Methodologies for the Analysis of Petroleum Hydrocarbons Extracted from Contaminated Soils

A thesis submitted for the degree of

Doctor of Philosophy

by

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March 2002

Preface

I hereby declare that, to the best of my knowledge and belief, the material presented in this thesis is original, except where due reference is made in the text. None of this work is submitted for any other degree or diploma in any other university.

Publications

(1) Barone, S.; Buddhadasa, S. C.; Bigger, S. W.; Orbell, J. D. Extraction of Hydrocarbons from Clay Soils by Sonication and Soxhlet Techniques, *Journal of The Japan Petroleum Institute*. 44, 6, 378-383, 2001.

(2) Thi, H. T.; Bigger, S. W.; Kruger, T.; Orbell, J. D.; Buddhadasa, S. C.; Barone, S. Identifying Deficiencies in the Environmental Chemistry Education Literature, *Journal of Chemical Education.* 78, 1693-1695, December 2001.

(3) Barone, S.; Buddhadasa, S. C.; Bigger, S. W.; Orbell, J. D. Method Dependency in the Measurement of BTEX Levels in Contaminated Soil, *Journal of Soils and Sediments*. 2 (3) 137-142 (2002). http://dx.doi.org/10.1065/jss2002.06.050.

(4) Barone, S.; Buddhadasa, S. C.; Bigger, S. W.; Evans, J.; Orbell, J. D. and Gibson E. Comparison of Field and Laboratory Methods for Measuring Volatile Organic Contaminants in Soil. *Journal of The Japan Petroleum Institute.* 45, 5, 271-278, September 2002.

(5) Bigger, S. W.; Orbell, J. D.; Buddhadasa, S. C.; Barone, S. A comparison Between the use of Dichloromethane, a Dichloromethane/Acetone Mixture, and Isopropanol, as Extractants Solvents in the Quantitative Analysis of Total Petroleum Hydrocarbon in Soil Samples, *Journal of the Japan Petroleum Institute*. 46, 1, 2003.

Conference Presentations

(1) Barone, S.; Buddhadasa, S. C.; Evans, J.; Hicks, C.; Neil, E. C. *Volatile Petroleum Pollution Testing Study using a Field Photo-Ionisation Detector (PID) Under Laboratory Conditions*, First International Conference, Contaminants and the Soil Environment, Australasia – Pacific, Adelaide, South Australia, 18 – 23, February 1996, p 155-156.

(2) Buddhadasa, S. C.; Santhakumar, N. *Coode Island Analytical Study*, International Symposium on Environmental Chemistry and Toxicology, Sydney, Australia, 14 – 18 July 1996, p 27.

(3) Barone, S.; Buddhadasa, S. C., Magore, B. *Simultaneous Analysis of Purgable Petroleum Hydrocarbons to Obtain BTEX and C_6 to C_9 Fractions in Contaminated Soils, Sediments and Waters using Purge and Trap Gas Chromatography with Mass Selective Detection*, Australian Symposium on Trace Analysis and Environmental Monitoring, Sydney, Australia, 12 – 15 October 1997, p 15.

(4) Barone, S.; Buddhadasa, S. C., Magore, B. *Application of External, Internal and Surrogate Standards for the Analysis and Confirmation of TPH (C_{10}-C_{36}) in Contaminated Soil and Water*, Australian Symposium on Trace Analysis and Environmental Monitoring, Sydney, Australia, 12 – 15 October 1997, p 16.

(5) Barone, S.; Buddhadasa, S. C. *Comparison of the Flame Ionisation Detector and the Mass Selective Detector for Gas Chromatographic Detection and Quantification of Total Petroleum Hydrocarbons in the C_{10}-C_{36} Range*, International Symposium on Analytical Science, Melbourne, Australia, 4 – 9 July 1999, p 345.

(6) Barone, S.; Buddhadasa, S. C. *Comparison of Dichloromethane/Acetone (1:1) and Isopropanol as Solvents for the Extraction of Total Petroleum Hydrocarbons in the C_{10}-C_{36} Range from Contaminated Soils Using Gas Chromatography with Flame Ionisation Detection*, International Symposium on Analytical Science, Melbourne, Australia, 4 – 9 July 1999, p 346.

(7) Barone, S; Buddhadasa, S. C.; Gibson, E. *Comparison of TPH (C_6-C_9) Concentrations Achieved by Two Detectors Using Purge and Trap Sampling*, Contaminated Site Remediation : from Source Zones to Ecosystems, Melbourne, Australia, 4 – 8 December 2000, p 313-320.

(8) Bigger, S. W.; Orbell, J. D.; Buddhadasa, S. C.; Barone, S. *Australian Approaches to Improving Methods for the Analysis of TPH Contamination in Soil*, 17 World Congress of Soil Science, Bangkok, Thailand, 13-21 August 2002, Proceedings iv.

Abstract

Australian research into TPH and BTEX test methods has, to date, not been coordinated and no standard methods have been agreed to. Overseas research also lacks acceptable solutions for the standardisation of TPH and BTEX methodologies. Since Australia carries out many thousands of analyses of TPH and BTEX on contaminated soils annually research into and assessment of current methods is required to demonstrate the effects on outcomes of method choice. In the Australian context the problem of developing standard methods for the analysis of hydrocarbon contamination of soil, and establishing a more scientific basis for commercial operations has been addressed in this thesis. In particular, problems associated with establishing TPH and BTEX analysis have been critically examined with a view to exposing shortcomings and suggesting possible solutions.

The study includes an assessment of the relationship between measurements in the field and in the laboratory for TPH (C_6-C_9) and BTEX; an area where there are known to be frequent disagreements. This study confirms this problem and aims to educate practitioners of the limitations of field measurement.

Studies on the choice of extraction technique includes the assessment of Soxhlet, sonication, tumbling and soaking on TPH (C_{10}-C_{36}) measurements. These techniques are employed across many laboratories in a non-standard way. This work will demonstrates the variability in measurements that can arise and recommends suitable extraction techniques. Specific areas investigated are as follows. The optimisation of solvent ratios - most laboratories in Australia use a variety of mixed extraction solvents. Therefore it is important to determine if this results in significant differences in measurement. Another area investigated for a given set of extraction conditions is the influence of soil moisture content on measured TPH (C_{10}-C_{36})

concentrations. The variation in extraction cycles has also been addressed with a view to minimising analysis time.

The choice of GC detectors such as the FID and the MSD to determine TPH (C_6-C_9), TPH (C_{10}-C_{36}) and BTEX levels has been investigated. It has been demonstrated that comparable concentrations of TPH and BTEX are measured using the different detectors. The comparison between different BTEX techniques namely P&T GCMSD, Headspace GCMSD and solvent extraction GCFID commonly used in Australia are also assessed to determine and recommend if one method is more suitable than another in obtaining proper concentration estimates. A method has been developed and validated to simultaneously determine TPH (C_6-C_9) and BTEX since it has been shown that when two methods are used for these analysis the results cannot be readily related to each other.

A study has been conducted to establish the most suitable extraction solvent, among DCM/acetone v/v, (1:1), DCM alone or isopropanol, for TPH (C_{10}-C_{36}) extraction from soil. It was concluded that the DCM/acetone is the superior solvent closely followed by DCM alone, the least effective being isopropanol.

For two extraction techniques compared by assessing the TPH (C_{10}-C_{36}) concentrations obtained from clay soils, Soxhlet extraction was capable of producing higher recoveries than sonication. However, the statistical variation of TPH (C_{10}-C_{36}) concentrations extracted from sandy soils and soils containing very low clay content had very little variation upon varying extraction technique from Soxhlet to sonication to tumbling. It was found that varying the DCM/acetone (v/v) ratio between 1:9 and 9:1 made no difference to TPH (C_{10}-C_{36}) extraction; single or multiple sonication extractions made no difference to TPH (C_{10}-C_{36}) extraction; changes in the moisture content from 3 to 21% does not influence TPH (C_{10}-C_{36}) extraction by sonication.

Studies were conducted to determine appropriate roles for GCFID vs GCMSD in TPH analysis. It was demonstrated that the TPH (C_{10}-C_{36}) concentrations obtained by GCFID with a given set of calibration standards were statistically different to those obtained by the GCMSD. The GCFID required a lesser number of calibration standards to obtain more reliable TPH (C_{10}-C_{36}) concentrations compared to the GCMSD. However the GCMSD produced more reliable identification of the TPH (C_{10}-C_{36}) components in any given sample. During the volatile TPH (C_6-C_9) analysis this finding was again confirmed, this time by using a split detector system on samples purged and trapped prior to the GC step then analysed by GCMSD and GCFID.

For volatile BTEX it was demonstrated that P&T GCMSD is a superior method to headspace GCMSD and solvent extraction GCFID. Therefore the same method was modified and developed for the analysis of TPH (C_6-C_9). The method was then validated and shown that concentrations obtained for TPH (C_6-C_9) and BTEX on any given sample of soil was technically comparable and the analysis can be simultaneous carried out.

Acknowledgements

I wish to express my sincere gratitude to the following persons and organisations for their contribution towards this work.

Principal Supervisor, Associate Prof. John D. Orbell, Co-Supervisors, Associate Prof. Stephen W. Bigger of the Victoria University of Technology and more recently Dr. Brett Yeomans Executive Officer-Scientific Programs, Australian Government Analytical Laboratories (AGAL), Canberra for undertaking the supervision and co-supervision of this project, patient guidance, enthusiastic support, tremendous encouragement, warm friendship, commitment and many contributions in the preparation of the thesis and publications.

I would like to acknowledge Dr. Sandra Hart, Australian Government Analyst for approving and granting the funds necessary for the project and the keen interest and enthusiasm, and the AGAL staff including Dr. Rod Miller (Team Leader, National Analytical Reference Laboratory (NARL) Perth), Mr. Paul Armishaw (Senior Chemist, NARL Perth), Mr. Danny Slee (Senior Chemist, AGAL Sydney, Mr. Sebastian Barone (Environmental Residues, AGAL Melbourne), Mr. Neil Menz (Food Composition, AGAL Melbourne), Mr. Nobert Strobel (Food Composition, AGAL Melbourne) and a very special thanks for Mr. Roger Cromie who frequently assisted me in data handling techniques and Microsoft Word and Excel applications. Furthermore, I also wish to thank my colleagues at AGAL, NARL and the Victoria University for their assistance throughout the course of the work.

Most importantly I thank my wife and son, my parents, sisters and brother for their support, encouragement and continual love.

This thesis is dedicated to my parents

Abbreviations and Terms

AGAL	Australian Government Analytical Laboratories
AIP	Australian Institute of Petroleum
ANZECC	Australian and New Zealand Environmental and Conservation Council
BFB	4-Bromofluorobenzene
BTEX	Benzene, Toluene, Ethyl benzene and ortho-, meta and para- isomers of Xylenes
C_{10}-C_{14}	Fraction of Hydrocarbon Measured from the beginning of n-C_{10} to the end of n-C_{14}
C_{10}-C_{36}	Fraction of Hydrocarbon Measured from the beginning of n-C_{10} to the end of n-C_{36}
C_{10}-C_{40}	Fraction of Hydrocarbon Measured from the beginning of n-C_{10} to the end of n-C_{40}
C_{15}-C_{28}	Fraction of Hydrocarbon Measured from the beginning of n-C_{15} to the end of n-C_{28}
C_{29}-C_{36}	Fraction of Hydrocarbon Measured from the beginning of n-C_{29} to the end of n-C_{36}
C_6-C_9	Fraction of Hydrocarbon Measured from the beginning of n-C_6 to beginning of n-C_{10}
C_8-C_{21}	Fraction of Hydrocarbon Measured from the beginning of n-C_8 to the end of n-C_{21}
CCC	Calibration Check Compound
CV (%)	Coefficient of Variation, Measure of the Spread in a Group of Results Calculated by Dividing the Standard Deviation by the Mean (can also multiply by 100 to obtain a percent value)

DCM	Dichloromethane
DELMTAS	Department of Environment and Land Management Tasmania
DEPWA	Department of Environmental Protection Western Australia
DRO	Diesel Range Organics
ECD	Electron Capture Detector
EICP	Extracted Ion Current Profile
EILs	Ecologically-Based Investigation Levels
EQL	Estimated Quantification Limit
FID	Flame Ionisation Detection
GC	Gas Chromatography
GCECD	Gas Chromatography with Electron Capture Detection
GCFID	Gas Chromatography with Flame-Ionisation Detector
GCMS	Gas Chromatography Mass Spectrometry
GCMSD	Gas Chromatography with Mass Selective Detector
GRO	Gasoline Range Organics
HHPID	Hand Held Photo Ionisation Detector
HIL	Health-Based Investigation Level
HP	Hewlett Packard
IS	Internal Standard
kg	Kilogram
kPa	Kilo Pascal
MS	Mass Spectrometry
MSD	Mass Selective Detection
NARL	National Analytical Reference Laboratory
NATA	National Authority of Testing Authorities
NEPM	National Environmental Protection Measure
EV	Electron volts
m/z	Mass to Charge Ratios

Amu	Atomic Mass Units
EI	Election Impact
P&T	Purge and Trap
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PEG	Polyethylene Glycol
% RSD	Percent Relative Standard Deviation
PID	Photo-Ionisation Detector
ppm	Parts Per Million
PTFE	Polytetrafluoroethylene
QC	Quality Control
R	Average Recovery
RF	Response Factor
r.f.	Reference Frequency
RRT	Relative Retention Time
R_t	Retention Time
SAEPA	South Australian Environmental Protection Authority
SD	Standard Deviation which is the Deviation from the Mean Value of a Population
Semi-volatile TPH	Total Petroleum Hydrocarbon Determined in the C_{10}-C_{36}
SFE	Supercritical Fluid Extraction
Soaking	A Procedure where a Test Portion of Soil is Placed with Solvent (without Agitation) to Extract the Target Chemical to be Analysed
Sonication	A procedure where a Test Portion of Soil is Mixed with Solvent and Placed in an Ultrasonic Bath and the Soil is Agitated at 40 kHz by Vibrating 40,000 Times per Second) to Facilitate the Extraction of the Target Chemical to be Analysed

Soxhlet	A procedure where a Test Portion of Soil is Extracted with Solvent in a Soxhlet Apparatus to Facilitate the Extraction of the Target Chemical to be Analysed
SPCC	System Performance Check Compound
S_R	Standard Deviation of Recovery
SS	Surrogate Standard
SW-846	Series of testing Methods Published by the United states Environmental Protection Authority
TCE	Trichloroethene
Tetraglyme	Tetraethylene Glycol Dimethyl Ether
TIC	Total Ion Chromatogram
TPH	Total Petroleum Hydrocarbon
Tumbling	A Procedure where a Test Portion of Soil is Mixed with a Solvent and Turned End Over End to Facilitate the Extraction of the Target Chemical to be Analysed
U	Uncertainty
UCM	Unresolved Complex Material
ULP	Unleaded Petrol
USA	United States of America
USEPA	United States Environmental Protection Agency
VicEPA	Victorian Environmental Protection Authority
VOC	Volatile Organic Compounds
Volatile TPH	Total Petroleum Hydrocarbon Determined in the C_6-C_9 range
v/v	Volume/Volume
w/v	Weight/Volume

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Chapter One : Introduction

1.1 Soil Contamination by Petroleum

Petroleum is the fossilised organic remains of microscopic marine plants and animals that settled to the sea floor millions of years ago[1-5]. Products derived from petroleum are complex mixtures containing primarily hydrocarbons[1-5], and other material including compounds containing atoms such as sulfur, nitrogen, or oxygen and even small concentrations of metallic constituents[1]. Classes of hydrocarbons in petroleum are given in Figure 1.1[1].

The hydrocarbon fractions of petroleum which contaminate soil and which are environmentally significant require monitoring under legislation in many countries around the world. The monitoring parameter most widely used is the so-called Total Petroleum Hydrocarbon (TPH). In some parts of Europe, this parameter is referred to as the "Mineral Oil Content". In Australia, various methods are in use for determining TPH. The TPH fraction can be divided into sub-groups including the TPH (C_6-C_9), TPH (C_{10}-C_{36}), TPH (C_{10}-C_{14}), TPH (C_{15}-C_{28}), TPH (C_{29}-C_{36}), and benzene, toluene, ethylbenzene, ortho, meta and para xylenes, referred to as TPH/BTEX. The polycyclic aromatic hydrocarbons, which are also a fraction of TPH are referred to as PAH. Petroleum products are obtained from the distillation of crude oil or blends from distillation fractions[2]. Examples of major products are gasoline, naphtha/solvents, aviation gasoline, jet fuels, kerosene, diesel fuel, fuel oils and lubricating oils. Due to the large number and variety of components in petroleum, characterisation is conducted using the boiling range of the mixture and the carbon number rather than referring to individual components[1]. For example, diesel is regarded as the fraction boiling between 200-325 °C and is represented as C_8-C_{21}. A description of the various fuels derived from petroleum mixtures is given in Figure 1.2 and the accompanying notes.

Since the widespread use of petroleum products, soil contamination has caused significant and complex problems. Such contamination may be generated, for example, by the activities of factories, service stations and oil refineries[6-9]. The extent and character of these problems is

now being recognised throughout the world. Countries including North America, The Netherlands, Canada, Australia, France, Germany and Japan have established soil quality guidelines, which are directed towards ensuring that this contamination is identified and ultimately remedied[9-18]. High concentrations can affect ground water and may be toxic to humans[19-31]. The problem is especially significant at a time when many contaminated sites are being re-developed and used for housing. Contamination of soil, water and air by petroleum products is generated in a number of ways. Service stations, railway yards, air force bases, airports, factories, oil refineries, terminals, depots and other facilities have inherent environmental liabilities[6-9]. The common causes of contamination at service station sites generally include underground storage tank ruptures, cracked or broken fuel lines, tarmac and forecourt rainwater runoff, workshop accidents and, most frequently, motorists overfilling their petrol tanks[9]. Apart from the unpleasant smell, leaking petroleum products can be explosive, toxic to humans, animals and plants, and can cause pollution in creeks, rivers, bore waters and ground water wells, foreshores, and forests[7]. The major hydrocarbon parameters tested in soil collected from oil industries contaminated sites are TPH and BTEX[7-10]. They are given a higher priority compared to other types of industrial contaminants due to their abundance in the environment, higher mobility through the soil into ground water and demonstrated toxicity to humans and animals[19-31].

