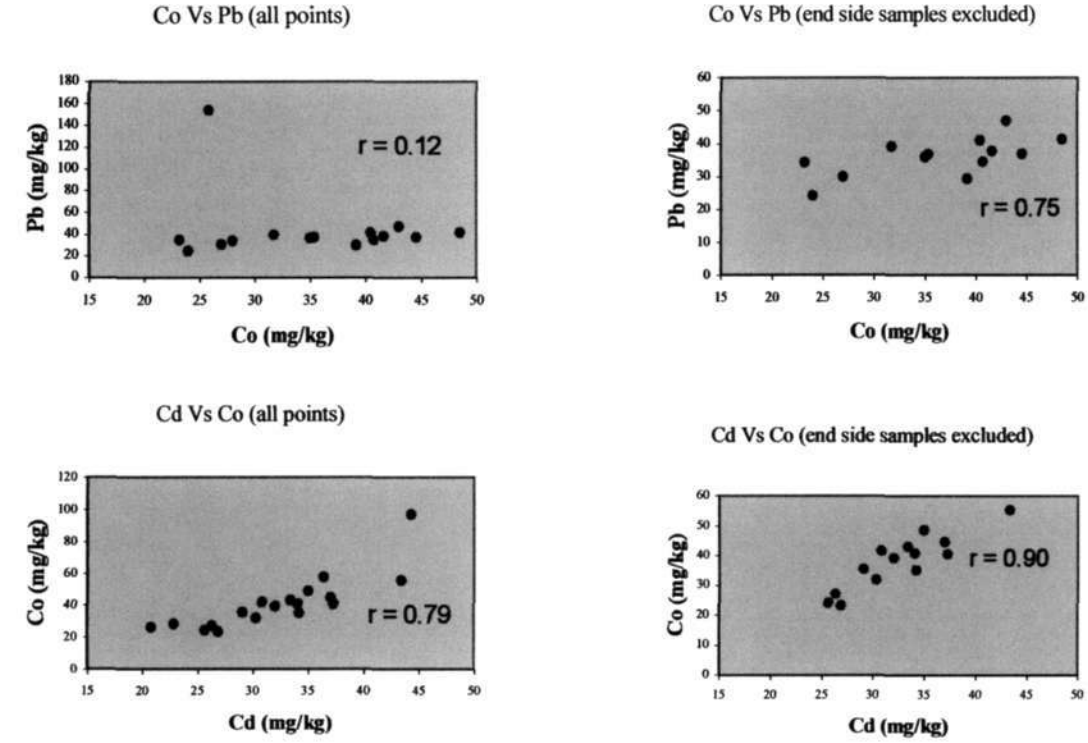


Figure 4.12 Correlations of Co with Cd and Pb for all sampling points and sandy soil samples from the westside of the runway.

In general, the correlation matrices between the heavy metals indicate that all the heavy metals, except zinc, come from the same source, in this case the activities of the aircraft on the runway. Though aircraft activities produce pollutants that contain zinc, the trends of the levels of zinc and correlation coefficient results of zinc with the other metals suggests that the dominant source of zinc pollution in the soils close to the runway is independent from the aircraft activities on the runway.

Comparison of the results with the South African guidelines for the maximum permissible contents of these metals in soils[170] shows that Cd and Co concentrations of all samples and the Pb and Zn concentrations of 86% of the samples were above these guidelines (2 mg/kg Cd, 20 mg/kg Co, 6.6 mg/kg Pb and 46.5 mg/kg Zn). In addition, the concentration of Cr was significantly above these guidelines (80 mg/kg Cr) in 51% of the samples. These results confirm that the soils adjacent to the runway are contaminated by the heavy metals.

CHAPTER 5

ORGANIC COMPOUNDS (PESTICIDES): EXPERIMENTAL, RESULTS AND DISCUSSION

5.1 INTRODUCTION

There is much concern about the possible contamination of the surrounding soils and groundwater by pesticides and fuel oils used by the tenant companies at the airport in Pietermaritzburg. This is because some of the effluents containing pesticides and fuel oils used in the day-to-day activities of these tenant companies find their way to the soil in waste water flow or are flushed by rainwater into nearby water courses.

A study was thus carried out to qualitatively assess the contamination of the soils in the vicinity of these tenant companies, particularly in the crop sprayers ditch and maintenance hangers drain which are highly susceptible to contamination by the organic chemicals used in the maintenance and crop sprayer hangars.

5.2 EXPERIMENTAL: MATERIALS AND METHODS

5.2.1 Sampling

Samples for determining the level of organic pollutants, from the activities of the crop sprayer and aircraft maintenance organisations, were taken over two areas (Figure 5.1).

- First, samples were taken along the ditch that extends from the aircraft maintenance and the crop sprayers' hangars down to the fence. From this sampling area 11 samples were taken along the ditch at distances between 15 and 25 meters (Table 5.1) where there is sufficient soil for sampling using a bucket auger.

- The other sampling area was the downward-sloping side adjacent to the drain opening on the aircraft washing area next to the Oribi Flying Services Maintenance hangar. From this sampling area two samples were taken, at 2 meters and 30 meters from the drain opening along the down slope.

To get a representative sample of every sampling point, three sub-samples, 1 meter apart (where it was possible), were taken from the top 0-15 cm of the soil using a bucket auger and subsequently mixed. Approximately 1 kg of the composite sample was taken for each sampling point. The samples were collected in glass bottles. The bottles were then covered by putting aluminium foil between the bottles and the lid to prevent possible adsorption of analytes on the plastic lid. Each sample was labelled and its site description recorded.

Table 5.1 Sampling points description

Sample No.	Distance from crop sprayer hangar (m)	Sampling point description
310	-	At outlet of the crop sprayer hangar drainage pipe (left)
309‡	5	Crop sprayer ditch, outlet of hangar drainage pipe (right)
308	25	Crop sprayer ditch
307	40	Crop sprayer ditch, 5 m up from junction with runway ditch
306	45	Runway ditch, 5 m up from junction with crop sprayer ditch
305†	60	Crop sprayer ditch
304	75	Crop sprayer ditch
303*	-	Control sample, 10 meter from sampling point 302
302	95	Crop sprayer ditch, 2 meter from the fence
301	120	Crop sprayer ditch 2 meter from the fence
311	-	4 m from drain outlet of the maintenance hangar (Pacair)
312	-	At outlet of drain from maintenance hangar apron (Oribi Flying Services) 5 m from tarmac.
313*	-	50 m from tarmac apron in front of the maintenance hangar (Oribi Flying Services)

* Sample 303 and 313 are taken as a control for samples from the crop sprayer and Pacair maintenance hangars, and for sample from Oribi Flying Services maintenance hangar and washing apron respectively.

† Samples taken from very shallow topsoil on shale.

‡ Samples taken from very wet, waterlogged ground.