The contamination of soil by constituents of petroleum hydrocarbons presents a major problem to countries throughout the world. Given the indispensable significance of oil and petroleum to the whole process of industrialisation and the use of motorised fuel engines, it is hardly surprising that industrialised countries such as The Netherlands, United Kingdom (UK), Australia and the United States of America (USA) have given great emphasis to identifying and remediating such contamination[10-17]. The problem of contamination is also great in developing countries which, in their attempts to achieve rapid economic growth, often

ignore the consequences of soil contamination, and usually lack both the expertise and the resources which would enable them to address such problems[18].

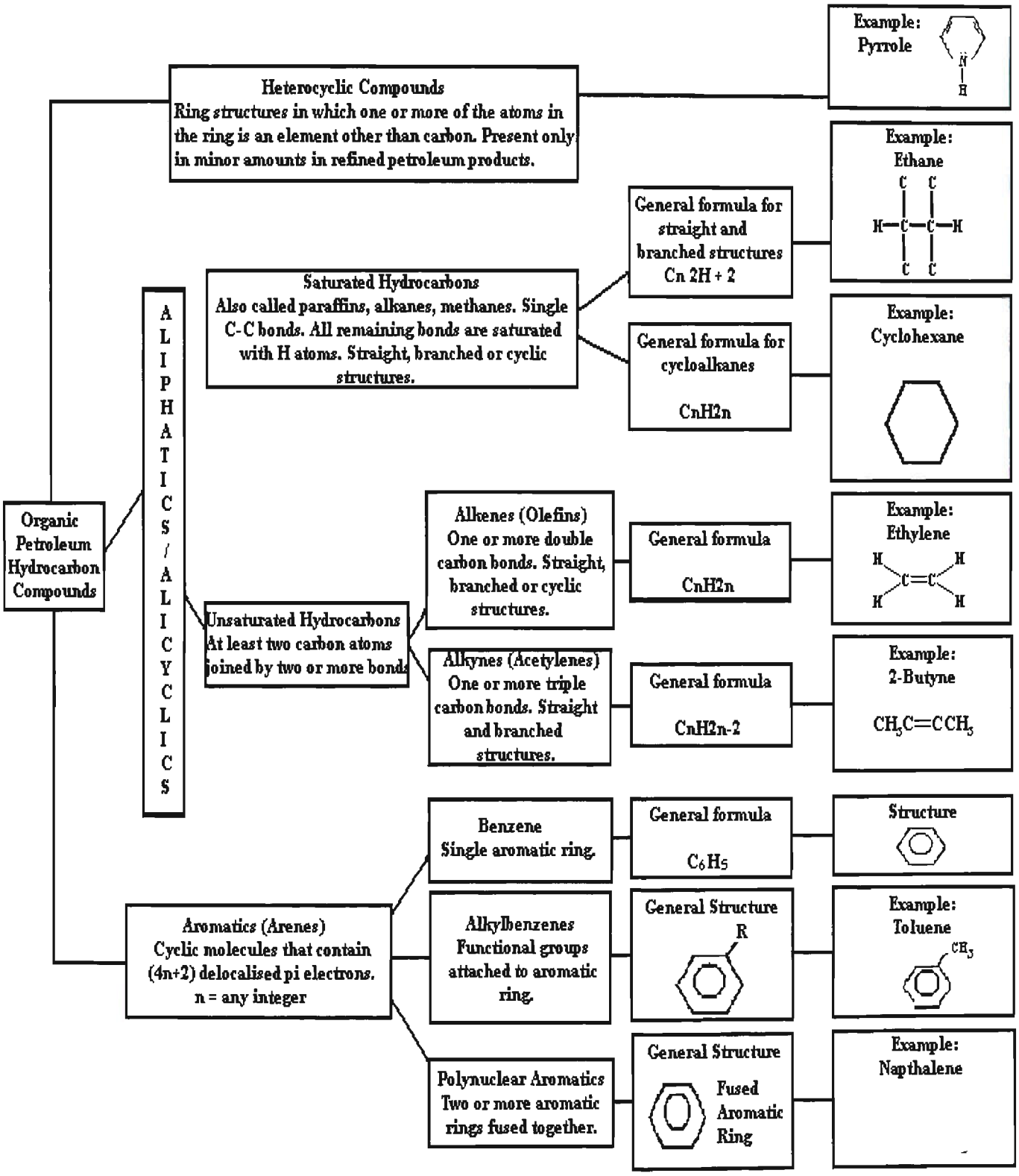

Figure 1.1: Classes of hydrocarbons (Weisman W. 1998)[1].

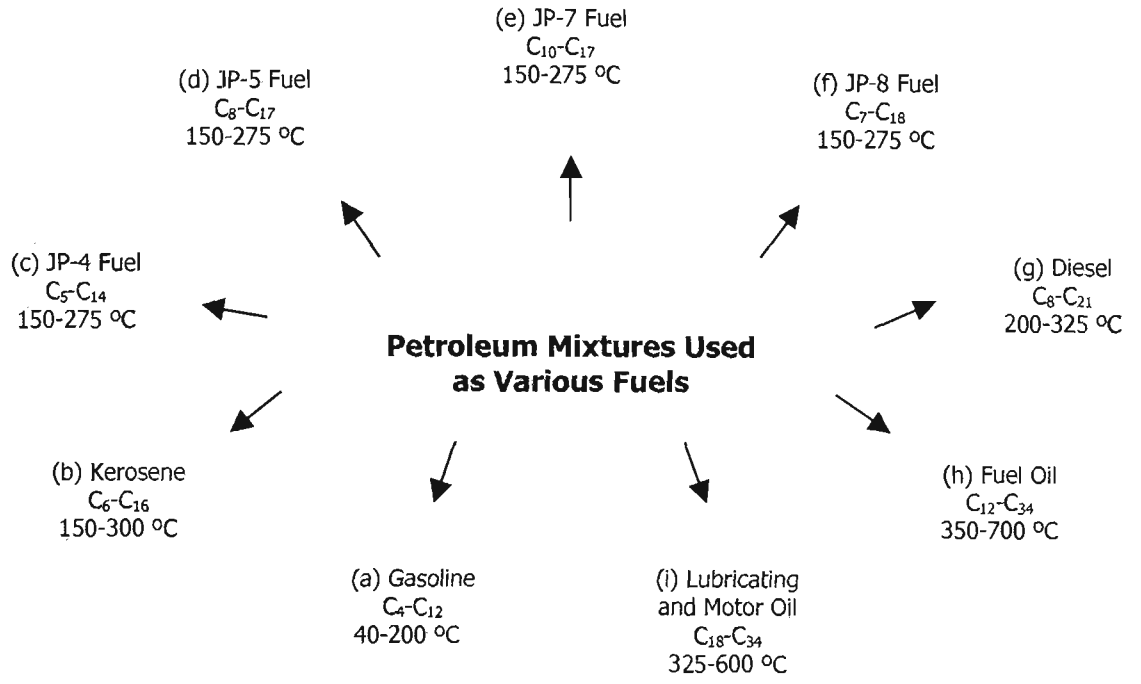

Figure 1.2: Petroleum mixtures used as fuels. Descriptive notes on each of these are provided in Appendix 1[1].

1.2 What is Total Petroleum Hydrocarbon (TPH) ?

There are no consistent definitions for TPH. The most commonly referenced method for analysing hydrocarbon contamination in soil is known as "*n*-hexane extractable material (HEM)" which is the definition used by the United States Environmental Protection Agency (USEPA) SW-846 series, method 9071B 5. Method 9071 B specifies extracting contaminated soil with *n*-hexane, drying and evaporating and determining the residue by gravimetry[4-5]. Due to the difficulty in obtaining a solvent, which can selectively remove the required TPH from soil, co-extraction of a range of compounds (including animal lipids, pesticides, ethers, alcohol, amino acids, carboxylic acids, aldehydes and ketones) occurs. Therefore, when an analysis of soil is conducted using gas chromatography (GC), unless individual components are identified, the TPH concentration is assumed to be the total response by the flame ionisation detector (FID) falling within a specified chromatographic range. In Australia and in many other parts of the world there are no uniform definitions for TPH [32-37]. One of the definitions used in Australia for TPH is the parameter computed by summing the total

chromatographic area between normal hexane (n-C_6) peak and normal hexacontane (n-C_{36}) peak. This is called TPH (C_6-C_{36}), although the soil extracts may contain non-hydrocarbons which are also detectable by GCFID. Fractions of TPH reported for soil contamination assessments are listed in Table 1.1. Some of the European countries extend the range to TPH (C_6-C_{40}). In some states of the USA TPH is defined according to the fuel type i.e. diesel range organics, gasoline range organics, etc. There is little or no consistency in the way that hydrocarbon contamination is determined in Australia and most likely in many other parts of the world. For example TPH in many Australian states are defined as total petroleum hydrocarbons. However the real definition due to the extraction techniques used is the total solvent extractable material.

Table 1.1: Reported TPH fractions.

TPH Fraction	Sources
C_6-C_9 Including BTEX	Gasoline and solvents
C_{10}-C_{14}	Distillates, components of kerosene, jet and diesel fuel
C_{15}-C_{28}	Fuel oil and lubricants
C_{29}-C_{36}	Sealant for roofing and road material

Components within each of the fractions presented in Table 1.1 are required to be confirmed to avoid reporting non-hydrocarbons as TPH. BTEX is one significant group of hydrocarbon components within the TPH (C_6-C_9) fraction. There are a number of analytical methods used for the BTEX and TPH analysis in soil around the world[38-53]. Important factors used in the selection of a method includes cost, availability of technology and expertise. Some of the more popular methods applied in testing TPH and BTEX are based on the USEPA SW 846 series of methods[5,54-60]. They include the analysis of BTEX by purge and trap (P&T), extraction and detection by GC with photoionisation detection (PID), FID or mass selective detection (MSD).

The P&T technique is unique for extracting volatile components by replacing them from a given sample with an inert gas and concentrating the volatile material in a trap made out of a stationary phase. These components are desorbed by heating the trap and transferring them to a GCMSD, a GCFID or a GCPID. In particular the analysis of TPH fractions C_6-C_9, C_{10}-C_{14}, C_{15}-C_{28} and C_{29}-C_{36} is usually performed by solvent extraction and detection is by GCFID. Consideration should be given to the analysis of the TPH (C_6-C_9) fraction since it contains BTEX and many volatile components similar to BTEX. Therefore the P&T technique is required to be applied for both BTEX and the TPH (C_6-C_9) fraction to obtain results which are comparable. For example, the BTEX concentration of contaminated soil is a part of the TPH (C_6-C_9) fraction because BTEX contains aromatic hydrocarbons which lie within the carbon numbers of the fraction. If BTEX is determined by P&T extraction and GCMSD analysis but TPH (C_6-C_9) is determined by a different method such as that used for the analysis of semi-volatile TPH (C_{10}-C_{36}) fraction (which is a common practice), then the concentration of BTEX can appear greater than the TPH (C_6-C_9). This is due to P&T being the better technique for the analysis of volatile components involving minimum losses. Instrument distributors such as Hewlett-Packard (HP), OI Analytical, Tekmar and Perkin-Elmer are developing and changing analytical approaches to TPH and BTEX analysis by updating instrumentation when appropriate. For example, the static and dynamic headspace extraction methods used in BTEX extraction is a major recent development with its automation and increased capacity to handle large numbers of samples in batch processes[61-62].

The accuracy of a site assessment is crucial in determining the subsequent stages of clean up. Additionally, the coherence and effectiveness of the assessments are largely dependent on the validity of the analytical techniques used in testing the contamination[11]. This whole process poses enormous and, as yet, unresolved problems. In broad terms, TPH concentrations may vary considerably depending on:

(i) the techniques used to identify and collect samples from the field;

(ii) the way the analysis is conducted;

(iii) the nature of the constituents in the soil;

(iv) the manner in which the soil is prepared for analysis; and

(v) the amount of moisture present in the tested soil sample[10].

The current literature acknowledges this problem, and research has been conducted on some of these aspects[12,63]. For example, the ways in which the baseline construction for the quantification of TPH was investigated since it has been a contentious issue in Australian Laboratories. Figure 1.3 contains a pair of chromatograms one with integration done on baseline-to-baseline and the other on peak-to-peak. Of these two baseline construction techniques the more accurate technique is suggested to be the baseline-to-baseline integration technique[1]. The baseline-to-baseline integration represents the total area between a retention time range which includes all components eluted in the chromatogram. There are many unresolved peaks which are an important part of the chromatogram because petroleum contains large numbers of isomers and compounds which co-elute. Therefore to avoid underestimation of TPH the baseline-to-baseline integration method needs to be applied.

There is a growing concern among professionals involved with contaminated site assessments regarding the analytical approaches used in determining TPH in contaminated soil[32-37]. Significant variation in methods with variations in results is a major issue. In this regard, a study conducted by the Victorian Environmental Protection Authority (VicEPA) in 1996 highlights the need for a standard method for the analysis of TPH[11-12,63]. To establish standard methods valid data is required on the performance of the various existing methods.

1.3 Petroleum Hydrocarbons and Health Hazards

A number of hydrocarbons have been identified to be significant health hazards to humans. They range from benzene and hexane, which are volatile hydrocarbons to benzo(a)pyrene,

which is a semi-volatile PAH. Some examples of health hazards are classified according to types of hydrocarbon are listed in Table 1.2[19-30].

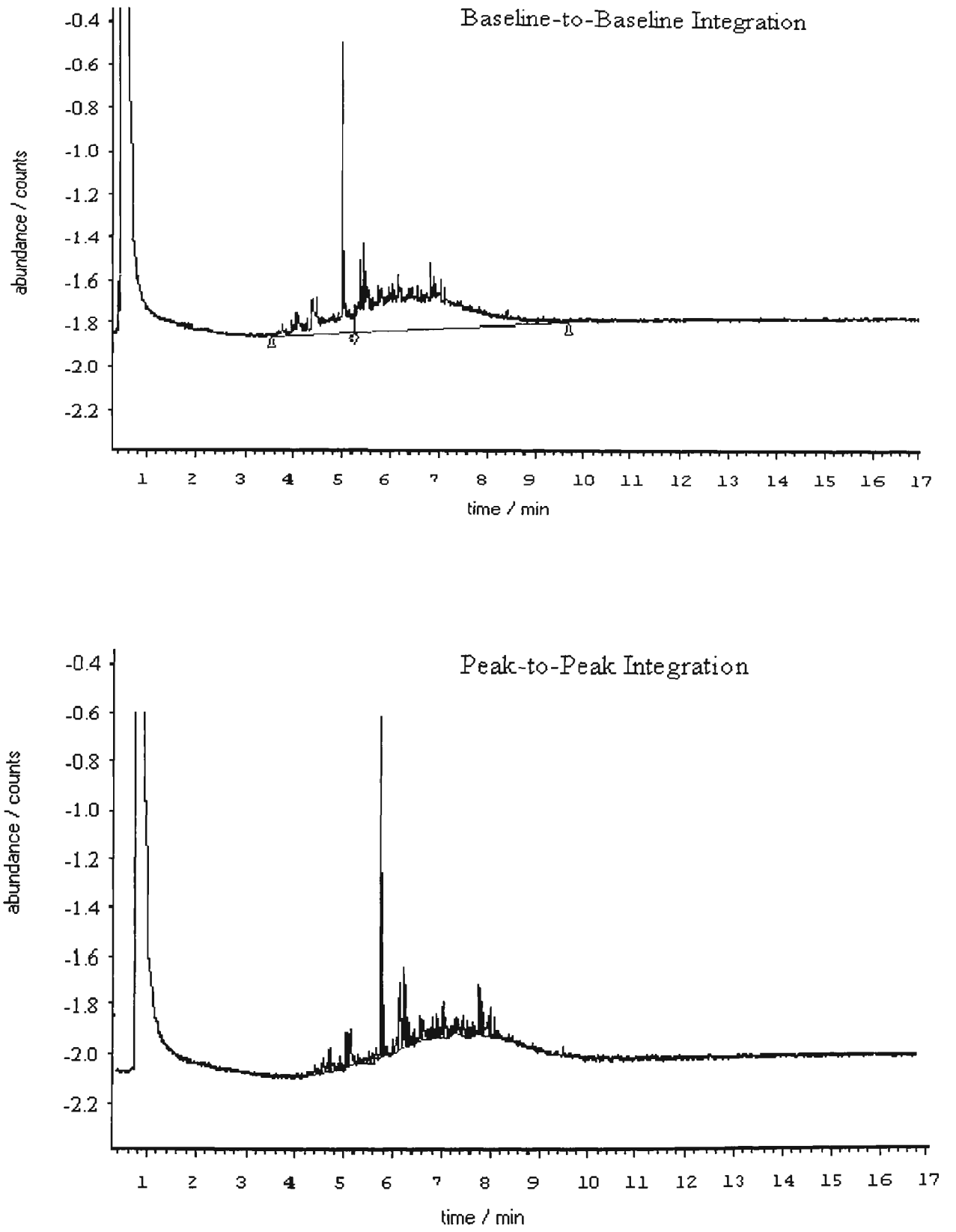

Figure 1.3: Baseline-to-baseline and peak-to-peak integration of TPH.

1.4 Environmental Fate of Hydrocarbon Contaminants

The environmental fate of TPH and BTEX is one of the most important issues confronting environmental authorities around the world due to possible paths of transformations. Petroleum products released into the environment undergo changes with time and these changes are called "weathering"[1]. Figure 1.4 gives an example of the effect of weathering on the chromatogram of diesel[1]. The weathering process includes evaporation[1], leaching of TPH and BTEX by transfer to an aqueous phase through solution and entertainment[1], chemical oxidation[2] and microbial degradation[2].

Table 1.2: Hydrocarbons and health hazards.