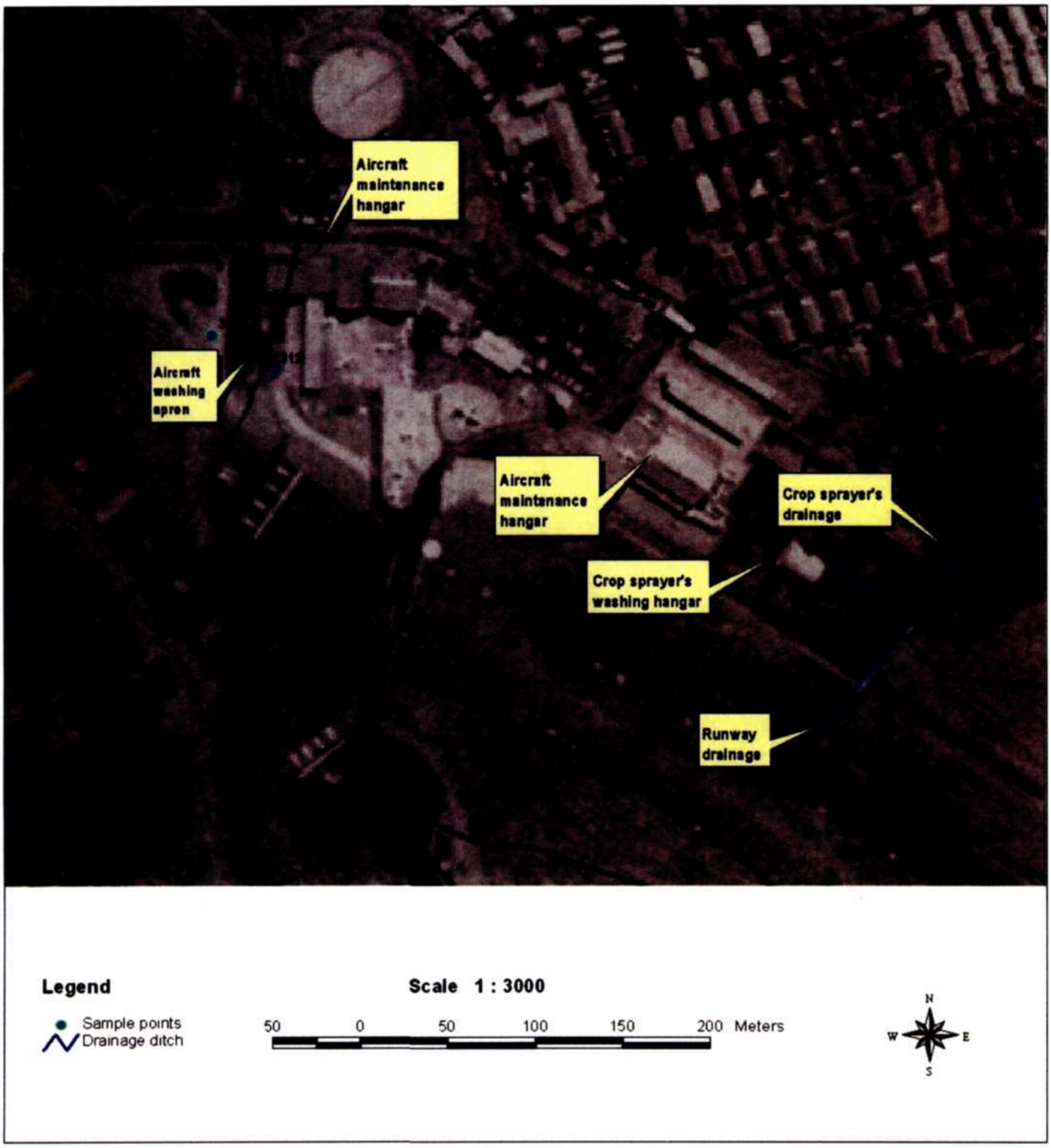


Figure 5.1 Sampling site and sampling points for organic chemicals.

5.2.2 Sample drying and grinding

Most of the samples were wet; hence, they were spread over cardboard boxes and air-dried at room temperature (approximately 25 °C) for 4-5 days. Stones, foreign materials and plant materials were removed from the soil samples and they were then ground using a mortar and pestle. Two portions of the soil were taken for each sample and were sieved using a 1.0 mm and 0.5 mm pore size sieves (Laboratory test sieve BS410/1986, Serial No. 311641, Endecotts, London, England) for soxhlet extraction and organic matter determination respectively. The soil that passed the 1.0 mm and 0.50 mm size sieves was collected in a properly labelled glass bottles, and was covered by putting aluminium foil between the bottle and the lid.

5.2.3 Organic matter determination

The air dried soil samples that had been sieved using the 0.50 mm sieve were used for organic matter determination in the samples using the Walkley-Black oxidation procedure as described in chapter 4 (section 4.1.4).

5.2.4 Soxhlet extraction

10 g of the dried soil sample that passed through the 1.0 mm sieve was blended with 10 g of anhydrous sodium sulfate and then placed in a porous extraction thimble (Whatman Cellulose extraction thimbles single thickness, inside diameter 28 mm x 80 mm external length). The extraction thimble was then placed in the sample holding siphonable chamber of the soxhlet extractor apparatus (Figure 5.2). An extraction solvent was prepared by mixing equal volumes of acetone (BDH, HiPerSolv for HPLC) and n-hexane (BDH, HiPerSolv). 300 ml of the extraction solvent was placed in a 500 ml round bottom flask containing two clean boiling chips.

The flask was placed on the heating mantle (electrothermal, UK, serial No. 10609162-3), and then attached to the sample holding siphonable chamber and the condenser (Figure 5.2). The power in the heating mantles was set such that the solvent was and condensed at 4-6 cycles/hour. Each sample was extracted for 16-24 h.

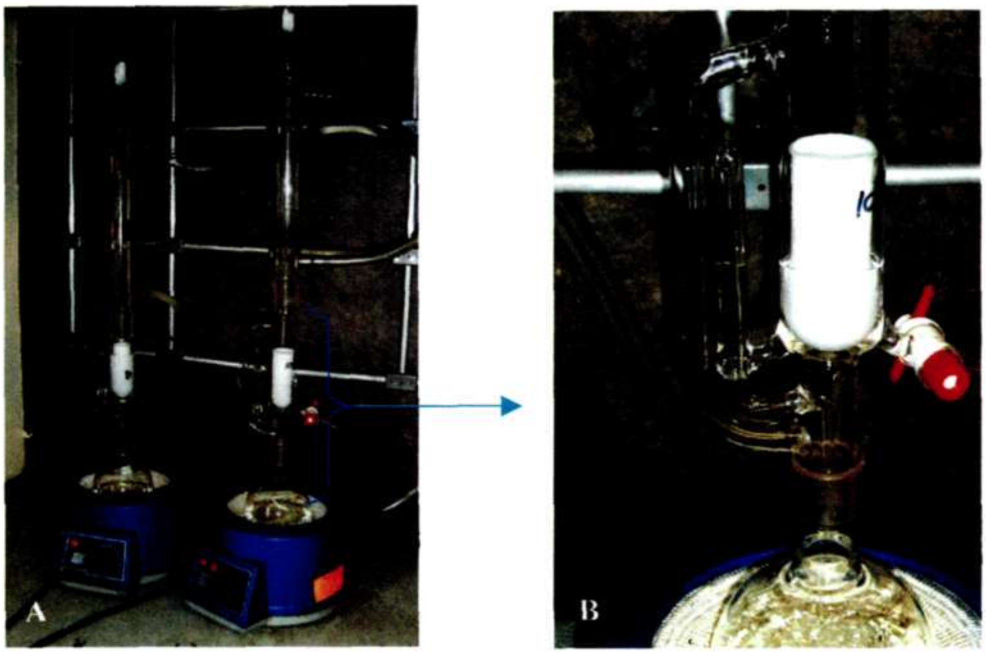


Figure 5.2 The soxhlet extractor apparatus set-up (A), and the extraction thimble (white) inside the siphonable chamber of the soxhlet extractor apparatus (B).

5.2.5 Sample drying and concentration

The extract was dried, by passing it through a drying column containing about 10 cm of sodium sulfate. Both the extractor flask and the drying column were washed with 100 ml of extraction solvent (1:1 acetone/n-hexane) to ensure the complete transfer of the extract.

A Kuderna-Danish (K-D) concentrator was assembled, by attaching a 10 ml concentrator tube to a 500 ml evaporation flask. The dried sample was collected in the K-D concentrator. After adding two clean boiling chips to the K-D concentrator, it was attached to a three-ball Snyder column pre-wetted with about 1 ml of hexane through the top of the column.

The K-D apparatus was placed on a hot water bath (80-85 °C) so that the concentrator tube was partially immersed in the hot water and the hot vapour bathed the entire lower rounded surface of the concentration flask. The vertical position of the apparatus and the water temperature were adjusted in such a way that the concentration processes was completed in 10 – 20 min, at a distillation rate at which the balls of the column actively chattered, but the chambers did not flood.

The K-D apparatus was removed from the water bath when the apparent volume of the liquid reached 1 - 2 ml, and it was allowed to drain and cool for at least 10 min. The Snyder column was then removed and the flask and the lower joints of the concentrator were rinsed with 1 - 2 ml of hexane.

5.2.6 Sulfur cleanup and nitrogen blow down

Sulfur has solubility characteristics similar to organochlorine and organophosphorus pesticides and can cause analytical interferences in the GC/MS analysis of these pesticides. To eliminate sulfur from an extract and prevent the masking of the pesticides in GC/MS analysis, a sulfur cleanup was done for the sample extracts using the EPA method 3600.[153]

A tetrabutylammonium (TBA) sulfite reagent was prepared by dissolving 3.39 g tetrabutylammonium hydrogen sulfate in 100 ml organic-free reagent water (ultra-pure water). 25 g of sodium sulfite was then added to the solution and stored in an amber bottle.

Each sample solution extracted and concentrated using EPA method 3500[151] was transferred to a 50 ml clear glass bottle, 1.0 ml of TBA sulfite reagent and 2 ml of 2-propanol were added, and the bottle was shaken for at least 1 min after capping the bottle with a glass stopper. This was followed by the addition of 5 ml organic-free reagent water (ultra-pure water) and then shaking the solution for at least 1 min. The mixture was then allowed to stand for 10 min, during which time the solution separated into two phases.

The hexane layer (top) containing the sulfur-cleaned sample, was then collected in a 50 ml conical flask and placed in a warm water bath (approximately 35 °C) and its volume was reduced to approximately 1.5 ml using a gentle stream of clean and dry nitrogen to evaporate the solvent. Finally the extract obtained was transferred to a properly labelled vial with a PTFE-lined screw cap, and stored in a refrigerator for future analysis of the target analytes using gas chromatography/mass spectroscopy (GC-MS).

5.2.7 GC/MS

5.2.7.1 Standards

The qualitative determination of the organic chemicals in soils around the crop sprayer and maintenance hangars was done for the pesticides and fuel that were amenable to GC analysis. Standard solutions of these compounds were prepared from pesticide solutions that were used by the crop sprayer company and fuels used by the aircraft. These compounds are:

- Pesticides
    - Amistar™ (Azoxystrobin 250 g/l, Syngenta, South Africa),
    - Kemprin 200 EC (Cypermethrin 200 g/l, KEMPTON CHEMICALS, Kempton Park, South Africa),
    - Decis® (Deltamethrin 25 g/l, Aventis CropScience South Africa),
    - IMPACT® (Flutriafol 125 g/l, Cheminova, Denmark),
    - Fusillade (Fluazifop-p-butyl 125 g/l, Zeneca Agrochemicals SA, South Africa), and
    - Punch-xtra® (Flusilazole 125 g/l and Carbendazim 250 g/l, DuPont, USA).
- Fuels
    - Av gas and
    - Jet A1

The concentration and solvent used to prepare the standards used in the qualitative determination of the organic chemicals by GC/MS are given in Table 5.2. Pesticide grade solvents (acetone BDH, HiPerSolv) and n-hexane (BDH, HiPerSolv) were used to prepare all the standard solutions.

Table 5.2 The concentrations of the chemicals (active ingredients), and solvents used in the preparation of the standards for qualitative determination of organic compounds in soil samples from crop sprayer and maintenance hangars by GC/MS.

Chemical (Trade name)	Active ingredients	Active ingredient (g/l)	Solvent	Concentration of standard
Amistar™	Azoxystrobin	250	Acetone	1 g/l
Kemprin 200 EC	Cypermethrin	200	Acetone	0.5 ml/l
Decis®	Deltamethrin	25	Acetone	0.5 g/l
IMPACT®	Flutriafol	125	Hexane	0.6 g/l
Fusillade	Fluazifop-p-butyl	125	Acetone	0.1 ml/l
Punch-xtra®	Flusilazole Carbendazim	125 250	1:1 Acetone/ hexane	0.6 g/l
Jet A1	-	-	Hexane	0.5 ml/l
Av gas	-	-	Hexane	0.5 ml/l

5.2.7.2 GC/MS analysis of the standards and samples

Each sample extract was run twice consecutively on the GC/MS (Figure 5.3), with operating conditions as given in Table 5.3. The results (chromatograms) of the second run (injection) of each sample were used for qualitative determination of the target analytes. The mass spectrum for each of the peaks obtained in the chromatogram of each sample was compared against the library data of the GC/MS computer data library for qualitative identification. The results obtained from the library search of the peaks for the target analytes were confirmed by comparing the retention times of the peaks in the chromatograms obtained from the GC/MS analysis of each sample with the retention times of the standards for the target analytes.

Table 5.3 The operating conditions and instrument specifications of the GC/MS used in the qualitative analysis of organic chemicals.