Hydrocarbon	Health Hazards
Benzene [19]	Can produce interference in the formation of red blood cells in the bone marrow linked with leukaemia in individuals having long-term occupational exposure
Fractions of catalytically cracked petroleum oils and coal tars	Tests conducted on mouse skin have shown tumourigenic potential
Air containing particles of semi-volatile hydrocarbon fractions between C_{10} and C_{16} can contain higher concentrations of PAH[20,24,27,29]	Potentially carcinogenic
Semi-volatile olefins can also decompose by photo oxidation producing peroxides	Can cause tumours
PAH containing 4, 5 and 6 benzenoid rings[20,24,27,29]	Implicated as a factor in causing lung cancer

The rate of weathering is highly dependent on environmental conditions. For example, gasoline can evaporate readily in a surface spill, while gasoline released below 3 m of clay topped with asphalt will tend to evaporate slowly and the weathering process may not be detected for years[1]. Leaching processes carry TPH and BTEX into ground water by their dissolution in rainwater mass flow. Aromatic compounds, especially benzene and its derivatives, are the most soluble fraction of petroleum[6]. During a storm event, benzene can

reach ground water quicker than the other petrol components. Therefore if the ground water is tested after such an event, benzene can be detected much earlier than the other components[1].

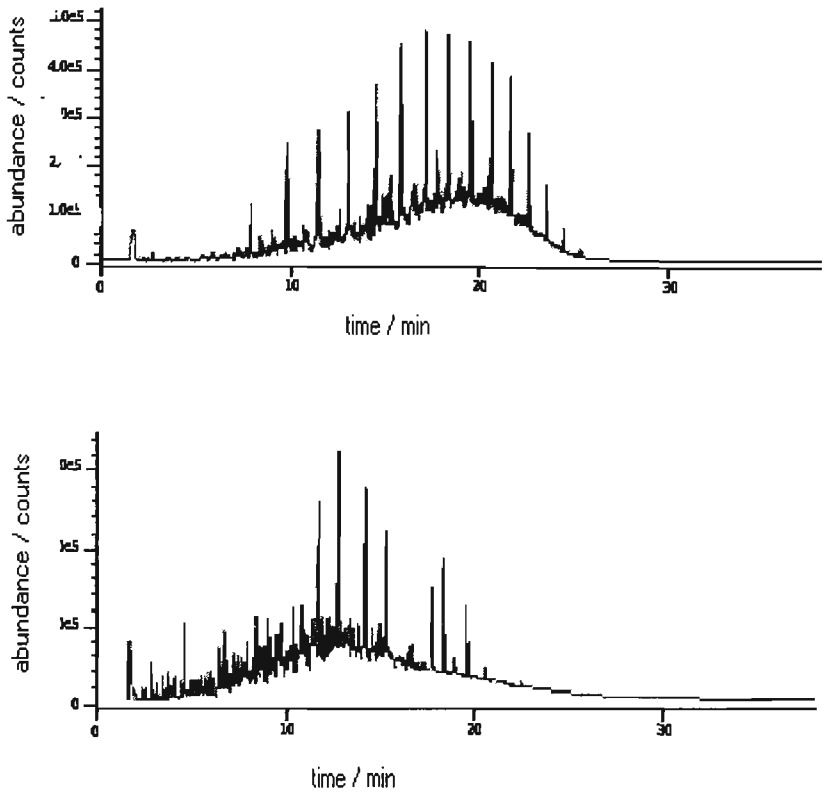

Figure 1.4: Un-weathered (top) and weathered (bottom) profiles of diesel (Weisman, 1998)[1].

The major problem confronted by different approaches to TPH analysis world-wide is the lack of comparative data between methods used for the analysis of an any given parameter. If a number of specific methods are tested against each other by statistically comparing results of TPH using contaminated these results can be used to present a better understanding of the capability of each of the methods. This information is essential if specific methods are to be implemented for TPH and BTEX analysis. The Netherlands legislation, although one of the first in the world, does not provide a standard method for such testing. Similarly the UK, Germany, France, Canada, USA, Japan and Australia do not have standard TPH and BTEX test methods specified by legislation [2-37]. In the USA and the UK there are a significant

number of petroleum hydrocarbon impacted sites. Figure 1.5 depicts examples of human exposure pathways[21].

The evaluation and remediation of these sites are also regarded as difficult due to the complexity of the regulatory, scientific and economic issues. For example, in the USA most of these investigations are regulated on a state by state basis with different requirements in investigation methodology, action levels, and clean-up criteria[33]. Therefore, there is a demand for the evaluation of analytical methods to obtain comparisons between data to properly nominate suitable methods for TPH and BTEX analysis. Although the above countries have not specified or legislated the required methods of analysis, most have nominated the concentrations of TPH and BTEX in soil which requires the implementation of a clean-up. Due to variation in methods used in obtaining the TPH and BTEX concentrations, these specified concentrations may not be determined accurately and consistently.

1.5 TPH and BTEX Assessments

1.5.1 Assessment in the Netherlands

One of the first countries to address hydrocarbon contamination in soil was The Netherlands. Soil protection policy in The Netherlands identified major categories of contaminated sites which was presented at the first International Conference on Contaminated Soil in 1985[17]. This work was called "Dutch Soil Contamination Criteria" and was also referred to as the "Soil Clean-up Interim Act".

The publication contains a list of soil contaminants with concentrations specified for background, further investigations, and clean-up. The action values for BTEX and mineral oil are included in this list. This document refers to TPH as mineral oil. During the time this publication was prepared the analysis was based on infrared (IR) spectrometry after a freon-based extraction. Since freon was banned from use due to greenhouse issues the Dutch Soil Contamination Criteria changed to GCFID analysis of soil extracts. Although there are no

official standard definitions for mineral oil the "unofficial" definition in the Netherlands is the GCFID chromatographic area between *n*-C_{10} and n-C_{40} obtained by the solvents used for the extraction. The extraction is carried out using a mixture of acetone and petroleum ether and the clean-up is achieved with Florisil™. BTEX analysis is carried-out either by using the headspace or a P&T sampling with a GC analysis.

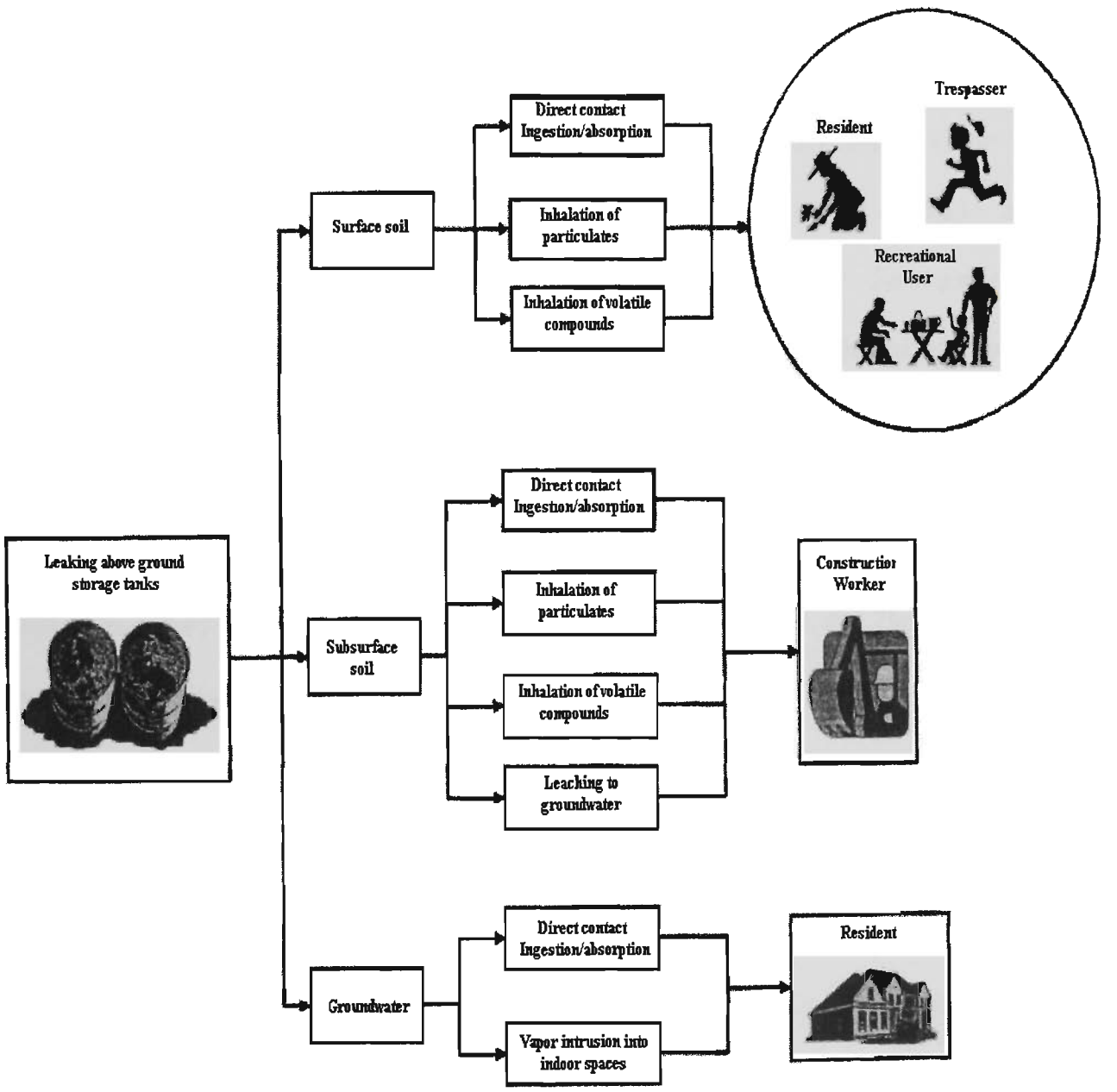

Figure 1.5: Exposure to hydrocarbon contamination (Vorhees *et al.* 1999)[21].

These initial criteria applied in the Netherlands were used in establishing most of the UK, European, Australian and the USA soil clean-up criteria. The Dutch criteria were based on defined levels, including background level of contaminants (A level), investigation threshold (B level) and the action level (C level); the C level indicating that clean-up and management

plans are required to be implemented. An updated version of "Dutch Soil Contamination Criteria", called the "New Dutch Soil Contamination Criteria" was presented to Australian scientists at a seminar in November, 1994[31] as a part of a seminar series to environmental scientist around the world. This presentation included more recent criteria and priority setting in The Netherlands, the history and overview, ecotoxicologically-based methodology and human health-based criteria[31]. The new Dutch criteria defines the concentrations as A, B and C levels in a similar manner to the previously published criteria. Furthermore, the C level concentrations are regarded as quite critical and are termed the "intervention values" which indicate serious soil contamination with unacceptably high risk to humans and the environment. The contaminants listed in the Dutch guidelines, especially the organic species, are much more detailed and comprehensive than those in most other guidelines around the world. The Dutch guidelines have specific values for benzene, toluene, ethylbenzene, xylene, fuel and mineral oil, which are useful as indicative contamination levels for site assessments. Presently, the Dutch B levels are used as reporting limits for environmental testing in Australia since they are more comprehensive. However, the levels for TPH are classified under Dutch guidelines only as fuel and mineral oil.

The Dutch criteria officially do not specify the values for TPH by carbon chain number (which relates to boiling point, not length is the commonly used reporting processes within Australia and a number of other countries) and do not specify testing methods. The TPH carbon chains are grouped in ranges C_6-C_9, C_{10}-C_{14}, C_{15}-C_{28} and C_{29}-C_{36} for contamination site assessment in Australia.

Another important drawback of the listings in the Dutch criteria is the lack of appropriate update with respect to expanding the list of contaminants, as data become available. This is particularly important in regard to the volatile hydrocarbons which are present in petroleum products and may include iso-octane, 2-methylpentane, hexane, 1-ethyl-2-methylbenzene,

1,3,5-trimethylpentane, methylcyclopentane, heptane and 1,2,4-trimethylbenzene. These components are commonly detected during site assessments. Netherlands have standard methods NEN 5732 for volatile TPH and NEN 5733 for mineral oil C_{10}-C_{40}.

1.5.2 Assessment in UK

In the UK there is no standard method for either TPH or BTEX analysis in soil. TPH is measured by solvent extraction and GCFID analysis[32]. BTEX is usually analysed by adapting a P&T or headspace with a GC method. The solvents used for extraction of TPH (C_6-C_{40}) include dichloromethane (DCM), DCM/acetone, pentane or pentane/acetone. Due to the lack of comparative data, a standard method is not currently available. In the UK, there is no legislative requirement as contaminated land assessment is based on a risk assessment process. In essence, this requires that testing be undertaken for potentially hazardous contaminants, which may be present on a particular site, as identified by a desk study of the site history. Within the UK, at present, the regulator, the Environment Agency, does not prescribe methods. This leads to the use of a wide variety of methods and conditions, and poor data comparability. The UK Environment Agency is presently producing performance standards for the analysis of contaminated soils and, as in the case of The Netherlands, during many personal communications the author has determined the need for substantial amounts of data on method comparisons prior to implementing standard methods[32-37]. As examples the assessment of data obtained by various extraction methods, detection methods, and quantification methods of TPH in contaminated soil needs to be clearly known prior to the implementation of a standard.

1.5.3 Assessments in Germany and Japan

In Germany, TPH is referred to as THC and usually analysed by IR. The legislators are currently introducing TPH and BTEX analysis by GC[34]. This suggests that Germany is in an

early stage of development with regards to such analysis. In Japan, the analysis (based only on oil and grease) is performed by gravimetric methods across various laboratories[35].

1.5.4 Assessment in USA

In the USA, each state regulates TPH and likewise sets its own analytical requirements[33]. The TPH working group[1] has kept track of some of the individual state's requirements, some of which are presented in the TPH working group documentation (volume 5)[21] and include Massachusetts, Alaska, Louisiana, North Carolina, and Michigan. The lack of standardisation in the USA as well deficiencies in the TPH analysis is clearly evident[21].

1.5.5 Assessment in Australia

The expansion of contaminated sites in Australia began with European settlement in the early 1800s and the subsequent increase in agricultural and industrial practices. The total number of contaminated sites in Australia is not accurately known[7]. According to 1995-1996 estimates by state environmental protection authorities, there are in excess of 30,000 sites in the most populous states of New South Wales (NSW) and Victoria (Vic) and approximately 400 in Tasmania (least populous state)[7]. The majority of these sites are contaminated by TPH. These statistics published by the Victorian State Environmental Protection Authority (VicEPA) have not been collected by the environmental agencies since 1998[36-37]. Therefore presently there are no compiled data on the number of existing contaminated sites, percentage proportion of total areas, the distribution of contamination and actual risks posed due to the existing contamination. Among the various classes of contaminated sites, the ones most frequently assessed include those that arise due to petroleum hydrocarbon contamination by land used for automobile service stations, refineries, gas works and fuel storage areas[8-9].

According to the Australian Institute of Petroleum (AIP), the Australian oil industry began the rationalisation of service station sites in the early 1970s[8]. At the time, there were about 20,000 operating service stations in the country. In 1994 there were about 9,000 service

stations estimated to be operating. According to the indicated trend, by the first half of 2002 there will be approximately 6,500 stations in operation. Among the decommissioned service station sites, those with elevated levels of petroleum products could pose unacceptable risk to human health and the environment, especially if the land use is changed from industrial to housing development[7-9]. Therefore, prior to re-development, planning authorities such as local councils require site assessment and remediation where necessary as part of the conditions of redevelopment approval[10]. Assessment of old service station sites should conform to the Australian and New Zealand Environmental and Conservation Council (ANZECC) and National Health and Medical Research Council (NH&MRC) draft guidelines[7] and the National Environmental Protection Measure (NEPM) for assessment of site contamination[10]. A major part of the assessment involves the testing of soils collected from these sites for BTEX and TPH contamination.

1.6 Australian Guidelines

The assessment of TPH and BTEX in Australia comes under the legislation of individual states. Each state or territory has its own environmental regulator, which implements the guidelines. The conclusions of a VicEPA study conducted on the analysis of TPH and BTEX are[11]:

(i) a wide range of analytical methods are used for the measurement of TPH and BTEX;

(ii) the type of data and sensitivity varies with each technique;

(iii) positive and negative biases are possible when necessary precautions are not taken; and

(iv) inter-laboratory and methodology variations can lead to widely differing assessments of site contamination.

Therefore, there is a need for a standardised procedure for TPH analysis[11]. Areas that need standardisation include:

(i) solvents such as acetone, DCM and methanol that are used in soil extractions for the analysis of BTEX and TPH;

(ii) extraction techniques such as sonication, Soxhlet, and tumbling;

(iii) clean-up techniques prior to the determination steps;

(iv) calibration standards that are used in the determination of such species as n-alkanes and aromatics;

(v) chromatogram baseline construction method for the determination and identification of the amount of TPH present; and

(vi) confirmation techniques such as GC coupled to MS.

The VicEPA review did not consider the use of an internal standard (IS) in the semi-volatile TPH (C_{10}-C_{36}) analysis because of the difficulty in determining such a peak using a GCFID among the range of peaks which are commonly found in TPH. The study described the unusual chromatographic profiles found in TPH analysis especially the semi-volatile fraction consisting of unresolved complex material (UCM). Due to the UCM most TPH peaks cannot be baseline separated. Therefore the IS can be lost or co-eluted with TPH components making the identification and detection very difficult by a GCFID analysis. Figure 1.6 contains a chromatographic profile of TPH containing the UCM, which includes an aggregation of components.

Contributing to the lack of standardisation across Australia is the fact that environmental protection is a state responsibility and each state has its own policy on site assessment and related measurements. The organisations tabulated in Table 1.3 have all published various soil criteria.

The ANZECC/NH&MRC have recognised the need to develop an Australian approach to the assessment and management of contaminated sites in the form of national guidelines[7]. The objectives of the ANZECC/NH&MRC guidelines are to provide a framework for the proper

assessment and management of contaminated sites. The framework is designed to ensure the implementation of standards for all contaminated sites and to provide assurance to the community that public health and environmental concerns are being addressed.

The guidelines comprise three parts:

(i) a policy document summarising the strategic framework for the assessment and management of contaminated sites;

(ii) a supporting document providing background information and methods for assessing and decontaminating potentially contaminated sites; and

(iii) recommended soil quality criteria. The long-term aim of the guidelines is to include information on specific levels similar to the Dutch criteria (A, B and C)[17] and types of contaminants.