Instrument	ThermoFinnigan, Model K07300000000080, S. No. 20031445, Milan, Italy.
Injector	
Split mode	Splitless
Split flow (ml/min)	50
Splitless time (min)	0.75
Injected volume (μl)	1.0
Washing solvent	Acetone
Pre injection solvent cycle	2
Post injection solvent cycle	2
Carrier gas	Helium (99.995%, AFROX, South Africa)
Carrier gas flow (ml/min)	2.0
Column	EC-5, Serial No.306187, Alletech Associates, USA. (5% phenyl, 5% methyl polysiloxane)
Length (m)	30
Internal Diameter	0.32
Film thickness (μm)	1.00
Column Oven	
Initial temperature (°C)	60
Hold time (min)	20
Final temperature (°C)	300
Rate (°C/min)	10
Equilibration time (min)	0.5
Mass Spectrometer	Trace GC 2000, PolarisQ A1/AS 3000.
Source temperature (°C)	200
Damping gas flow (ml/min)	0.3
Micro scans	3
Max Ion time (ms)	25
Polarity	Positive
Ionisation mode	EI
Scan mode	Full scan
Mass range (amu)	50.0-600.0

Figure 5.3 ThermoFinnigan GC/MS apparatus Model K07300000000080 used in the analysis of the organic chemicals.

5.3 RESULTS

5.3.1 Organic matter

The results of the organic matter content analysis of the soil samples, obtained from the Walkley-Black oxidation procedure, are given in Table 5.4. The results show a wide range in the organic matter content (3.8-9.4%) of the soil samples. The highest organic matter content was found in sample 310, which was taken from the outlet of the crop sprayer hangar drainage pipe. Sample 305 showed the lowest organic matter content. The statistical analysis results show that there is a significant difference in the organic matter contents of the soil samples at 95% confidence level (Fpr < 0.001) with a least significant difference (l.s.d) of 0.39%. The % organic matter content results of the soil samples are shown graphically in Figure 5.4.

Table 5.4 Organic matter content (%) of soil samples from the crop sprayer and maintenance hangars.

Sample No.	Distance from the crop sprayer's hangar (m)	% Org matter
310	-	9.4
309	5	6.5
308	25	4.8
307	40	6.1
306	45	7.5
305	60	3.8
304	75	7.0
303	-	6.7
302	95	4.4
301	120	6.8
311	-	5.5
312	-	6.3
313	-	4.6
	Fpr	<0.001
	l.s.d	0.4
	s.e	0.2

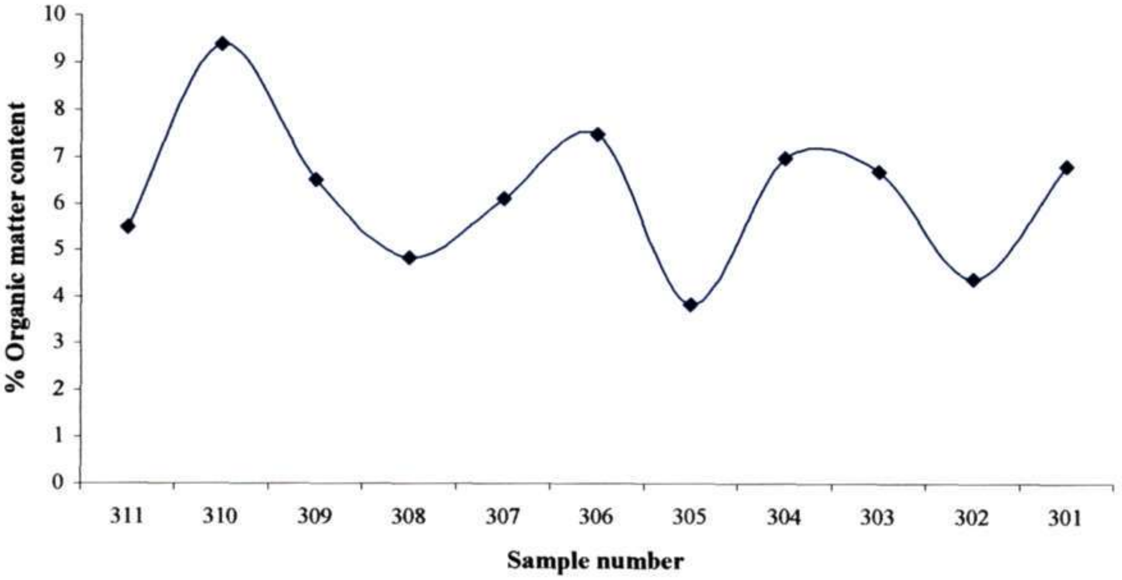


Figure 5.4 Organic matter content of the soil samples from the crop sprayer and maintenance hangars.

5.3.2 GC/MS analysis results for standards

The target analytes and retention times of the peaks for the active ingredients of the pesticides are given in Table 5.5. Figures 5.5, 5.6 and 5.7 show typical chromatograms of the standards obtained from the GC/MS analysis of the standard solutions, prepared as described in Table 5.2. The labels (numbers) in the chromatograms show the retention times of the peaks for the respective standards in the chromatograms.

Table 5.5 Retention times for the active ingredients of the pesticides used as standards.

Chemical (Trade name)	Active ingredients	R_t (min)*
Amistar™	Azoxystrobin	31.77
Kemprin 200 EC	Cypermethrin	27.60, 27.75 and 27.94
Decis®	Deltamethrin	30.58 and 31.12
Fusillade	Fluazifop-p-butyl	22.23
Punch-xtra®	Flusilazole	22.10

*: Retention time of the active ingredient in the pesticide.

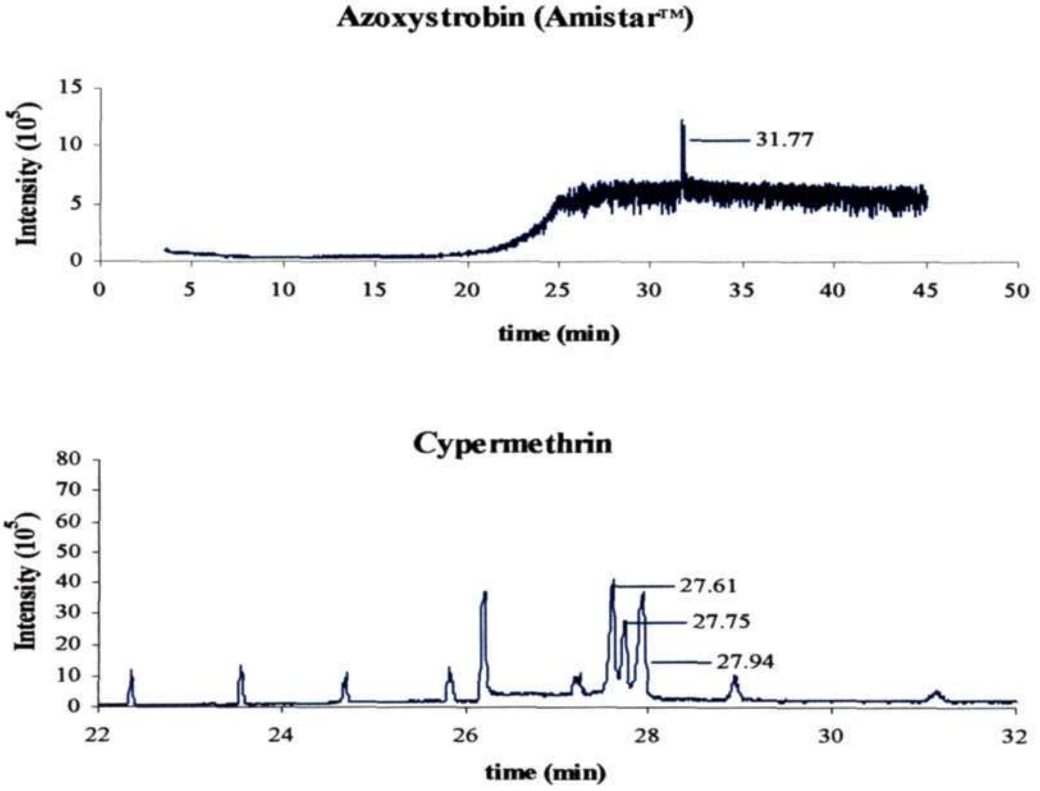


Figure 5.5 Chromatograms of the pesticides Amistar™ and Cypermethrin used as standards for qualitative analysis of organic chemicals.

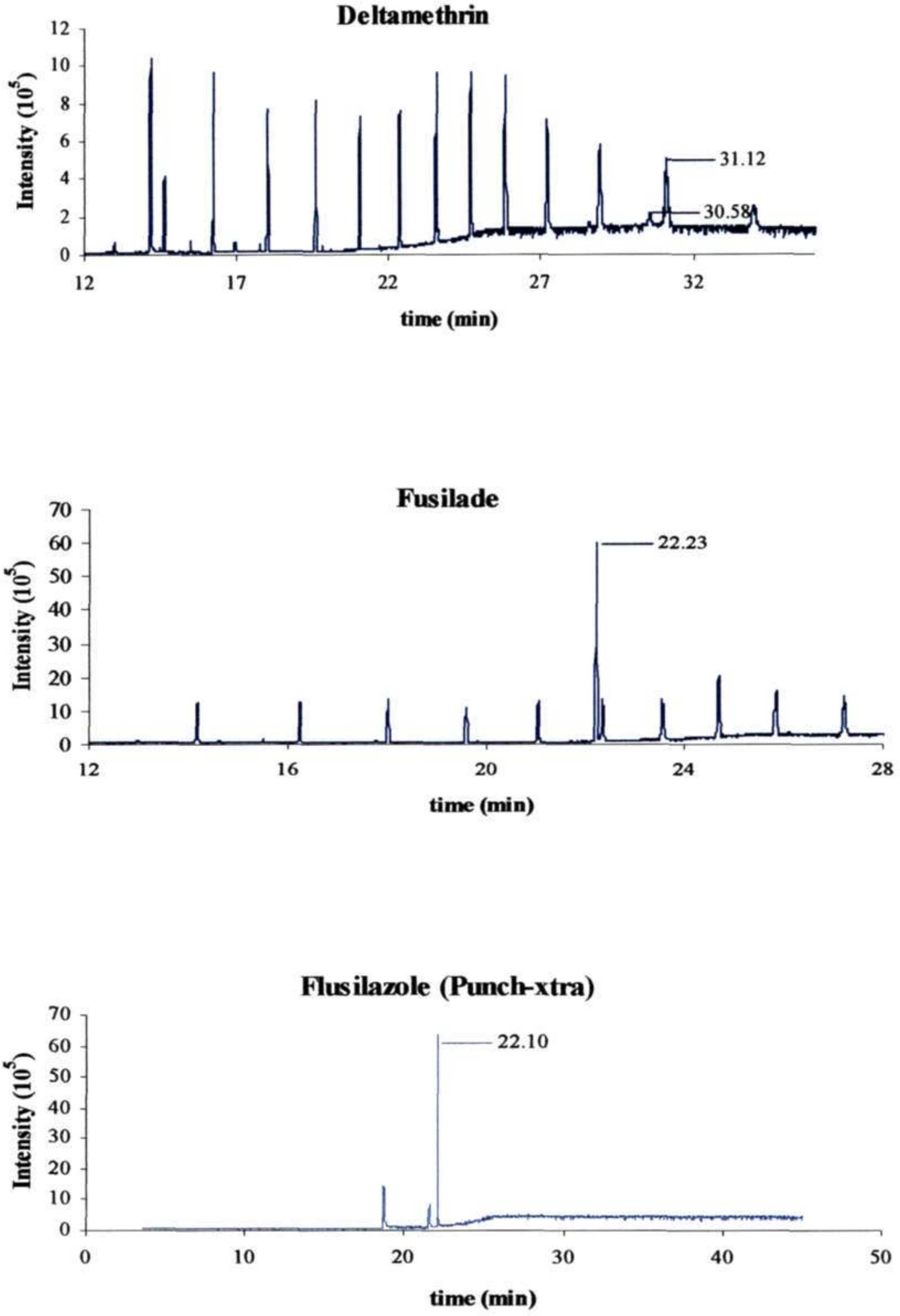
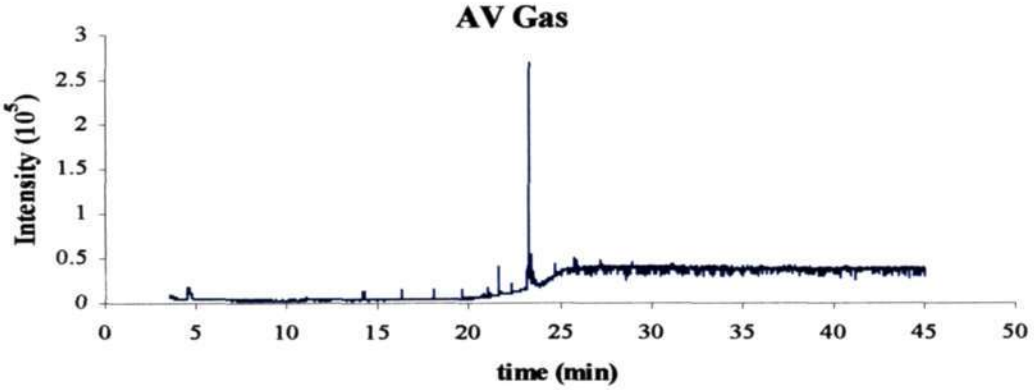


Figure 5.6 Chromatograms of the pesticides Deltamethrin, Fusilade and Punch-xtra® used as standards for qualitative analysis of organic chemicals.