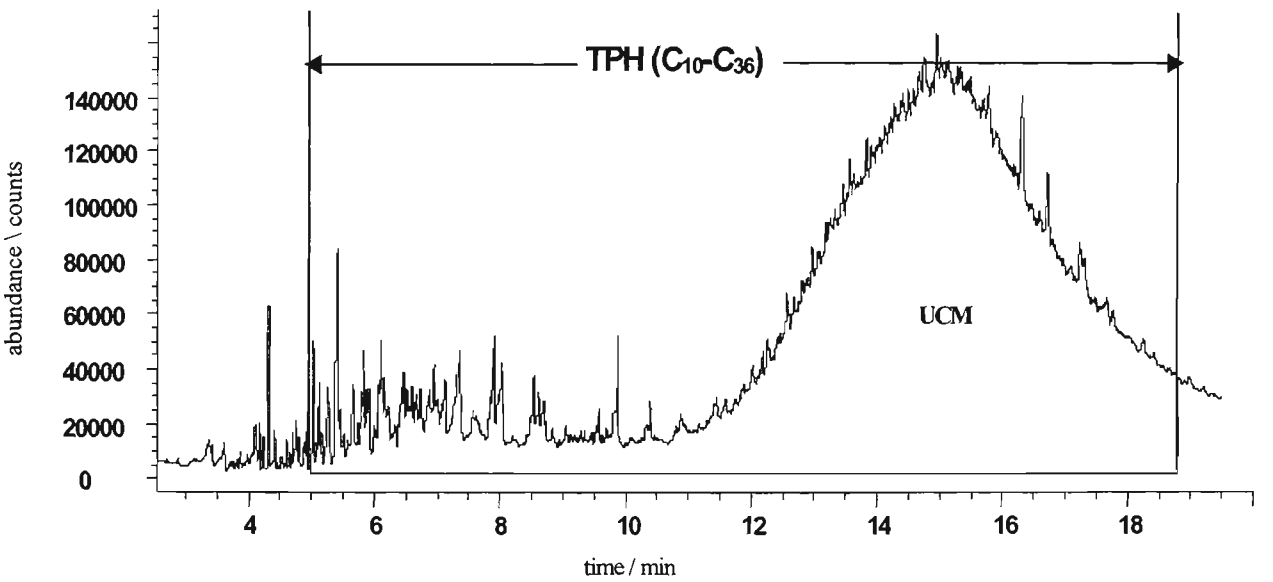

Figure 1.6: TPH chromatogram containing UCM.

The levels will include A level for Australian soils which best represent background concentrations; this being defined as the level of contaminants typically found in the locality away from a specific activity or site. Since A levels are regarded as background levels these should be achieved after the clean-up of a contaminated site. Classifications for action are presently being developed and these include B and C levels. The B level will represent an

investigation threshold. The C level will be used to classify those soils that require specific management strategies.

Current ANZECC/NH&MRC guideline values referring to BTEX and TPH are limited to values for benzene and toluene. Therefore, these guideline levels for BTEX and TPH analyses cannot be used comprehensively in their present form. Therefore similar to the Dutch criteria, the A, B and C levels for components such as the benzene, toluene, ethylbenzene, xylene and the TPH fractions (C_6-C_9, C_{10}-C_{14}, C_{15}-C_{28} and C_{29}-C_{36}) needs to be established urgently for application to Australian situations. The guidelines do not specify analytical methods and therefore a range of methods are used for TPH and BTEX analyses. This may lead to the possibility of variations in calibration standards used for the analysis, detection, and even the reporting procedures between different laboratories.

Table 1.3: Organisations involved in Australian site assessments.

Organisation	Document
New South Wales Environmental Protection Authority (NSWEPA)	Guidelines for Assessing Service Station Sites
VicEPA	Guidelines for Assessing Contaminated Sites
National Environmental Protection Council (NEPC)	Guidelines for Assessing Contaminated Sites
Queensland Department of Heritage (QLDDH)	Guidelines for Assessing Contaminated Sites
South Australian Environmental Protection Authority (SAEPA)	Guidelines for Assessing Contaminated Sites
Department of Environmental Protection Western Australia (DEPWA)	Guidelines for Assessing Contaminated Sites
National Association of Testing Authorities (NATA)	Accredits Laboratories and Methods Used for Testing
Australian Government Analytical Laboratories (AGAL)	Testing for TPH and BTEX,
National Analytical Reference Laboratories (NARL)	Reference Materials and Conducting Proficiency Studies
Commercial Laboratories	Analysis
Universities and Tertiary Institutions	Research and Development

1.6.1 Guidelines for Service Station and Distribution Depots

Guidelines for service station and distribution depots were prepared by a working group established by the AIP[9]. These guidelines are applicable to any oil industry site irrespective of ownership or occupancy, and include a policy statement that recommends procedures for identifying and managing contaminated sites. They do not replace statutory regulations, which vary between states. The guidelines state that the levels specified should be used as minimum levels and should be read in conjunction with the 1992 ANZECC/NH&MRC recommendations[7].

The AIP guidelines identify hydrocarbon contaminants and specify common products that are easily distinguished by hydrocarbon chain lengths. These are represented by gasoline TPH (C_6-C_9) and BTEX, distillates (C_{10}-C_{14}), fuel oil and lubricants (C_{15}-C_{28}) and asphalt and tars (>C_{28}) chains. This identification system is unique to service station and distribution depot guidelines. Although the BTEX components are included, the service station guidelines fail to consider the additional aromatic hydrocarbons found in gasoline, which may have significant toxicity. Furthermore, the guidelines do not specify the analytical techniques which should be employed for soil analysis thereby leaving open options in the selection of methods, which may generate variation in results.

1.6.2 Contaminated Site Guidelines for Service Stations

These guidelines were prepared by the NSWEPA in December 1994[8] for assessing and remediating service station sites in order to provide ongoing environmental protection and to minimise the risk to public health. The guidelines specify threshold concentrations in soils for "sensitive" land use. The volatile TPH fraction, C_6-C_9 and the BTEX components are designated relatively low threshold concentration values compared to TPH fractions between C_{10}-C_{14}. The guidelines define approximate ranges for petroleum hydrocarbon fractions i.e.

C_6-C_9 as petrol, C_{10}-C_{18} as kerosene, C_8-C_{21} as diesel, > C_{18} as lubricating oil. However, the recommended analytical methods fail to detail confirmation techniques that are critical for the determination.

The VicEPA survey indicates that current guidelines vary considerably in terms of standards. The guidelines are ambiguous and are open to interpretation especially in BTEX and TPH analytical methodology. They can function effectively only if implemented by a consistent, uniform and accurate set of analytical techniques. Similarly, the North American, Canadian and British guidelines have significant differences between different states or regions and these differ to Australian guidelines. For example, the measurement of TPH in North America is reported as either gasoline range organic (GRO) and diesel range organic (DRO) using calibration standards of reference gasoline and reference diesel. The Australian way of reporting TPH is by using normal alkane calibration standards and the concentration referred to as TPH (C_6-C_{36}). This in itself can be misleading unless the definition is changed because the total material extracted from the soil by the solvent is assumed to be TPH.

1.6.3 National Environmental Protection Measure

The National Environment Protection (Assessment of Site Contamination) Measure 1999 (NEPM) was established and published to standardise site assessment guidelines across Australia[10]. Schedule B of the measure contains ten sub-schedules numbered from B (1) to B (10). Sub-schedule B (1) covers the investigation levels for soil and ground water. It recommends the application of investigation levels for soil assessment for a particular site and proposed land use, on a site-specific basis. Thus professional judgement will necessarily form a part of the decision. Furthermore, soil assessments are to be carried out by determining health-based investigation levels (HILs) and ecologically-based investigation levels (EILs). For example, if the values for TPH based on NSWEPA criteria for a given site are exceeded, then an appropriate site-specific assessment is required. When soil concentrations exceed the

site-specific response levels, the actions will include informing landowners and users about the nature of contamination and applying appropriate site management plans, to affect large-scale remediation. Volatile contaminants such as BTEX in soil are considered as "complicated" due to their complex environmental interactions and the absence of a generally accepted model that can be used to determine maximum exposure levels.

The moisture content determination of a soil and the conversion of a contaminant concentration on a moisture-free basis are not discussed under the results reporting criteria. These details are included under the pre-treatment Sections 5.3.2 and 5.3.3.2 of the document. The quality assurance work conducted on a sample matrix by spiking a known concentration of TPH has only a limited value depending on the level of natural TPH contamination in the sample. When TPH is spiked (at the limit of reporting which is a relatively low concentration) into a soil sample heavily contaminated with TPH, the spiked amount will be completely masked by the gross contamination already present. Therefore matrix spikes will provide only a very limited amount of information unless testing is done on contaminant free soil or lightly contaminated soil. The NEPM discusses the confirmation of the TPH and BTEX by a second technique such as the GCMSD. These confirmatory techniques should be included in quality assurance protocols to minimise the possibility of false BTEX positives. Minimum reporting requirements on analytical results need to be clearly specified, to obtain uniformity across laboratories.

1.7 Characterisation of BTEX and TPH in Soil

Chi-Yuan Fan *et al.*[13] reviewed various analytical techniques available for the analysis of contaminated soils. The review considered the application of GCPID and GCFID for the analysis of TPH. The GCPID was used in determining the volatile components, especially the BTEX. The confirmation technique, which required the application of GCMSD, was not discussed in that study. The use of GCMSD in place of either GCFID or GCPID for the

confirmation of BTEX is important to avoid the inaccurate identification of the non-hydrocarbon components from the hydrocarbon components. The GCFID identifies components in a given sample extract only by retention time. The GCMSD has the advantage of identifying the specific ions in addition to the retention time. Additionally, a GCFID profile of a polychlorinated biphenyl (PCB) mixture and a GCFID profile of a weathered, mixed, petroleum hydrocarbon can be misidentified as TPH without a GCMSD confirmation using selected ions.

Xiang *et al.*[42] conducted a study on TPH and BTEX in gasoline and diesel contaminated soils by capillary GCMSD. Multiple groups of ions were monitored to obtain reliable data. The study did not consider the possible variations of responses by the GCMSD and the GCFID when the TPH standards and samples were analysed nor did it consider the possible variations in the concentrations that been determined. This variation between detector responses needs to be tested to determine if the concentrations of TPH from the two techniques differ significantly.

The Manchester Environmental Laboratory has published a method on the analysis of semi-volatile petroleum products in contaminated soil and water[39]. The method enables identification of the TPH by pattern matching of semi-volatile components and the quantification using various types of semi-volatile TPH mixtures. These mixtures included kerosene, diesel, jet fuels, fuel oil, lubricating oil, hydraulic fluids, mineral oils and insulating oils. The study attempts to identify the presence of these mixtures in unknown sample extracts and then quantify the concentrations using an IS. The IS is used to negate the uncertainty due to possible injection volume errors during the analysis of a batch of samples. The application of an IS in TPH analysis appears to be futile with a GCFID. Previous work carried out by Magore *et al.*[64] has shown the difficulty in identifying the IS among the peaks generated by TPH during GCFID analysis. Therefore, to apply the IS for TPH analysis it

requires a more complex detector system such as the GCMSD and compounds containing unique ions. The research carried out for this thesis avoided the use of IS with the GCFID but monitored the errors due to injection volume by measuring the response of a calibration standard frequently within a batch of analysis.

Characterisation of C_6 to C_{35} petroleum hydrocarbons in soil was conducted by Rhodes[38]. The method involved extraction, of the TPH with n-pentane and determination by GCFID. Interference by other organic compounds including vegetable and animal oils, organic acids, chlorinated hydrocarbons, phenols and phthalate esters were discussed in that study. Confirmation by the GCMSD was not used in that method. The identification and confirmation of the TPH in Rhodes paper is by matching the peak patterns of the unknown samples with the peak patterns of the known fuel oils. Standards such as kerosene and petrol were used as the calibration standards. However, the method does not resolve situations when the petroleum hydrocarbons are partly degraded or mixtures containing various fuel oils at unknown ratios (i.e. kerosene and diesel). The chromatograms of weathered diesel in Figure 1.4 demonstrate the difference between weathered and pure diesel. Therefore, using pure hydrocarbon products such as diesel, kerosene and petrol to confirm TPH is of limited value for soil which are contaminated by various TPH products over a period of time. This current study has used specific hydrocarbons of known concentrations as the calibration standards for most of the work.

Rhodes does not use the P&T technique for the sampling of the C_6-C_9 volatile fraction. Using the same extraction as for the C_{10}-C_{36} (semi-volatile) TPH fraction can cause substantial losses of the C_6-C_9 fraction due to the volatility of the components. This loss of volatile hydrocarbons will generate inaccurate data. The method uses pentane to extract TPH from contaminated soils. However, pentane is not efficient in removing all the TPH from the soil because the polarity variation between the moisture content in the soil and the pentane limits

the ability of pentane to reach the TPH within the soil. The study addresses such issues by determining changes in concentrations with changes in methods.

The Total Petroleum Hydrocarbon Working Group sponsored by the Association of American Railroads, BP Oil Company and the United States Air Force Armstrong Laboratory, Occupational Medicine Division, published a five-volume series consisting of TPH and BTEX research[2-3,5-6,21]. The first volume comments on the possible variations in concentrations with various analytical techniques. However, it does not recommend the use of GCMSD as a requirement to confirm TPH. The section relating to the GC resolution is of high significance to hydrocarbon analyses. This is due to petroleum being made up of many compounds each with its own set of isomers, especially those above the n-C_8. These compounds are known to be difficult to separate due to co-elution with components with similar retention times. The UCM are legitimately a part of the petroleum signal, and unless regulations specify otherwise, should be quantified. Quantifying UCM requires a baseline-to-baseline integration mode rather than a peak-to-peak integration mode. This series of books, although informative and interesting as an overall study of TPH, do not contain a critical assessment of analytical methods. Most Australian laboratories typically use the UCM in their calculation of TPH in Australia.

Nadim *et al.* (1997)[65] presented a comparative study of TPH from soil and water extracts using IR and GCFID. They extracted semi-volatile TPH contaminated soil with Freon-113 and DCM. The extracts were then analysed by IR and GCFID. For the GCFID study an IS was not applied and the identification of TPH was achieved by observing the peak pattern and relating it to a known TPH profile such as diesel. The calibration standards were normal alkanes. The conclusions of the study were that DCM is a better solvent than Freon–113 in extracting TPH, especially the heavier components. The GCFID results were more reliable than those achieved by IR. This was due to "outside interference" causing unacceptably

higher concentrations. The paper did not discuss reasons for excluding the IS or if there were any steps taken to compensate for the IS. The normal alkanes used as external standards in the study were not detailed by nominating the components and the concentration ranges.

Guerin, (1999)[66] conducted a number of comparison studies of PAH analysis in Australia and concluded that DCM/acetone (1:1, v/v) mix is a better solvent than hexane/acetone (3:1, v/v). Although the extraction was carried out for 48 h, that study did not specify the number of extraction cycles/h required to obtain the above result. Additionally, the study did not measure the optimum time required to obtain the maximum extraction which can be 4-8 hours. An extraction time of 48 h appeared to be somewhat higher and impractical for commercial testing requirements, which usually require faster turnover times. Additionally, Guerin's study did not specify the number of contaminated soils that were analysed although the extractions were conducted in duplicate.

The Guerin's study did not include alcohols, which are used as a common solvent in the extraction of lighter TPH fractions. The sonication extraction was not applied continuously over the 48 h period but intermittently for 2 min for every hour after the first 15 min sonication. Therefore, the extraction may have taken a longer time than necessary. The minimum power of the ultrasonic bath required to obtain the optimum extraction was not specified in that study. The clean-up technique used with hexane appears to be of concern due to the limited solubility or TPH and PAH in hexane. Additionally, the use of GCFID for the determination and confirmation of PAH is inadequate. To confirm individual components such as BTEX or PAH among the possible range of peaks commonly found in TPH extracts, GCMSD is essential. The study concludes that sonication extraction is a more effective technique than Soxhlet extraction. One of the reasons given is that during Soxhlet extraction there are possible losses of the more volatile PAH. However, this statement was not validated by multiple analysis of contaminated soil samples to overcome possible errors due to non-

homogeneity. The study does not state the required rate of extraction but mentions that the stronger binding of PAH requires good extraction efficiency to obtain good recoveries. The procedure used in monitoring surrogate spikes is not detailed. The paper discusses the possible presence of tar particles amongst the soil in the shape of balls, which can further limit homogenisation. However, the ways to achieve homogeneity in such situations are not discussed.

Work carried out by Vandegrift and Kampbell (1988)[67] on the analysis of JP-4 jet fuel concludes that acceptable recoveries were obtained for spiked, medium-grained sand for a number of hydrocarbons including 2-methylhexane, heptane, toluene, 3-methylheptane, octane, m/p-xylenes and a number of other volatile and semi-volatile hydrocarbons. Recoveries for benzene, ethyl benzene and o-xylene are not reported in the study. Additionally, there was no testing of clay-type soil, which is regarded to be more difficult for the recovery of hydrocarbons. No IS was included in this method and no vapour separation techniques, such as the static headspace or the P&T technique, were applied prior to the GCFID analysis to maximise the recovery of the volatile BTEX.

Roe and co-authors (1989)[68] published a study on manual headspace analysis of volatile aromatic compounds in gasoline from ground water and soil. The work does not discuss recovery rates or present any validation data on the method.

A study by Richards and Campbell (1998)[69] on the comparison of supercritical fluid extraction (SFE), Soxhlet and sonication methods for the determination of priority pollutants in soil concluded that among the 18 components of acid and base, neutral types tested, almost all the components produced higher recoveries by the Soxhlet extraction technique compared to the sonication extraction.

Trends in P&T was discussed in a paper authored by Abeel *et al.* (1994)[70]. The detailed explanation of various aspects and stages of the analysis using the complex P&T technique was informative but did not include application details for volatile TPH analysis.

Xie and co-workers (1999)[71] conducted a study on TPH quantification and interpretation in sediments by GCMSD, and compared the results with a rapid field method. It was found that the use of an IS produces reliable results but the paper does not discuss the need to use GCMSD in order to accurately identify the IS among the other components when present as a cluster of peaks. Further more, data obtained by the GCMSD and the relationship between the responses due to the calibration standards and the responses due to the sample components were not discussed.