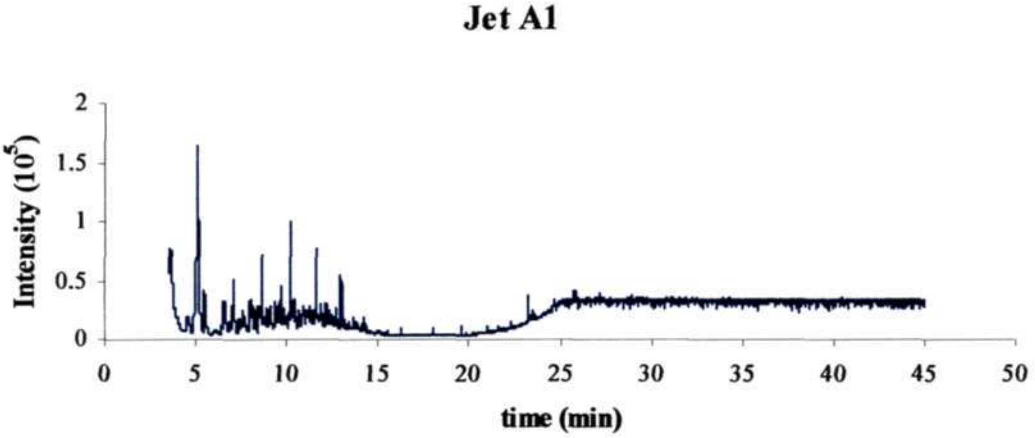


Figure 5.7 Chromatograms of the fuels Jet A1 and Av gas used as standards for qualitative analysis of organic chemicals.

5.3.3 GC/MS analysis results for samples

Punch-xtra® (Flusilazole) and Fusillade (Fluazifop-p-butyl) are the only pesticides that were detected. However, these two pesticides were not detected in all the soil samples from the crop sprayer and maintenance hangars. The results of the qualitative determination of the target analytes in the samples, using GC/MS, are given in Table 5.6.

The chromatograms obtained from the GC/MS analysis of the samples and the peaks for target analytes are shown in Figure 5.7 and 5.8. The chromatograms given in Figures 5.8

and 5.9 include only the chromatograms for the soil samples where the pesticides were detected. Two chromatograms for a single soil sample are presented in the figures; one showing the whole chromatogram (left) and a second (right) extract from the chromatogram enlarged to show the peaks of the target analyte and its retention time.

Table 5.6 Analytes detected, their retention times in the standard and samples.

Sample No.	Chemical name	Active ingredient	Standard's retention time (min)	Sample retention time (min)	Prob. (%)
301	-	-	-	-	-
302	-	-	-	-	-
303	-	-	-	-	-
304	Punch-xtra®	Flusilazole	22.10	22.09	88.86
305	-	-	-	-	-
306	-	-	-	-	-
307	Punch-xtra®	Flusilazole	22.10	22.08	83.42
308	Punch-xtra®	Flusilazole	22.10	22.09	90.77
309	Punch-xtra®	Flusilazole	22.10	22.10	92.14
	Fusillade	Fluazifop-p-butyl	22.23	22.23	86.78
310	Punch-xtra®	Flusilazole	22.10	22.09	89.33
	Fusillade	Fluazifop-p-butyl	22.23	22.23	95.37
311	Punch-xtra®	Flusilazole	22.10	22.11	90.24
312	-	-	-	-	-
313	-	-	-	-	-

Prob (%): A probability factor based on the differences between the adjacent best matches found during the library search (hits). The hits are arranged in order of how well they match the library spectrum.

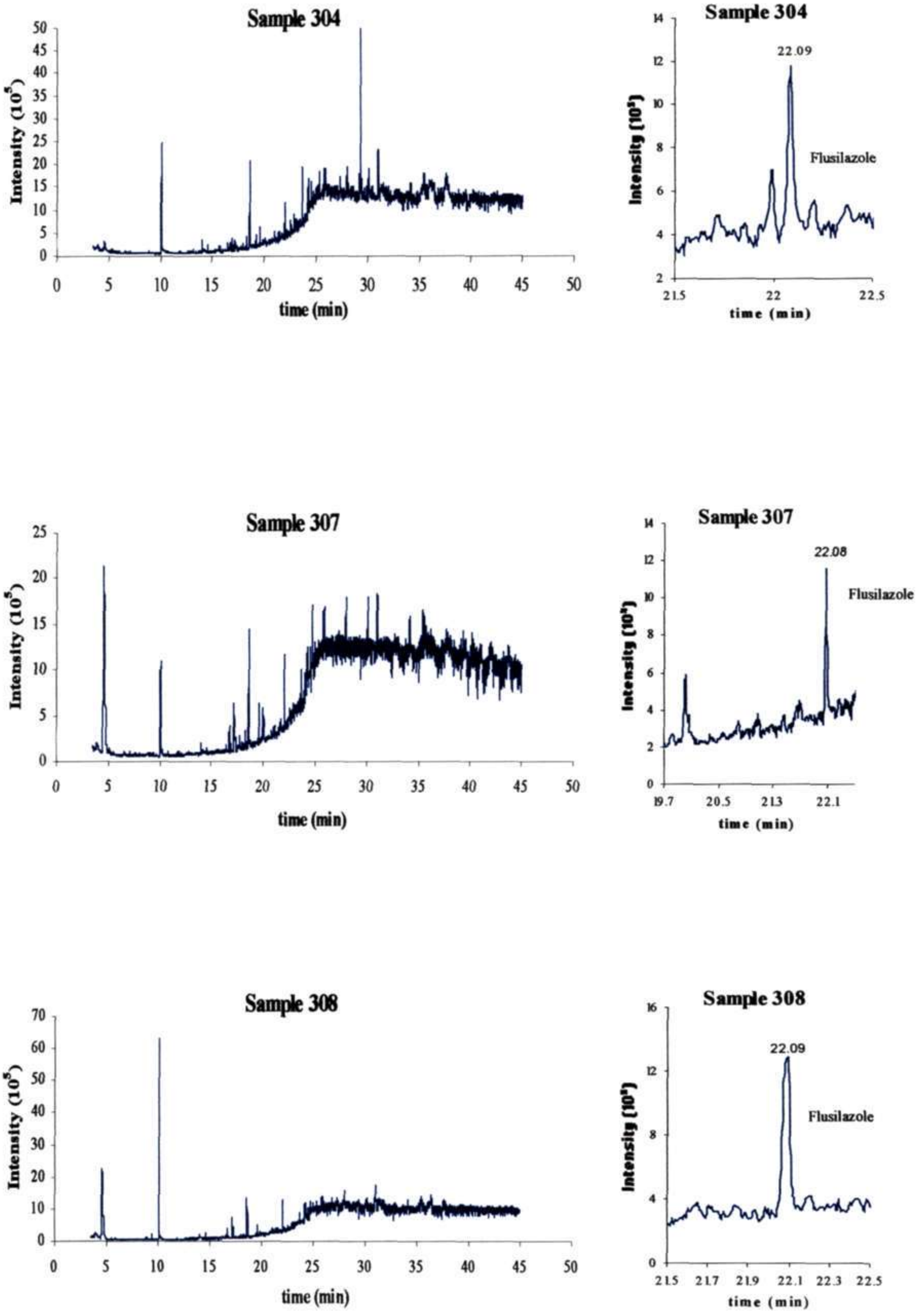


Figure 5.8 GC/MS chromatograms for samples 304, 307 and 308.

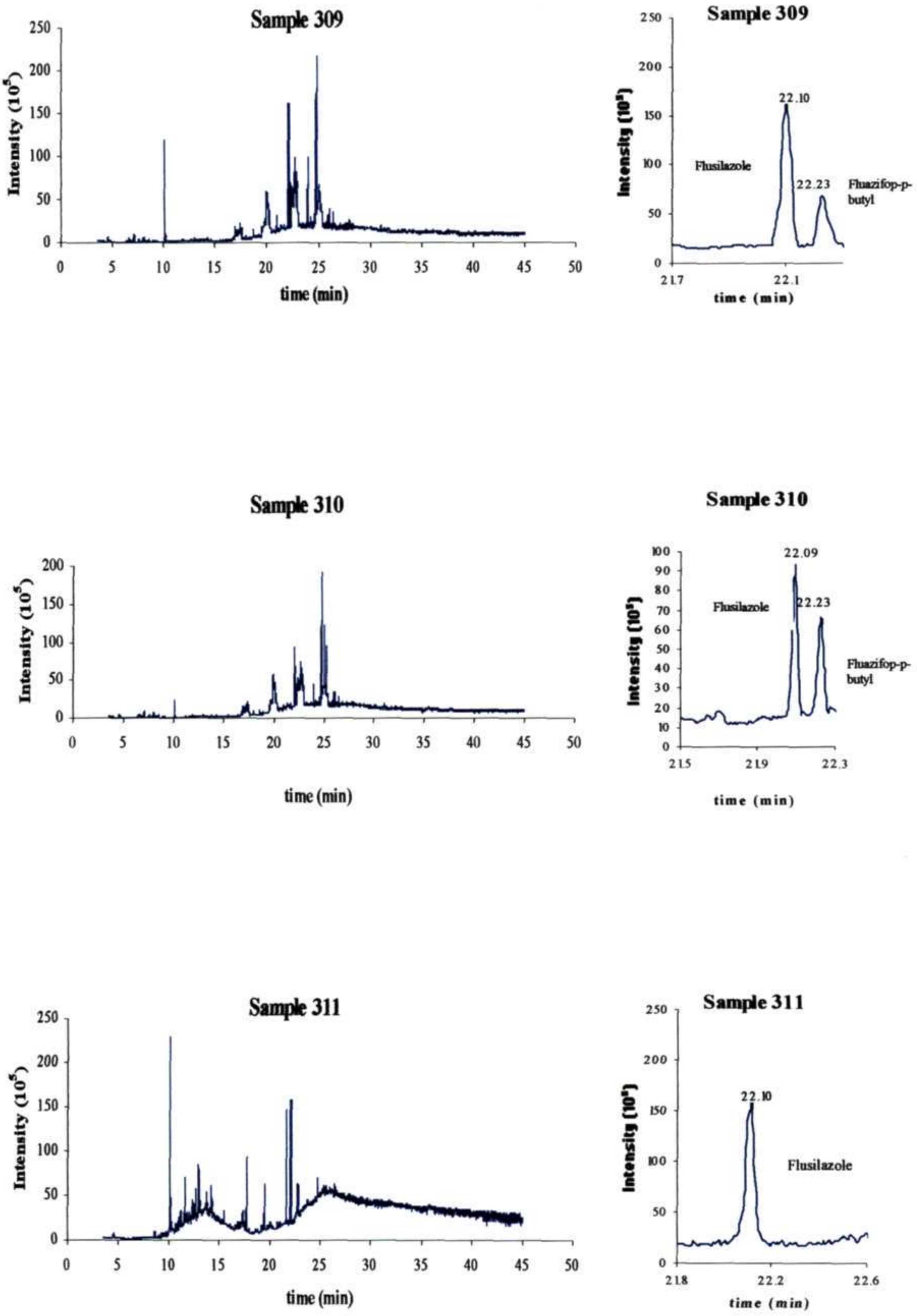


Figure 5.9 GC/MS chromatograms for samples 309, 310 and 311.

5.4 DISCUSSION

The organic matter results obtained show that the soil samples have significantly different amounts of organic matter, at 95% confidence level. These differences in the organic matter content of the soil samples may be due to the difference in the soil texture (type) of the soil samples collected. Sample 305 exhibited the lowest amount of organic matter (3.8%) since this soil sample contained a large amount of coarse-textured soil and gravel. Sample 310, on the other hand, showed the highest organic matter content (9.4%). This sampling point was a small drain hole located immediately next to the crop sprayer hangar, where the spray aircraft and the pesticide-mixing vessel are washed. Thus, the accumulation of organic chemicals in the pesticides (solvents, surfactants, active ingredients, etc), plus the lubricating and fuel oils from the pesticide mixing vessel and spraying aircraft washing effluents might be the reason for the high organic matter content of the soil from this sampling point.

From the pesticides used by the crop sprayer, Azoxystrobin (Amistar™), Cypermethrin (Kemprin 200 EC), Deltamethrin (Decis®), Flutriafol (IMPACT®), Fluazifop-p-butyl (Fusillade) and Flusilazole (Punch-xtra®) were chosen for the analysis since these pesticides require only solvent extraction prior to analysis by GC/MS. Ethephone and glyphosate were excluded from the analysis since they require derivitization prior to analysis by GC/MS.[171,172] Furthermore, the library (NIST/EPA/NIH mass spectral library)[173] of the GC/MS computer used in the analysis did not include the data for Flutriafol, thus identification (confirmation) of the peak and the retention time of Flutriafol was not possible.

Azoxystrobin, Cypermethrin and Deltamethrin were not detected in any of the soil samples. This may be due to the rate of degradation of the pesticides. The persistence of organic chemicals in the environment has been shown to be directly related to the rate of their degradation processes.[47] Thus, the results obtained may be attributed to the contribution of different degradation mechanisms, such as photodecomposition, hydrolysis, volatilisation and microbial degradation, to the selective disappearance of these pesticides from the sampling area.