The work conducted by Schwab *et al.* (1999)[72] on the extraction of petroleum hydrocarbons from soil included the extraction by mechanical shaking and comparing the results with Soxhlet extraction. However, the types of soil and the volatility of the TPH components present in the soil was not discussed. The conclusion of the work is that the shaking method appeared to produce comparable TPH concentrations to the Soxhlet extraction method. The analysis of TPH using GCFID included an IS. The technique used to identify the IS and the results obtained by using it were not specified.

Ilias (1992) investigated the isolation, identification and quantification of fuel contaminants in soil[73]. The method is claimed to work for a range of fuels from low to high boiling point. However, a major limitation of the method is its use of fuels such as petrol and kerosene as standards for the assessment of contamination levels in soil. Any given fuel, such as petrol, contains a group of hydrocarbons that are collectively called a "hydrocarbon profile". When fuels are exposed to the environment as a contaminant in soil, various physical, chemical and biochemical processes change the original profile and so it will not be comparable to the original profile of the material due to weathering as described in Section 1.4. It is therefore

possible to generate inaccurate identification and quantification if petrol and kerosene are used as standards. Figure 1.7 represents an example of a crude oil determined by the GCFID using a temperature program to efficiently elute the components[74].

A number of studies related to TPH have been undertaken at the Australian Government Analytical Laboratories (AGAL) to address the concerns highlighted by various state environmental authorities of Australia. The studies are still under review and they include investigations into topics included in Table 1.4.

Table 1.4: Studies undertaken at AGAL on TPH analysis

Topic	Study Aims	Results
Stability of BTEX in soil †	Assessment the losses during transport and storage.	Loss of BTEX was controlled using Teflon™ -lined screw caps.
Homogenisation ††	Determine the importance of homogenisation.	Variability of TPH concentrations were reduced down to 21-50% upon homogenisation.
Storage stability †††	Determine if there are substantial losses of BTEX within 8 days.	No substantial losses within 8 days.
Possible reasons for variation in TPH concentrations	Determine reasons for statistical variation in TPH concentrations among laboratories.	Difference in instrumentation and conditions. Baseline construction technique. Grouping of TPH. Integration technique. Calibration standards used.

† Losses of volatile petroleum components (BTEX) from types of environmental field sampling jars[75]. The results of this study suggest that jars with Teflon™-lined screw caps contain BTEX components and those with metal screw caps generate a 50% loss. The study was not extended to investigate the variations in losses due to variations in temperature, the variations in BTEX concentration with variation in holding times in the jars, or the way the jars were transported from the field to the laboratory;

†† The variability of laboratory sub-sampling by means of five soil samples contaminated with petroleum hydrocarbons. Homogenisation was achieved by stirring the soils with glass rods[76]. The results of the study show that the variability of TPH within sub-samples is reduced by 21-50% upon homogenisation. The study was limited to five contaminated soil samples and did not investigate the losses on spiked samples. Since many of the homogenisations were conducted on clean soil spiked with TPH, the possibility of naturally contaminated soils not being totally homogenised was not considered in this study;

††† The study of storage stability of unleaded petrol spiked into water and stored at 4 °C and 20 °C for eight-days showed that, within experimental error, there is no substantial losses[77].

‡ study of factors affecting the quantification of petroleum hydrocarbons using GCFID which found that methodology remains un-standardised and therefore is subject to the discretion of the analyst[78].

‡‡ the variations in results between laboratories which are due to differences in instrumentation and conditions, the way the baselines are constructed, the way the TPH groups are integrated, and the types of calibration standards used. An important factor, which was not investigated during the AGAL study, is the possible variation in TPH (C_6-C_9) during sub-sampling for soil, due to limitations posed by the presence of volatile components.

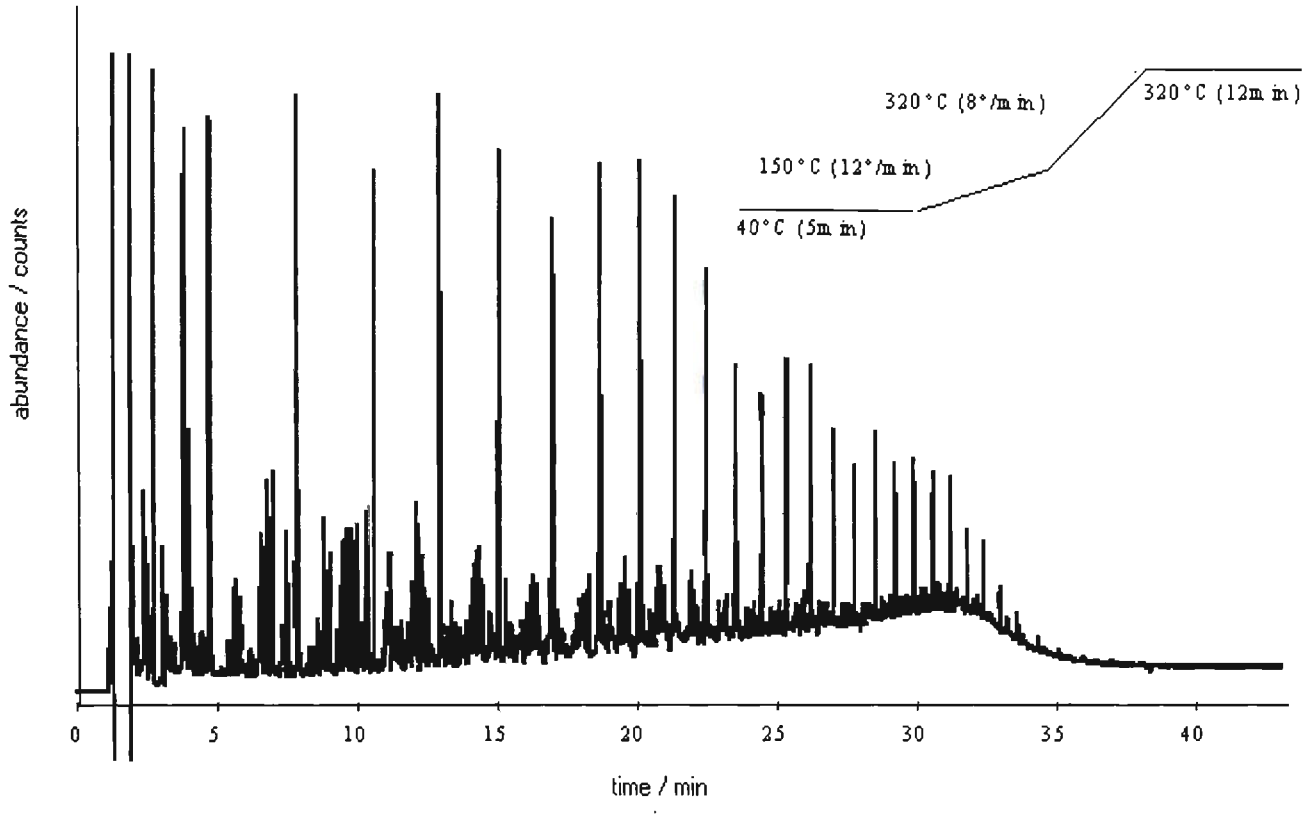

Figure 1.7: Example of a crude oil chromatogram with a temperature program (Worral, 1996)[77].

It has been noted that various studies presented in this review shoes contradictions in findings for example Guerin[66] concludes that the sonication is more efficient to soxhlet extraction, Richard and Cambell[69] states the oppersit from Guerin, Schwabb[72] demonstrates that shaking is similar to soxhlet and no reports are presented between the GCMSD and the GCFID determinations.

1.7.1 International Standards Technical Committee

The International Standards Organisation Technical Committee (ISO/TC 190) consists of members from Germany, Australia, The Netherlands, Japan, Norway, France, Finland and the UK. This committee is currently setting a standard method for mineral oil (TPH) analysis. The committee met and discussed the first draft (16703 ISO/TC190/SC3/WG6) at the meeting of working group 6 in Brisbane, Australia in November 2000[63].

The method defined TPH as the total peak area between n-C_{10} and n-C_{40}. According to this method the soil extracts are to be cleaned-up using Florasil™ to remove polar material prior to GCFID analysis. This ISO method is applicable to mineral oil contents between 100-10,000 mg/kg soil expressed as dry matter. The extraction of soil in this method is based on sonication or by shaking, then removing the polar components, which are regarded as non-TPH, using Florasil™. The mineral oil content is determined by GCFID. Soxhlet extraction is not used. Although n-C_{10} and n-C_{40} hydrocarbons were suggested to be used as an IS, they were used as TPH components to determine the start and the end of the TPH fraction which is referred to as the "boundary". It appears that this step was taken to avoid possible errors due to incorrect identification of the sample components with the internal standards.

The low solubility of the n-C_{40} will contribute to errors if care is not taken in determining the required conditions to solubilise the alkane before the analysis. If the n-C_{40} is used as an IS, it could affect the calculation of the concentration due to its partial solubility at room temperature. Also the clean-up technique is highly likely to remove PAHs which are relatively polar compared to aliphatic components. Similar clean-up techniques are used in USEPA methods to separate aliphatic hydrocarbons from the aromatic hydrocarbons[78]. This issue requires investigation to avoid removing the hydrocarbons with polar, non-hydrocarbon material. Compounds which are non-polar and still non-hydrocarbons such as chlorinated material will not be separated from the hydrocarbons by this clean-up technique.

1.7.2 Standards Australia Working Group

Standards Australia is an organisation which co-ordinates the establishment of standard methods for analytical testing in Australia. Working group CH/8/2/2 was set up in 1997 to formulate methods for the analysis of TPH (C_6-C_{36}). The members included most of the commercial laboratories of Australia conducting TPH and BTEX analysis, Australian environmental consultants, NATA and VicEPA. The need for a standard method is due to

inconsistent laboratory methods and practices that are driven by economic considerations rather than technical requirements. The members agreed to create a benchmark method, one of the investigations conducted for this study was the application of an IS to check the consistency of the analytical steps including the injection volume, instrument sensitivity and retention times for chromatographic systems. The uncertainty in identification and confirmation of an IS by the GCFID during the TPH analysis was a major drawback. There are a number of published TPH methods, which do not include an IS which were discussed previously in this chapter. Although some methods propose the use of hydrocarbons as IS they can provide misleading information especially if the IS co-elutes with material from the sample. This can be a common occurrence since the analyst does not know which type of material is present in the sample prior to the analysis. Therefore, to include an IS it is necessary to conduct a preliminary screening to investigate the region where the IS elutes and determine if this region is free of natural contamination by TPH. Using such procedures whilst conducting TPH analysis is impractical both in terms of time and cost. One way of addressing this issue is to use a GCMSD detector to monitor the ions of the IS. A radio-labelled IS such as acenaphthene-d_{10}, chrysene-d_{12} and perylene-d_{12} can be effectively used in such situations. Another way to address the problem is to avoid the use of an IS but use one of the calibration standards more frequently (eg. one in every four GCFID injections). Using this procedure the analyst can determine the response of two adjacent calibration standards and monitor if they hold within 10% which can be regarded to be well within experimental limits. Investigations conducted to determine the applicability of coronene as an IS were carried out by the committee[12]. Coronene is a high molecular weight PAH, which is not commonly found in TPH. During this investigation it was demonstrated that the applicability of an IS with the GCFID is inconsistent due to the wide range of TPH peaks and UCM elution. We are unaware as to the current status of the committee.

1.8 Significance of this Study

This research was designed to investigate reliable, economically viable and cost-effective techniques for TPH measurements in soil, giving consideration to optimum analysis time. Since no standard methods are currently implementsed to measure TPH and BTEX, the investigations were carried out after considering and reviewing a range of techniques. It is clear that very few comprehensive studies of the area of TPH analysis have been undertaken. To date only a few publications relating to TPH are to be found in the international literature. This research intends to assist in designing and conducting experiments to bridge gaps in areas that lacks information in TPH analysis. It will provide a better interpretation of data with the emphasis on the following areas of TPH analysis: field and laboratory measurements; the effects of using polar solvents to penetrate wet soil; the extraction of TPH from contaminated clay soils using Soxhlet and sonication extractions; the investigation and optimisation of TPH extraction conditions to improve efficiency; the development of a method to analyse volatile TPH by P&T; the comparison of volatile TPH concentrations determined by GCFID and GCMSD; and the comparison of three analytical techniques used for determining BTEX concentration in contaminated soil. By understanding the limitations of each procedure, the scientist can interpret the results with a higher degree of confidence. This, in turn, will result in a cleaner and safer environment. Additionally the outcomes of the study will also provide a more reliable basis for the improvement and development of appropriate future guidelines, leading to a cleaner environment.

Research carried-out in this thesis is documented in Chapters 2-9 which consists of a number of methods used in TPH analysis. Specific areas of research include comparison of a number of extraction and analysis methods, propose a method for the simultaneous analysis of BTEX and TPH (C_6-C_9), analysis of TPH contaminated soils by a range of methods and demonstrate data compatibility by evaluating data using various statistical techniques, demonstrate the responses between GCFID against the GCMSD for similar standards, specify procedures

taken to compensate for omitting IS when the GCFID is used, optimum extraction time studies, evaluate BTEX analysis by comparing various methods, comparison studies to overcome variations due to limited homogeneity in soil, assessment of static headspace against the P&T techniques, comparison of laboratory and field measurements used for volatile TPH measurements.

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Chapter Two: Comparison of Field and Laboratory Measurements for Measuring BTEX

2.1. Introduction

The first study in this series involves the investigation of field measurements with the corresponding laboratory measurements of volatile TPH components. This chapter therefore will examine a number of aspects of an initial stages of a TPH measurement which will include the sampling. According to the NEPM 1999 of Australia, "The appropriate use of investigation levels is an important component in the assessment of existing contaminated sites" and "Owners and occupiers of sites on which potentially contaminating activities are occurring are subject to the environmental protection legislation applying in each jurisdiction"[1]. In other words, to prepare for the transfer of title of a property, the owner must ensure that the condition of the property meets the relevant legislated criteria for the intended future use of that property[1-10]. The NEPM are based on the demonstrated toxicological properties of a range of volatile organic contaminants. For example, petrol contains a number of toxic components including benzene and toluene[11-15]. Such legislative requirements have spurred property owners in Australia and in many other countries around the world to seek cost-effective methods for assessing the impact of their activities upon the environment[1-10].

The NEPM also states that "Accurate data collection is the foundation for acceptable assessment of health and environmental risks associated with site contamination"[1]. When conducting an assessment of soil suspected to be contaminated by volatile or semi-volatile hydrocarbons, the challenge is to accurately quantify the composition, concentration and extent of the contamination that is present in the soil and to minimise the costs involved in the assessment. The recommended procedure is to conduct an initial assessment by sampling soil-gas concentrations at various locations on the site[16]. Usually, this involves the penetration of a vapour extraction probe into soil samples. Gas from each sample is extracted through the probe and analysed using an organic vapour analyser to determine the presence and the approximate concentration of hydrocarbon contamination at that location. The results

of this initial assessment are then used to determine the best locations for collecting representative soil samples for subsequent more rigorous analysis. A survey of twenty environmental consultants across Australia confirmed that hand-held photoionization detectors (HHPIDs) are in common use for such assessments. Such detectors measure, display and record the concentration of airborne photoionizable gases and vapours.

HHPID instruments are sensitive to a wide range of organic vapours. They are intended to cost-effectively screen soil with minimal disturbance, whilst ensuring that samples that best represent the condition of the soil are submitted for laboratory analysis. In particular, site assessors frequently use HHPIDs to measure relative concentrations of benzene, toluene, ethyl benzene and xylenes (BTEX). A limitation of this device is its variable sensitivity to factors in the soil and the environment, and its restricted range. Anecdotally, HHPID field measurements are also considered to show poor correlation with corresponding laboratory measurements. However, as a result of the drive to reduce the cost of quantifying the extent of soil contamination, there is an increasing tendency towards reliance on field measurements alone, with a decreased use of laboratory analysis and very limited legal requirements. An expectation has evolved on the part of property owners that, for a given sample, there should be a direct correlation between the measurement of a hydrocarbon concentration in the field and the corresponding laboratory measurement. While such an expectation would, on the face of it, seem justified, it is not surprising that such a direct correlation is problematic, due to the complexities associated with soil-gas concentration measurements[16]. Factors that may influence the correlation of field and laboratory data include weather conditions in the field, sampling procedures and sample characteristics (e.g. soil type, homogeneity and moisture content), handling and transportation factors (e.g. time between sampling and measurement), variations in field and laboratory protocols and the experience and expertise of personnel[17-22].

There are a number of laboratory methods specified by the United States Environmental Protection Agency (USEPA) Office of Solid Waste for determining BTEX components in soil[23-27]. Two of the methods frequently used are solvent extraction followed by purge and trap gas chromatography with detection by mass spectrometry (P&T/GCMSD)[27] and headspace analysis/GCMSD[24]. In the first method, hydrocarbon mixtures such as petrol are extracted from soil using a solvent (e.g. methanol) by mechanically shaking or sonicating. A portion of the extract is diluted in water, purged and trapped (P&T) to concentrate, and the compounds are then deposited onto an absorbent material and analysed by GCMSD[24,27]. Samples containing heavy oils, surfactants and relatively high analyte concentrations (i.e. 100 mg/L or above) can contaminate the trap if proper steps are not implemented. The headspace analysis method, recommended by the USEPA as a screening method for hydrocarbon analysis, is applied to soils by placing a sample in a closed vessel, maintaining sufficient room to allow the gas to expand out of the soil, whilst heating the vessel to drive the volatile components into the gas phase[24]. The potential for instrument contamination is minimised by this method as only the volatile compounds enter the GC. In Australia, as well as in many other countries, volatile hydrocarbons are frequently analysed in the laboratory using either P&T or headspace methods as described above. Additionally, soils may be extracted using a solvent such as dichloromethane (DCM) and the extract analysed by a GC coupled to a flame-ionisation detector (FID)[28]. These analytical techniques vary between laboratories and are usually chosen by the client, the consultant or the regulatory authority, with no specific guidelines directing a particular method.