Cypermethrin can be classified as a non-persistent pesticide in the environment (soil). According to The Royal Chemical Society, cited by Verschueren[174], the half-life of

Cypermethrin in soil is between 4 and 12 days. Similarly, several studies have shown that Deltamethrin is readily and quickly degraded in the soil, depending on the nature of the soil and temperature, and its half life generally ranges from 11 to 72 days.[175,176,177] It has been shown that Azoxystrobin is very susceptible to photolysis and degrades rapidly (soil half-life of less than two weeks), with photolysis being its major degradation pathway followed by microbial degradation.[178,179]

The continual input of the effluents to the soils in the sampling area may also result in a build-up of a select group of microorganisms in soil, capable of degrading these pesticides rapidly, thus resulting in enhanced degradation rates of the pesticides.[104] In addition, the dilution of the pesticides by the large volume of water used during washing has an impact on lowering the concentrations of these chemicals.

Another factor that influences the disappearance of the pesticides from the soil is the application rate (amount of pesticide applied in a given period of time). As more pesticide is used, the usage and washing of the pesticide mixing vessel and the spray aircraft increases, and so does the amount of the pesticide in the effluents from the crop sprayer hangar. In addition, the time of sampling in relation to the time of usage of these pesticides has a great impact on the detection of these pesticides, since the longer the time difference the more the pesticides will be degraded from the soil to concentrations below the detection limit of the GC/MS instrument. However, no properly documented data on the time of usage of these pesticides by the crop sprayers from the airport was available.

The relatively low usage of Cypermethrin and Deltamethrin (Table 5.7) suggests that they will consequently have a lower concentration in the washing effluents and they are less likely to be found at concentrations above the detection limit of the GC/MS. In contrast to the results obtained, Azoxystrobin was expected to have a relatively higher concentration in the effluents due to its relatively higher usage, and therefore expected to be detected in the soil samples. However, Azoxystrobin was not detected in any of the samples, and this may be attributed to its relatively short half-life (soil half-life of less than two weeks).

Table 5. 7 Usage of the pesticides and concentration of the ingredients.

Pesticide	Active ingredient	Usage (litres/year)	Concentration of active ingredient (g/l)
Amistar™	Azoxystrobin	12 000	2.5
Kemprin 200 EC	Cypermethrin	750	1
Decis®	Deltamethrin	750	3
Fusillade	Fluazifop-p-butyl	2 000	1
Punch-xtra®	Flusilazole	12 000	2.5

Note: "usage" refers to the amount of pesticide used by the crop sprayers from the airport.

The results of the GC/MS qualitative analysis of the soil samples confirmed the presence of Fluazifop-p-butyl (Fusilade, half-life 15 days[180]) in two samples (310 and 309) at locations close to the crop sprayers hangar. Flusilazole (Punch-xtra®, half life 251 days[181]), on the other hand, was detected in six samples (311, 310, 309, 308, 307 and 304) indicating it was spread over a wider area than is Fluazifop-p-butyl. The detection of Flusilazole in six of the samples can be ascribed to its longer half-life in soil (251 days), besides its high amount of usage. These results are in accordance with their usage as expected.

Considering the proximity of the sample location to the source of the pesticide effluents, it was expected that pesticides would be detected at sampling locations close to the effluent source (the crop sprayer hangar) rather than sampling locations at distances further from the point source. Flusilazole (Punch-xtra®), however, was detected in sample 304 but not detected in sample 305, which was located nearer to the pesticide effluent source. This can be attributed to the lower organic matter and clay contents exhibited by sample 305, and hence decreased adsorption of the pesticide on the soil. Several studies showed similar results on the effects of organic matter contents on pesticide adsorption. O'Connor *et al.* [65] reported that adsorption of 2,4,5-T tended to increase with an increase in organic content of the soil, suggesting that organic matter is an important contributor to the pesticide adsorption. Adams *et al.*[63] have reported that the organic carbon content determined the amount of lindane adsorption on soil.

The GC/MS chromatograms for all soil samples did not contain peaks characteristic of the fuel oils JET A1 and Av gas, which indicates that the concentration of these fuel oils in the soil samples was below the detection limit of the GC/MS. This can be attributed to the low number of aircraft getting serviced (ca. 64 aircraft/year), and hence there would be a low quantity of wastewater generated by aircraft maintenance activities in the maintenance hangars. In addition, the proper housekeeping and waste handling methods employed in both maintenance hangars have proved to be effective in reducing the concentration of the fuel oils in the effluent produced from the maintenance activities in the hangars.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Analysis of the total heavy metal content of the soils adjacent to the runway of Pietermaritzburg Airport (Oribi Airport) revealed that all samples contained significantly higher concentrations of Cd and Co than the mean baseline concentration of these metals in soils of South Africa as reported by Herselman *et al.*[166]. Moreover, 89% of the samples showed considerably higher concentration of Pb and Zn and 62% of the samples had Cr concentrations significantly above the baseline concentrations of these metals reported.[166] Similarly, Cd and Co concentrations of all samples and the Pb and Zn concentrations of 86% of the samples were above the South African guidelines for the maximum permissible contents of these metals (2 mg/kg Cd, 20 mg/kg Co, 6.6 mg/kg Pb, 46.5 mg/kg Zn) in soils.[170] In addition, the concentration of Cr was significantly above these guidelines (80 mg/kg Cr) in 51% of the samples. These results confirm that the soils adjacent to the runway are contaminated by the heavy metals.

Pearson's correlation coefficients between most of the heavy metals, a similarity in trends of the heavy metal concentrations in the east side of the runway and the noticeably higher concentrations of all the heavy metals at sampling points which correspond to the runway areas with a considerable number of tyre wear marks suggest that these heavy metals are originating from the different aircraft related activities. These include fuel combustion products, the tyre wear and other aircraft body abrasion (attrition). The trends in the levels of zinc and the correlation coefficients of zinc with the other metals suggest that the dominant source of zinc pollution in the soils close to the runway is independent from the aircraft activities on the runway.

The pesticides azoxystrobin, cypermethrin and deltamethrin, and the fuel oils Jet A1 and Av gas were not detected in any of the soil samples. This indicates that the effluents from the aircraft servicing activities at the two maintenance hangers and the crop sprayer's hangar did not contain significant amounts of these fuel oils or these organic chemicals were degraded by various degradation mechanisms in the soil. Fluazifop-p-butyl was detected only in two of the samples, both of which were taken close to the crop sprayer hangar. However, flusilazole was detected in 6 of the samples. The results show therefore that soils in the sampling area are contaminated by flusilazole.

Generally the housekeeping procedures put in place at both maintenance hangers in the airport are effective in controlling the fuel oils Av gas and Jet A1. However, pesticide contamination is occurring and better methods of control should be established.

This study was focused on the levels of heavy metals adjacent to the runway. Investigating the forms of occurrence of these heavy metals in the soil becomes an important aspect to predict the potential mobility of these heavy metals to ground water from soil. In addition, further studies on the levels of these metals in soils at the environs of the airport should be done to assess the extent of distribution of the heavy metals originating from the activities of aircraft in the airport.

Also, investigations need to be done on the availability of the pesticides surveyed in this study over a longer period of time. Moreover, further studies should also be conducted to quantify the pesticides detected in this study as well as to assess the levels of ethephone, glyphosate and flutriafol in the soils.

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