The goal of this study was to explore quality of the data when BTEX measurements from a HHPID are compared to the corresponding laboratory data. HHPID data from case studies (real field measurements) and from "simulated" field measurements have been used. In the former experiments, data from three different case studies were examined. These represent soil assessments carried out by a single environmental consultancy at three different locations

in Australia. The corresponding laboratory analyses were carried out at three independent laboratories where one or more of the above, frequently used, analytical techniques have been employed. In the latter experiments, various characteristics of the HHPID were investigated using simulated field samples; namely, BTEX-spiked water or soil. These experiments were performed under controlled laboratory conditions. The laboratory monitoring technique used in all of the above studies was headspace/GCMSD. Specifically, these studies include investigations into the linearity and sensitivity of HHPID response to spiked BTEX levels in pure water, dry sandy loam, dry silt and moist silt; the time dependency of HHPID response; and a comparison of the responses towards equivalent concentrations of BTEX and benzene in sandy loam. Water, silt and sandy loam were chosen for the simulated field experiments to provide a variation in relative pore space, that could affect VOC vapour release[16]. Thus, water was chosen because it has negligible pore space, silt because the pore space is relatively uniform throughout the sample and sandy loam because the pore space is usually not uniform throughout the sample.

2.2. Experimental Procedures

2.2.1 Materials, Reagents and Sample Preparation

Double distilled water, suitable for trace organic analysis, was used throughout. Certified grade (>99.98% pure) BTEX components were obtained from Ultra Scientific, Australia. Mixed BTEX standards were prepared from the individual components at a range of concentrations in double distilled water; namely 0.6, 1.2, 3.0, 6.0, 12, 30, and 60 mg/L. These mixtures were held at 4 °C for 1 h to maintain stability and to minimise evaporative loss. Premium grade silt of 30/60 mesh was washed in double distilled water, oven dried at 104 °C and tumbled to ensure homogeneity. The sandy loam (containing 15.4% w/w moisture[29-30]) was dried and homogenized in a similar way. A portion of the homogenized silt was deactivated (to reduce the available active sites) by the addition of 10% by weight of double

distilled water. Both the dry and the moisturized silt were spiked in 125 g lots at 1.2 and 6 mg/kg from an aqueous standard stock solution of 10 mg/L BTEX. The sandy loam was spiked in 125 g lots at 30, 70 and 170 mg/kg from an aqueous standard stock solution of 100 mg/L BTEX.

Measurements were carried out using a brand of HHPID that is in common use in Australia. Preliminary tests on this instrument confirmed a linear detector response of up to 500 mg/kg BTEX. For this reason, all laboratory experiments were designed to be within this range. For HHPID measurements, a 5.0 ml sample of spiked water or a 5.0 g sample of spiked soil was placed in a 20 ml glass headspace vial with a Teflon™ sleeve, an aluminium crimp top and an aluminium foil diaphragm. The vial was then heated in a water bath to 60 °C for approx. 10 min. Following the sample preparation, the cap was removed from the vial, and the PID probe inserted into the jar through the aluminium foil. HHPID readings were recorded until a decline in the concentration occurred. The maximum reading was recorded in ppm (benzene equivalent).

All spiked samples were satisfactorily monitored by headspace/GCMSD. A Perkin-Elmer HS-40 static headspace analyser was used along with method 5021[24]. A sampling protocol analogous to that described previously for the HHPID measurements was used (with 5.0 ml of saturated $CaCl_2$ solution being added to each soil sample). The samples were subsequently analysed using a Hewlett Packard 5970, Series 2, GCMSD according to the specifications of USEPA method 8260B[27]. The chromatographic peaks were identified by comparing the retention times of the BTEX components present in the calibration standard against the retention times of the components of the sample. Confirmation of each of the detected components was achieved by reference to the mass spectra database. Standards for the calibration of the headspace/GCMSD were prepared using the purity-known individual BTEX components weighed into a 100 ml calibrated standard flask and diluted with nanograde

methanol to obtain a 100,000 mg/L original stock. This was further diluted with nanograde methanol to obtain secondary stock solutions of 10,000 and 1000 mg/L. A mixture of internal standards consisting of dibromofluoromethane, toluene-d_8 and *4*-bromofluormethane (each at 50 mg/L) was applied to every analytical sample. Calibration of the system was carried out using 5.0 g of clean soil sample inside a 20 ml headspace vial, mixed with 5.0 ml of saturated $CaCl_2$ solution[31- 32]. Each vial was spiked with 50 µl of the internal standard mixture. Calibration levels of 0.2 mg/kg, 2.0 mg/kg and 20 mg/kg were achieved by spiking with 10 µl of the 1000, 10,000, and 100,000 mg/L BTEX stock solutions respectively. A reagent blank, in the absence of the BTEX standard, was used as the zero in the calibration curve. Analyses conducted in water used equivalent amounts to those used in the soil analyses.

2.3. Results and Discussion

2.3.1 Case Studies - Monitoring of HHPID Field Data by Laboratory Analysis

Sampling for the case studies were carried out in 125 mL glass jars filled to the top with soil collected from a hand auger from the pre-selected locations by the field scientist. Comparative data from the three case studies are presented in Table 2.1. The data have been presented in tabulated form because the correlations are considered to be too poor to be presented graphically. This is a rather disturbing outcome and highlights the problems associated with the reliability of field data. Specifically, for Case Study 1, these results were reported at the conclusion of a project that involved validation of soil decontamination activities on a property in Melbourne, Australia. The primarily clay soil at this property was contaminated predominantly with petrol. Soil samples analysed in the field using a HHPID produced measurements ranging from non-detect to 1390 ppm (benzene equivalent). The same soil samples tested in the laboratory produced results ranging from non-detect to 10 mg/kg. In this case, there is obviously no correlation between the HHPID measurements and the laboratory measurements. Indeed, the sample yielding the highest field measurement of

1390 ppm yielded a non-detect measurement in the laboratory. For Case Study 2, the results were reported at the conclusion of a project that also involved a land contamination investigation conducted in Melbourne, Australia. The primarily clay soil at this property was also contaminated predominantly with petrol. In this case, soil samples analysed in the field using a HHPID produced measurements ranging from non-detect to 2370 ppm.

Table 2.1: A Comparison between HHPID field data and the corresponding laboratory measurements for three different case studies involving the analysis of BTEX in soil.

Case Study 1			Case Study 2			Case Study 3		
Sample No	**PID Measurement (ppm)**	**Laboratory Measurement (mg/kg)**	**Sample No**	**PID Measurement (ppm)**	**Laboratory Measurement (mg/kg)**	**Sample No**	**PID Measurement (ppm)**	**Laboratory Measurement (mg/kg)**
1-6	0	0	1-12	0	0	1-4	Off Scale	0
7-9	0	0.1-0.2	13-32	5-450	0	5-14	Off Scale	0.6-34
10-20	10-1390	0	33	1190	0.1	15-18	130-1570	0
21-23	5-160	0.2	34-38	50-560	0.3	19-20	100-110	0.8
24-25	100	0.04-0.6	39-43	150-890	1.2	21-22	10-920	1.3
26-27	35-40	10	40-42	440-1310	2.6	23	10	1.5
28	350	0.6	43-47	40-1310	5.7	24	120	6.2
-	-	-	48	2010	14	25	110	6.7
-	-	-	49	2370	17	26-27	190	12.7-37
-	-	-	50	1450	37	-	-	-
-	-	-	51-52	895-2050	170	-	-	-

Note; Zero values represent non-detect.

The same soil samples tested in the laboratory produced results ranging from non-detect to 170 mg/kg. In this case, although the higher HHPID values tended to correspond to the higher laboratory results, there is clearly no correlation. These results reflect the outcome for the previous case study, with many false positive readings suggested by the PID values. For Case Study 3, the results are from soil samples reported at the conclusion of a project that involved a property in Melbourne, Australia, containing a silt-clay soil contaminated with a mixture of chemicals including phenol, trichloroethene (TCE), and benzene. Here, soil samples analysed in the field using a hand-held PID produced measurements ranging from non-detect to off-scale; the specified instrument range being 2500 ppm (benzene equivalent). The same soil samples tested in the laboratory produced concentrations ranging from non-detect to 34 mg/kg. As with the previous studies there is clearly no correlation between the HHPID and the laboratory data, and again there is a preponderance of false positives and inflated values.

The above three case studies illustrate the danger associated with relying too heavily on HHPID field measurements to quantify the amount of hydrocarbon contamination in soil, or even to confirm or rule out the presence of contamination. It is likely that the lack of correlation of the field and laboratory data may have been the result of a number of factors associated with outdoor sampling, most notably the weather. This study goes on to investigate how HHPID and laboratory data might correlate when field variables such as temperature extremes, humidity and wind are removed. Consequently, "simulated" field experiments were conducted and monitored as follows.

2.3.2 Linearity and Sensitivity of HHPID Response in Pure Water and Moisture-Free Sandy Loam

Water samples spiked with BTEX were prepared in bulk at 0.0, 0.6, 1.2, 3.0, 6.0, 12, 30 and 60 mg/L and stored at 4 °C for 2 h prior to analysis. Sub-samples were then taken for headspace/GCMSD analysis [30-36] and subsequent HHPID measurements. Appendix 2.6.1 and Figure 2.1 shows a linearity of detector response up to 60 mg/L and good agreement between the headspace/GCMSD readings and the expected (spiked) concentrations. This experiment serves as a check on the monitoring method. However, the GCMSD readings are slight underestimates of the spiked levels, probably due to evaporative loss. In spite of this, the monitoring method is considered to be satisfactory.

Figure 2.2 confirms linearity of response up to 60 mg/L when using the HHPID to measure the spiked samples. However, it should be noted that the HHPID readings have to be scaled down by a factor of ~34 (the slope of the response line) in order to reflect the real level of BTEX present. The data is shown in Appendix 2.6.2. Therefore, given the observed linearity of response, this outcome suggests that the actual concentration may be obtained from the HHPID measurement by the application of an "instrumental" or scaling factor. To determine whether this factor remains constant when the conditions of measurement change, a similar experiment was carried out where HHPID measurements were taken from samples of moisture-free sandy loam spiked at 30, 61 and 170 mg/kg with BTEX. The spiked concentrations were also satisfactorily monitored by GCMSD. Figure 2.3 confirms linearity of response up to 170 mg/l but, in this case, the HHPID measurements have to be scaled down by a factor of ~4.9 in order to reflect the spiked concentrations. The data is shown in Appendix 2.6.3. Therefore we conclude that the "instrumental factor" is indeed dependent on the conditions.

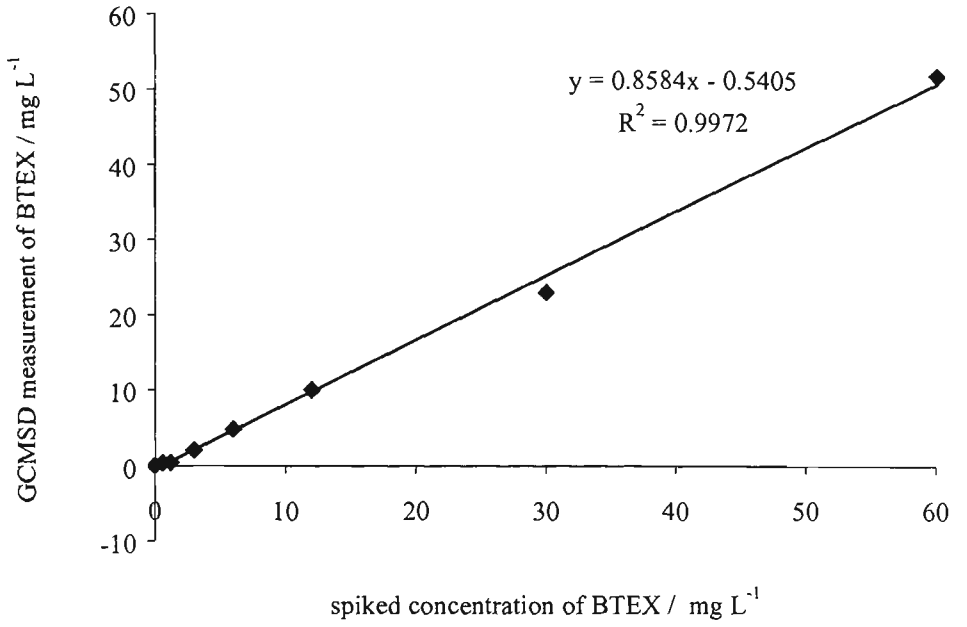

Figure 2.1: Headspace/GCMSD determination of BTEX-spiked water samples.

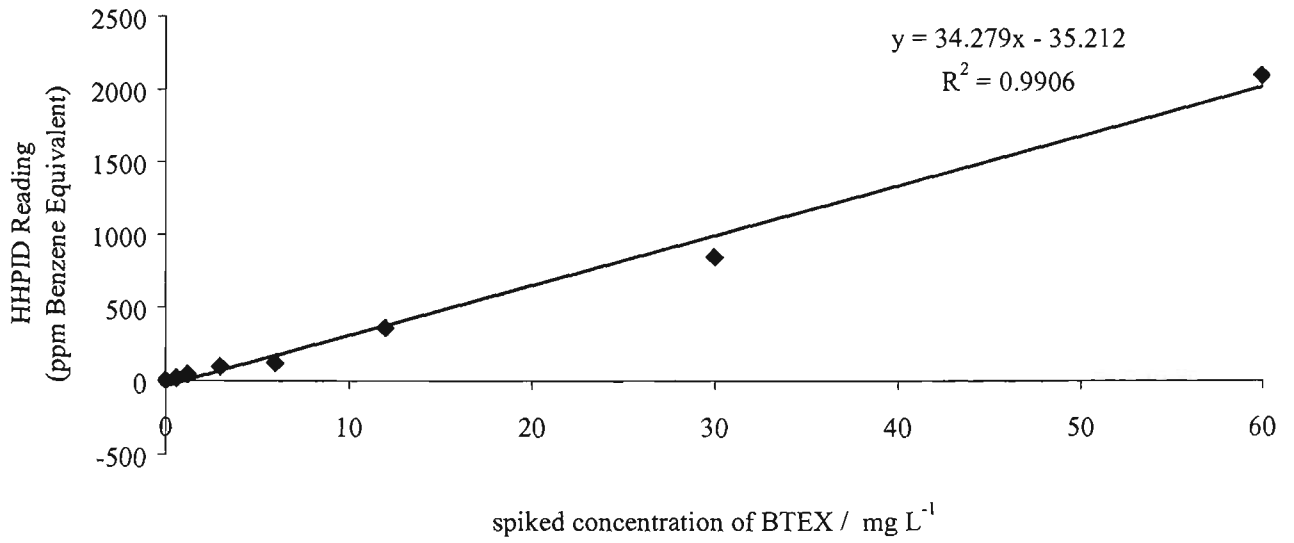

Figure 2.2: HHPID determination of BTEX-spiked water samples.

The above experiment suggests that the presence of water might have some amplification effect on the HHPID response. This notion has been explored further in the following experiment.

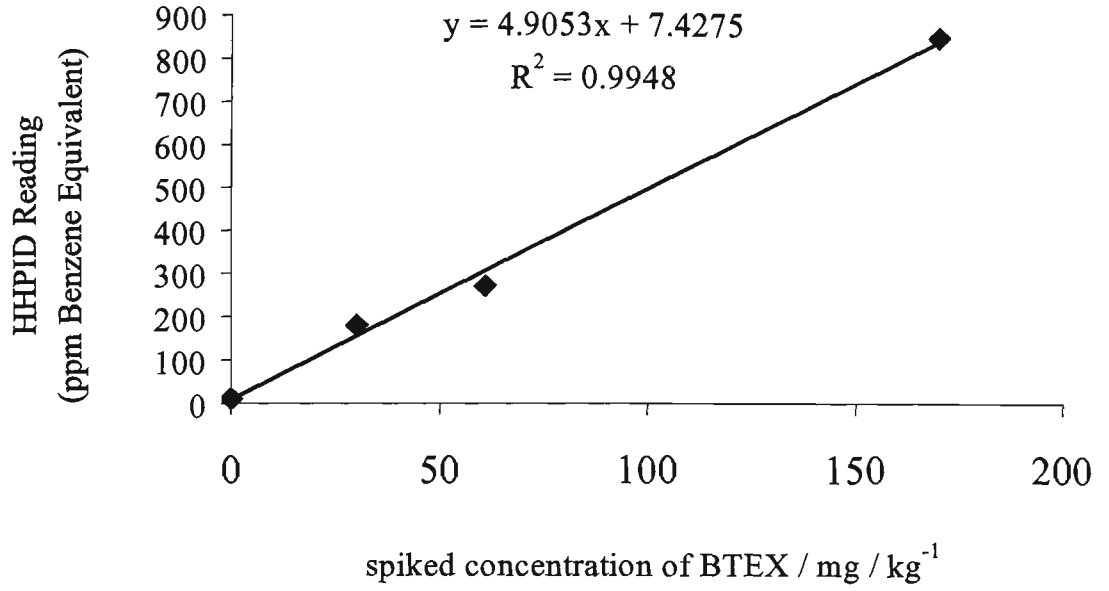

Figure 2.3: HHPID Determination of BTEX-spiked Sandy Loam.

2.3.3 The Effect of Moisture on HHPID Response

Clean silt was oven dried at 104 °C for 18 h. Blank HHPID measurements on the moisture-free silt confirmed non-detect readings. Moisture was applied to silt samples by the addition of 10% water by weight. The moisture-free and moisturised samples were both spiked in duplicate with 1.2 and 6.0 mg/kg of BTEX. The spiked concentrations were also satisfactorily monitored by GCMSD. Figure 2.4 depicts the comparative HHPID responses and the data shown in Appendix 2.6.4 and 2.6.5.

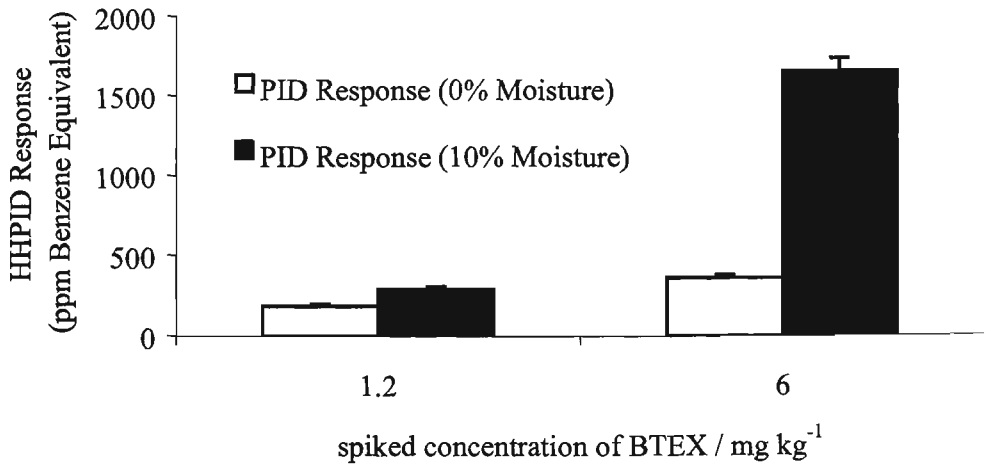

Figure 2.4: Comparative HHPID response towards BTEX-spiked silt of different moisture contents.

The results presented in Figure 2.4 indicate that the silt containing 10% moisture produced significantly higher HHPID readings than the same concentration with no moisture present. This outcome does suggest that water can amplify the HHPID response. However, there also appears to be other factors that might contribute to the sensitivity of response under various conditions. The data of Figure 2.4 may be represented as response lines so as to extract the slopes, Figure 2.5.

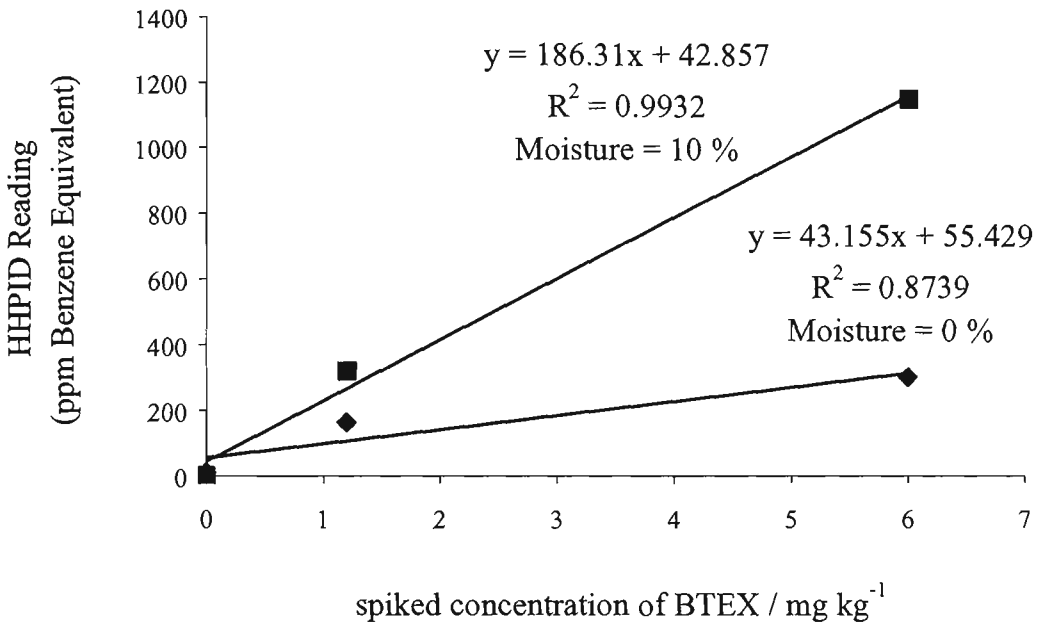

Figure 2.5: HHPID measurements of BTEX-spiked silt at different moisture contents.

The slopes of these lines represent the sensitivity of the HHPID measurement(s). It may be seen that these values are quite different, not only from each other, but also from the slopes obtained in Figures 2.2 and 2.3. These data are summarised in Table 2.2. This suggests that, under controlled conditions, the linearity of response is maintained for a variety of matrices and moisture contents but the sensitivity of the response depends very much on the particular combination of conditions. However, for a given set of conditions the response may be related to the actual BTEX level by an established "instrumental" or scaling factor.

Table 2.2: A comparison of the slopes of four different response curves for HHPID measurements of BTEX under different matrix and moisture conditions.

Matrix	Slope
BTEX-spiked water	34.279
BTEX-spiked sandy loam	4.9053
BTEX-spiked silt with 0% moisture	43.155
BTEX-spiked silt with 10 % moisture	186.31

2.3.4 Time Dependency of HHPID Response

Potential for VOC loss from samples during transport from the field to the laboratory, this study was conducted to assess HHPID response over time. The analyses were conducted on water samples spiked with BTEX, prepared in bulk at 0.0, 0.6, 1.2, 3.0, 6.0, 12 and 30 mg/L and stored at 4 °C prior to analysis. The first set of samples were equilibrated to ambient temperature, analysed immediately in quadruplicate, and the mean results were recorded. The second set of samples was also analysed in quadruplicate after a delay of 1.5 h and the mean results were recorded. Figure 2.6 shows the comparative histograms at each concentration. Although this appears to show an overall reduction in response over time, a two-tailed t-test[36] on the data shown in Appendix 2.6.6 indicated that this was not significant at the 95% probability level ($t_{calculated}$ = 2.14, $t_{critical}$ = 2.36). Further studies need to be carried out for time intervals longer than 1.5 h in order to ascertain when VOC loss becomes significant. Although this appears to show an overall reduction in response over time, a two-tailed t-test on the data indicated that this was not significant at the 95% probability level ($t_{calculated}$ = 2.14,

$t_{critical}$ = 2.36)[35-36]. Further studies need to be carried out for time intervals longer than 1.5 h in order to ascertain when VOC loss becomes significant.

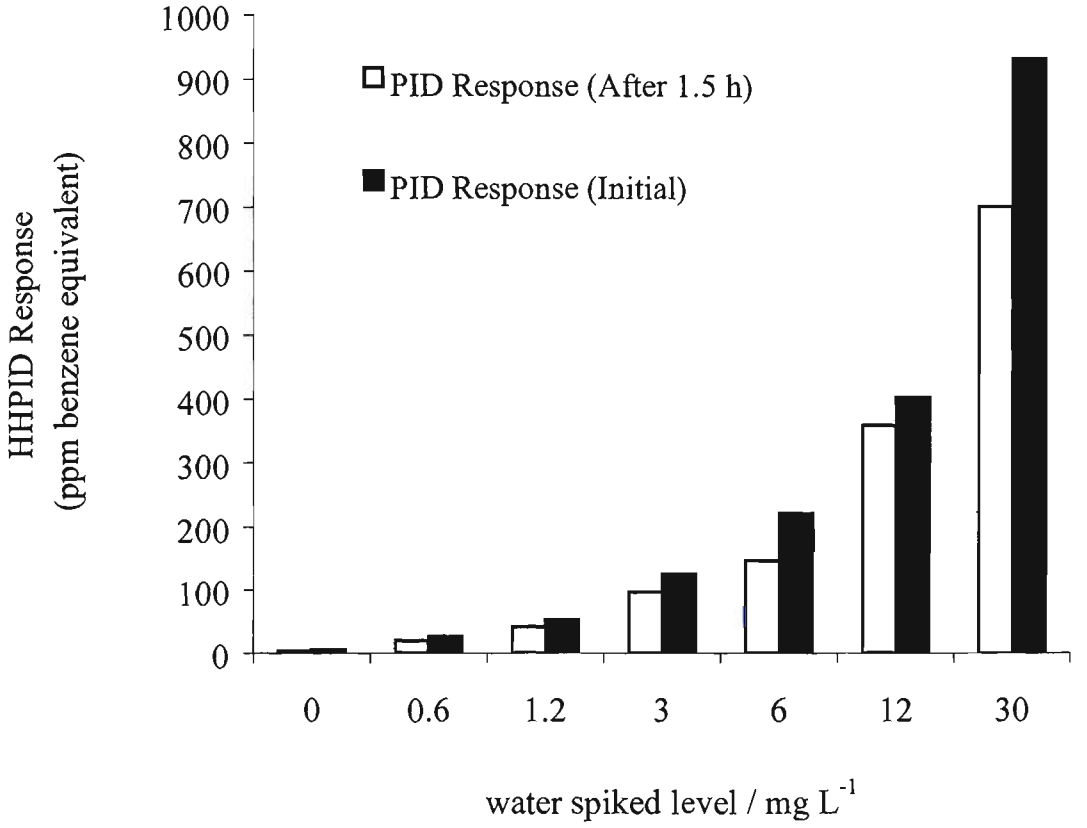

Figure 2.6: A comparison between HHPID measurements of BTEX-spiked water samples taken 1.5 h apart.

2.3.5 Effect of BTEX Mixture Component Interactions on HHPID Response

This study was conducted to investigate the effect due to multiple contaminants on HHPID measurements. The following results were obtained from analyses conducted on sandy loam spiked with 100 mg/kg BTEX as 6 replicates and 100 mg/kg benzene as 6 replicates. The HHPID measurement obtained for neat benzene was off-scale (>2,500 ppm) while the results of the sample spiked with BTEX was below 1000 ppm. This suggests that the presence of multiple contaminants in a sample might affect the rate of release of VOC vapour, although more detailed investigations into this phenomenon are warranted.

2.4. Conclusion

This study supports the widely held concern that field data from HHPID measurements, as currently reported by typical commercial operators, cannot be relied upon to reflect the true levels of VOC in soil. Our investigations would suggest that, even for simple screening, caution should be exercised especially in the light of the large number of exaggerated readings and false positives that were found. There are a number of factors that could influence both the linearity of response and the reliability of readings in the field. These include vagaries of weather, sampling procedures and sample characteristics (e.g. soil type, homogeneity and moisture content), handling and transportation factors (e.g. time between sampling and measurement), variations in field and laboratory protocols and the experience and expertise of personnel. An attempt was made to address some of these issues by carrying out controlled experiments in the laboratory (simulated field experiments) where HHPID measurements were made under a variety of conditions, monitored by headspace GCMSD. It was found that, although a good linearity of response can be achieved under various conditions of moisture and matrix, the sensitivity of response is very much dependent upon the particular combination of conditions. However, it is clear that, given a linearity of response, the actual concentration may be obtained from the HHPID measurement by the application of an "instrumental" or scaling parameter. Clearly, for linearity to be established in the field, corrections should be made for variations in moisture content and soil type, and for other parameters. There is also scope for the design of the HHPIDs themselves to be improved so as to better address some of these issues.

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Chapter Three: Comparison of Solvents for the Extraction of TPH (C_{10}-C_{36})

3.1 Introduction

The second study in this series involves the investigation of solvents used in extracting TPH. This step will be the continuation of the soil testing after the soils are collected from the field and submitted to the laboratory. This chapter therefore will examine a number of aspects of an initial stages of a TPH measurement which will include the sampling. This study is designed to investigate and demonstrate if there are statistical variations in TPH concentrations when soils are extracted using some of the more frequently used solvents. To obtain the TPH concentration in any given contaminated soil the extraction from soil is one of the initial steps[1-5]. The TPH, a 'lump' parameter, can be easily and rapidly measured and monitored in the laboratory. The term TPH is a widely used but loosely defined parameter, quantified by a number of methods determining the total compounds. It is anticipated that different extraction procedures might produce data which are difficult to compare[6-7]. Reporting TPH as a lump parameter is an accepted regulatory benchmark widely used to evaluate contamination[1,7-9]. Extraction of TPH can be conducted by various techniques. These include transferring TPH from soil into a solvent (for volatile and semi-volatile TPH)[10-15], heating the sample (static headspace)[16], or purging the sample with an inert gas (dynamic headspace)[17]. The last two techniques are specific for the determination of volatile TPH.

In Australia, the TPH is reported as volatile (C_6-C_9) and semi-volatile TPH (C_{10}-C_{36}) fractions[1,7-8]. The semi-volatile TPH is defined by some authorities as the diesel range organic (DRO) and quantified by summing the total response (including peaks and hums produced by aggregation of peaks) between *n*-C_{10} and *n*-C_{25} or in some cases *n*-C_{36}[1,18]. The current research will investigate the semi-volatile TPH obtained by sonication extraction, using three different solvents[7].

The extraction efficiency of TPH from soil depends on the solvent and the soil matrix. According to a surveys conducted by the VicEPA[17], solvents such as dichloromethane

(DCM), DCM/methanol (1:1, v/v), DCM/acetone (1:1, v/v), hexane/acetone (3:1, v/v), pentane/acetone (1:1, v/v) and various alcohols (including methanol and isopropanol) are used for soil extractions[1,6]. Figure 3.1 shows results of the VicEPA survey, which included 23 laboratories. The survey shows that there is a range of solvents currently used for TPH extraction across the laboratories. Although the use of freon was originally preferred due to the regulatory restrictions, alternative solvents have since been used due to there being very limited information available to help identify a specific solvent which can be used as a good substitute for freon. The TPH recoveries associated with a change of solvent needs to be investigated to establish comparability and highlight limitations due to various extraction efficiencies. In Australia and many other countries the variation is frequently observed during proficiency studies using split samples (i.e. samples regarded as portions taken from a single core sample) for the analysis of TPH[19].

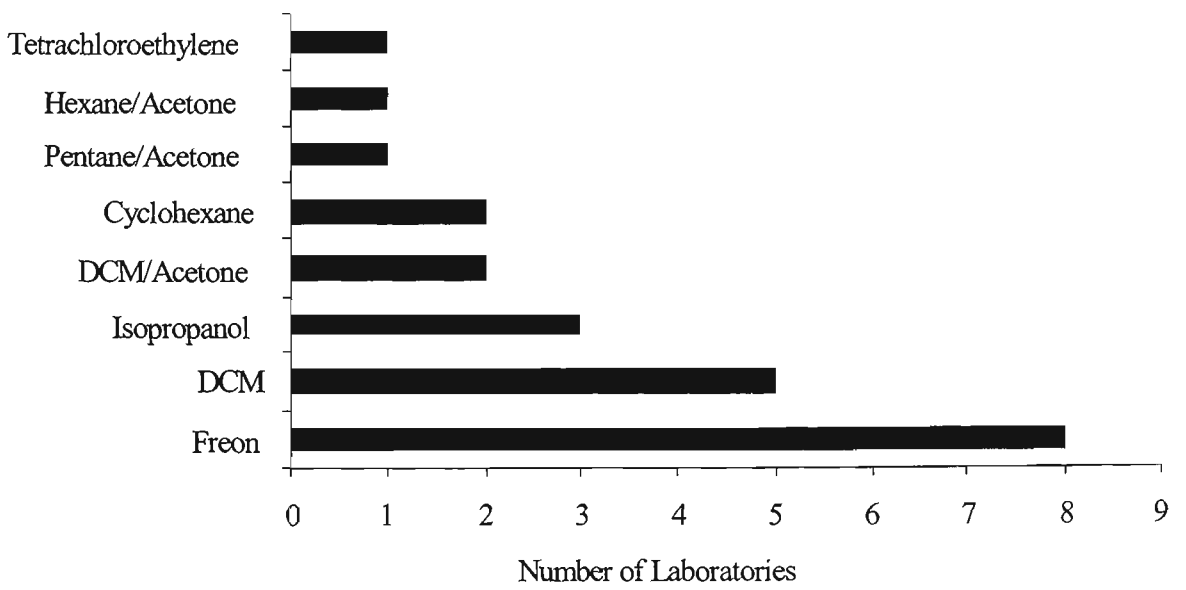

Figure 3.1: Solvents used for TPH extractions[7].

The extraction efficiency can be determined by matrix spikes or reference material containing TPH. A matrix spike is prepared by mixing a known concentration of TPH with clean soil thereby producing a quantitatively homogeneous, artificially contaminated soil. The TPH in

the soil can be measured and the percentage recovered calculated as a percentage. The TPH contamination in the spiked soil is an artificial system and may behave differently to naturally contaminated soil. A natural soil can contain numerous variables including non-uniform particles, moisture, clay content, and organic matter. Options available to homogenise natural soils without losing analytes are limited due to moisture and TPH instability. Conventional homogenisation methods such as drying followed by grinding and sieving cannot be applied to natural soils without the loss of TPH. Reference soils used in TPH proficiency studies are prepared by using conventional homogenisation methods because the losses during preparation are not considered to be important until the final preparation stage is reached. Therefore, when spiked or reference soils are extracted using various solvents and tested for TPH, the statistical variation in concentration can be within the acceptable limits of experimental uncertainty. To observe variations of TPH concentrations with a change of solvent, natural soils need to be tested. Additionally, a reasonable number of samples are required to obtain a data population sufficient for statistical analysis. For the research conducted in this chapter, seventy eight contaminated soils were extracted with three different solvents. The resulting concentrations were statistically analysed to determine the relationship between the TPH recoveries.

The three solvents were chosen from the survey in Figure 3.1 after discussions with many experts in the TPH field[20-22]. Factors including cost, regulatory requirements, extraction efficiency, toxicity and availability of the solvents were considered as important. For example Freon-113 was the preferred solvent but it was removed from production, distribution and use due to its ozone depleting properties[1,7]. Since then, DCM has been the solvent of choice for semi-volatile TPH analysis due to its high extraction efficiency and relatively low cost[1]. The use of DCM/acetone (1:1, v/v) was chosen by some Australian laboratories with minimum data to support the choice[7-8]. Alcohols such as methanol and isopropanol were also chosen to improve the penetration into moist soil due to there being a

difference in polarity between the moisture and DCM. The relatively low toxicity, lower disposal cost and concerns over release of chlorinated hydrocarbon residues into the environment were considered to be the advantages of isopropanol over DCM[23-27].

3.2 Materials and Methods

3.2.1 Apparatus

Glassware was purchased from Lab Supply Australia and cleaned by soaking overnight in a 2%, w/w Pyroneg™ solution, rinsed with water, soaked for 2 h in a 2%, w/w chromic acid solution then washed with water, rinsed with acetone and air dried before use. The glassware included 250 mL jars with screw cap lids and Teflon™ liners, 1 L jars with screw cap lids, glass rods (typically 6 mm diameter, 15 cm length); volumetric flasks of various volumes and glass pipettes ranging from 0.5-20 mL, calibrated prior to use. Glass GC vials (2 mL) were purchased from Proscience (Melbourne, Australia) with Teflon™ lined crimp caps and a crimper. A Branson 8210 ultrasonic bath, with a capacity to hold twenty extraction jars, 950 W and 47 kHz was used for extracting the TPH. A centrifuge, (MSE Microcentaur) was used for separating the fine soil particles from the suspension.

3.2.2 Chemicals and Reagents

Acetone, isopropanol and DCM (Omni Solve, chromatography grade) and granular anhydrous sodium sulfate were obtained from Crown Scientific (Melbourne, Australia). Table 3.1 contains a summary of properties of the DCM, acetone and isopropanol[23]. Millipore water, further purified by passing it through four cartridges of a milli-Q ultra cartridge system, was used to rinse glassware. The glassware cleaning solutions (2%, w/w in water) included, chromic acid and Pyroneg™ powder purchased from Diversey Lever Australia (Melbourne). The TPH (C_{10}-C_{36}) was defined as the total area of peaks between the retention time of the start of the n-C_{10} peak to the end-point of n-C_{36} peak.

3.2.3 Preparation of Standards

A number of hydrocarbons were chosen to represent the TPH (C_{10}-C_{36}). These normal alkane standards were purchased from Sigma, Supelco, and Ultra Scientific, Melbourne, Australia. They included 99% pure *n*-C_9H_{20}, *n*-$C_{10}H_{22}$, *n*-$C_{12}H_{26}$, *n*-$C_{14}H_{30}$, *n*-$C_{16}H_{34}$, *n*-$C_{18}H_{38}$, *n*-$C_{24}H_{50}$, *n*-$C_{28}H_{58}$, *n*-$C_{30}H_{62}$, *n*-$C_{32}H_{66}$, and *n*-$C_{36}H_{74}$. Each of the individual *n*-C_9H_{20}, *n*-$C_{10}H_{22}$, *n*-$C_{12}H_{26}$, *n*-$C_{14}H_{30}$, *n*-$C_{16}H_{32}$, *n*-$C_{18}H_{38}$, *n*-$C_{24}H_{50}$, *n*-$C_{28}H_{58}$, *n*-$C_{30}H_{62}$ were weighed and prepared as 10,000 mg/L standards with DCM in calibrated standard flasks. The *n*-$C_{32}H_{66}$ and *n*-$C_{36}H_{74}$ were difficult to dissolve and required the use of a small volume of carbon tetrachloride. The 10,000 mg/L solutions were diluted to achieve calibration and spiking mixed standards each containing 2, 10, 25 and 1000 mg/L hydrocarbon in DCM.

3.2.4 Preparation of Samples

Due to the relatively high volatility and instability of TPH, soils were not prepared using conventional soil preparation techniques such as drying, grinding and sieving to obtain total homogeneity prior to sub-sampling[28-30]. Therefore, to homogenise and prepare the soils, a delicate balance between optimum homogeneity with minimum losses was considered[24]. Soil samples were placed in 250 mL glass jars with screw tops and Teflon™ liners to minimise losses. These jars were placed in a refrigerator at 4 °C overnight prior to sampling by removal of the top 5 cm. Gravel, twigs or other material was removed from the jars. If the samples were free-flowing, sandy soil they were end-over-end shaken for 10 min and a composite was collected from different locations within the jar. If the samples were sticky (clay material) an apple corer was used to collect sub-samples from different locations within the jar to obtain a representative composite.

Table 3.1: Properties of solvents.

Property	DCM	Acetone	Isopropanol
	Dichloromethane	**Propanone**	**Popane–2-ol**
CAS number	75-09-2	67-64-1	67-63-0
Hazards Identification	Possible risk of irreversible effects.	Highly flammable, vapour/air mixture explosive	Highly flammable, Vapour/air mixture explosive
Handling	Under no circumstances eat, drink or smoke while handling this material	Precaution against static discharge	Precaution against static discharge
Form	Liquid	Liquid	Liquid
Colour	Colourless	Colourless	Colourless
Solubility in Water	Slightly soluble	Miscible in all proportions	Miscible in all proportions
Flash point	Non Flammable	-20 °C	12 °C
Stability	Stable	Stable	Stable
Toxicity	Carcinogen, category 3. Has been found to cause cancer in laboratory animals. May cause mutagenic activity or teratogenic effects.	No evidence of carcinogenic properties. No evidence of mutagenic or teratogenic effects.	No evidence of carcinogenic properties. Evidence of reproductive effects.
Ecological Information	Low bioaccumulation potential and aquatic toxicity.	No environmental hazard is anticipated if the material is handled and disposed of with due care.	No environmental hazard is anticipated if the material is handled and disposed of with due care.
Disposal Consideration	Residues are classified as special waste requiring special disposal requirements.	Residues are classified as special waste.	Residues are classified as special waste.
Current Price per 4L (Approximate)	$A 40	$A 35	$A 50

Obtaining representative soil samples was a challenge due to the heterogeneity of different soil matrices[24,29-30,33-35]. Additional difficulties were encountered with types of petroleum hydrocarbons in the soil due to the wide range of volatility, solubility, biodegradation and potential adsorption onto the soil of the individual constituents[35-37]. The current research focuses on TPH contaminated soil samples presented to the laboratory and so the field sampling was regarded to be beyond the scope of this work. The basis for using large sample numbers (i.e. 36 and 42) was to achieve statistically-based conclusions which offset possible random errors. Soils were prepared to draw representative and homogenous portions from a large repository, as needed for the comparative testing. Approximately 0.5 kg of each of the seventy eight contaminated soils were collected from decommissioned service station sites in and around Melbourne, Australia and the samples were individually homogenised. Soils were numbered sequentially and stored in 1 L glass jars at 4 °C. The possible losses during the homogenisation process were not investigated here since the study was designed only to determine TPH concentrations achieved by using each solvent.

3.2.5 Extraction Process

The TPH (C_{10}-C_{36}) from soil can be extracted either by shaking or vortrexing with solvent[1]. Adding a desiccant helps to break up the soil thus increasing the surface area available for the removal of bound TPH. The extraction efficiency depends on the soil type with clay soil requiring relatively more vigorous extraction conditions than sandy soil. Soxhlet extraction described by the USEPA SW-846 series method 3540[27-28] is regarded to be highly efficient. The sonication extraction technique based on USEPA SW-846 series method 3550 B [10-11] works by using sound waves to enhance analyte transfer from sample to solvent. Sonication extraction is regarded by most analysts to be a good substitute and a practical method for extracting TPH. Sonication requires relatively less time and solvents than Soxhlet extraction and is easier to operate.

3.2.6 Analysis of TPH (C_{10}-C_{36})

The semi-volatile TPH (C_{10}-C_{36}) fraction is subdivided into C_{10}-C_{14} (e.g. kerosene fraction), C_{15}-C_{28} (e.g. heavy kerosene and lubricating oils fraction) and C_{29}-C_{36} (asphalt fraction). Once the extraction is complete the extract can be analysed by gas chromatography with flame ionisation detection (GCFID). The cost differences between the solvents is moderate but the disposal cost of DCM residues is higher due to its toxicity. Isopropanol, a solvent with relatively low toxicity was compared with DCM/acetone (1:1, v/v) as requested by the Victorian Environmental Protection Authority (VicEPA) to limit the production of chlorinated solvent waste[31]. The aim of this study was to statistically compare the TPH (C_{10}-C_{36}) concentration obtained by extracting each contaminated soil using each of the three solvents. The toxicity and the environmental significance of DCM and the possible omission of DCM in future were considered to be significant factors for the isopropanol trial[32].

The GCFID analyses were conducted by using a Hewlett Packard (HP) 5890 Series II GC fitted with SGE BPX5 (25m × 0.22 mm I.D. × 0.25 μm film thickness) column, HP 7673A auto sampler, FID and HP Chemstation software. The GCFID conditions comprised an injector temperature of 325 °C, detector temperature of 350 °C, column head pressure of 175 kPa, oven temperature program at an initial temperature of 40 °C, initial hold time of 0.8 °C, temperature rate of 27 °C/min upto 100 °C, temperature rate of 35 °C/min upto 350 °C and a final hold time of 5 min. The GCFID was calibrated using the 2, 10, 25 and 1000 mg/L standards. The integration event timetable was programmed to calculate the TPH in the C_{10}-C_{36} ranges. The TPH (C_{10}-C_{36}) concentrations of 75 mg/kg or greater were collected for the data analyses. Samples that did not generate TPH (C_{10}-C_{36}) at or above 75 mg/kg were excluded from the study.

3.2.7 Moisture Analysis

The moisture content of each of the soils was assessed to obtain the TPH (C_{10}-C_{36}) concentration on a moisture-free basis. The soil weighing dishes (75 mm diameter and 25 mm deep) were placed inside a drying oven at 105 ± 5 °C for 1 h to remove traces of moisture. The dishes were removed from the oven and placed to cool inside a desiccator charged with silica gel. Using an analytical balance the empty dishes with lids were weighed and a 10 ± 0.1 g sample of soil was placed in each dish and the mass recorded. The dishes were removed and placed in the desiccator. This process was repeated until a constant weight was achieved with the removal of the moisture from the soil. Using this method the moisture content of each of the soils was determined in duplicate.

3.2.8 Soil Characterisation Using Northcote Bolus Manipulation

Soil texture was measured by the Northcote bolus manipulation process. The method assesses the behaviour of a small handful of soil, moistened and kneaded into a ball and pressed between the thumb and forefinger[37]. The method involved a sample of soil, sufficient in size to comfortably fit onto the palm that was moistened with water (a little at a time) and kneaded until a ball of soil was formed. The ball should just be wet enough to fail to stick to the fingers. More soil or water was added to attain the condition known as the sticking point. Kneading and moistening were continued until the soil ball was homogeneous, usually requiring a working time of 1 to 2 min. Following this procedure, the soil ball, or bolus, was ready for shearing manipulation, but the behaviour of the soil during bolus formation was also indicative of its texture. The behaviour of the bolus and the ribbon produced by shearing (pressing out) between thumb and forefinger characterised the texture. Nineteen grades of texture are identified by this method and they have been categorised into three main groups as defined by the behaviour of the moist bolus.

3.2.9 Comparison Studies

Two studies were conducted using TPH contaminated soil. The soil was extracted by sonication technique[9,10-11,13]. The contaminated soil samples were divided into two groups, one group containing 36 samples and the other containing 42 samples. The 36 soils were extracted as single samples for each solvent using DCM and DCM/acetone (1:1, v/v) and the 42 samples were extracted as single samples for each solvent using DCM/acetone (1:1, v/v) and isoproponol. The soils were prepared by weighing 10 g portions into 125 mL glass jars with screw cap lids and Teflon™ liners and 20 mL of respective solvents were added. The samples were mixed using glass rods and each jar was placed in the ultrasonic bath and sonicated for 10 min. The extracts were dried with anhydrous sodium sulphate (by adding approximately 10 g while mixing well with a glass rod) and the samples were placed in the ultrasonic bath for a further 1 h. Samples were allowed to settle from the solvent fraction and the supernatant was checked for suspended particulate or floating insoluble material. If these material were present, a portion of the supernatant was centrifuged at 13 000 rpm for 5 min. When the solution was clear a sample of the supernatant was transferred to a 2 mL glass crimp top GC vial and crimped immediately. The extract was analysed using the HP 7673A auto-sampler with a calibrated syringe containing a sampling sequence to deliver 1 μL with an accuracy of ± 0.001 μL.

The samples were analysed by GCFID in batches. Each batch contained extracts based on one solvent to avoid retention time and chromatographic variations. Each batch of samples contained calibration standards, one reagent blank representing the solvent, one soil blank extracted with the respective solvent and the soil extracts. Analysis of solvent and reagent blanks determined if there was interference by artefacts. Every one in four injections contained a 2 mg/L calibration check standard to monitor the response for changes and check for possible variations in the auto-injector. If the response of an adjacent pair of calibration check standards varied by more than 10% the analysis of the range was repeated. Internal

standards (IS) were not used with the GCFID. Further details regarding the exclusion of the IS are discussed in Chapter 4. Quality assurance studies were conducted by preparing a recovery sample. The recovery was prepared using contamination free soil (10.0 g) spiked with 500 μL of the 1000 mg/L recovery standard. The spike was delivered by injecting 500 μL of recovery standard just below the surface of the soil on the side of the jar through a calibrated 1000 μL syringe. The concentration of TPH in spiked soil was at 550 mg/kg. Once the spike was delivered into the jar the lid was closed and the contents of the jar were shaken for at least 10 min to obtain proper distribution. The percent recovery of TPH was determined by comparing the spiked amount with the recovered amount.

A calibration curve was prepared using 2, 10, 25 and 1000 mg/L TPH solutions. The 2 mg/L standard was used as the calibration check or the working standard. The acceptable recovery percentages were set between 80-120% based on USEPA-SW846 criteria[39].

The calibrations were performed whenever there were changes to the operating conditions. The calibration results were used to construct a calibration table to ensure that the FID was operating with minimum response factor variations. A calibration check standard (2 mg/L) was used to obtain the normal alkane retention times. The TPH (C_{10}-C_{36}) fraction was defined as the retention window of the beginning of the C_{10} peak and the end of the C_{36} peak and the total chromatogram was integrated using the baseline-to-baseline integration technique. Results for each sample were obtained directly from the calibration report and the result was corrected to account for the moisture factor.

The proper baseline construction was essential to obtain an accurate TPH concentration. Baseline drift during the oven temperature program was compensated by baseline subtraction using the column compensation function on the GCFID. Baseline-to-baseline integration mode rather than the peak-to-peak integration was used in the quantification to include the UCM. Peak-to-peak integration mode quantifies only the resolved individual hydrocarbons

omitting the contribution by the UCM. The TPH (C_{10}-C_{36}) fraction was calculated after setting the baselines over the appropriate retention time range. The integration event timetable was programmed to calculate the area between the designated time range for the fraction.

Due to the presence of a UCM in the chromatographic range the use of an IS was not practical. Additionally if an IS co-eluted with sample peaks accurate measurements would not be obtained resulting in significant errors. Therefore, in place of an IS the response of the 2 ng/μL calibration check standard between every four samples was monitored.

3.3 Calculations

A GC calibration factor was calculated to compensate for the moisture content, sample extraction volume and sample mass. The formula is:

$$\text{GC CalibrationFactor} = \frac{100}{[100-(\%\ \text{moist})]} * \frac{\text{Extraction Volume (0.020L)}}{\text{Sample Mass (0.010kg)}}$$

The TPH (C_{10}-C_{36}) concentration was obtained from the calibration report.

3.4 Results and Discussion

The results were calculated on a moisture-free basis and reported as TPH (C_{10}-C_{36}) in mg/kg of soil for each sample. Sample chromatograms are included below to demonstrate the unique TPH profiles obtained with a range of peaks including the UCM and demonstrating the need for a baseline-to-baseline integration technique to be used. Figure 3.2 shows a chromatogram of a TPH (C_{10}-C_{36}) sub-sample from a homogenised contaminated soil extracted with DCM/acetone (1:1, v/v) and Figure 3.3 shows a chromatogram of a second sub-sample from the same bulk sample extracted with isopropanol. These two chromatograms demonstrate the variation in extraction efficiency of the two solvents.

To conduct a comparison between solvents the paired t-test was used[40]. The t-test allows the determination of the variation between methods by restricting the swamping effect caused by differences between the individual soils. Adopting the null hypothesis that there is no significant difference in the mean concentration obtained by the two solvents, the mean of the differences was tested to confirm if they differed significantly from zero. If the numerical value for the t-critical obtained for (n-1) degrees of freedom is greater than the calculated t, the null hypothesis is retained and the methods would be deemed to be statistically comparable. If the calculated t is greater than the $t_{critical}$ then the null hypothesis is rejected and the two methods would be deemed to be not comparable.

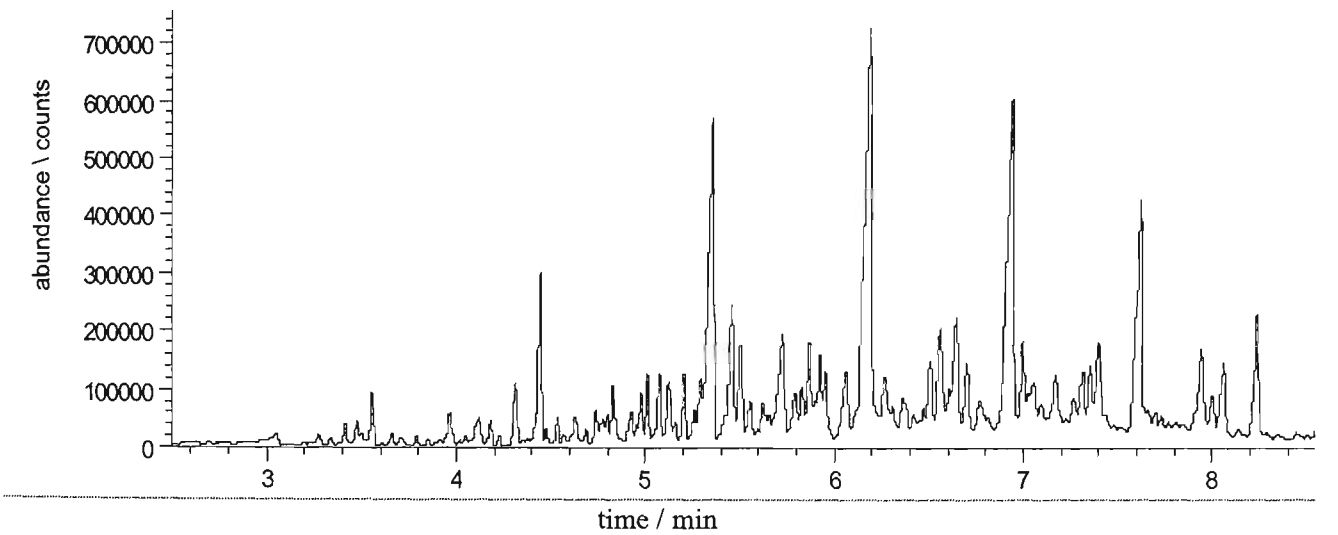

Figure 3.2: Sample chromatogram of soil extracted by DCM/acetone (1:1, v/v).

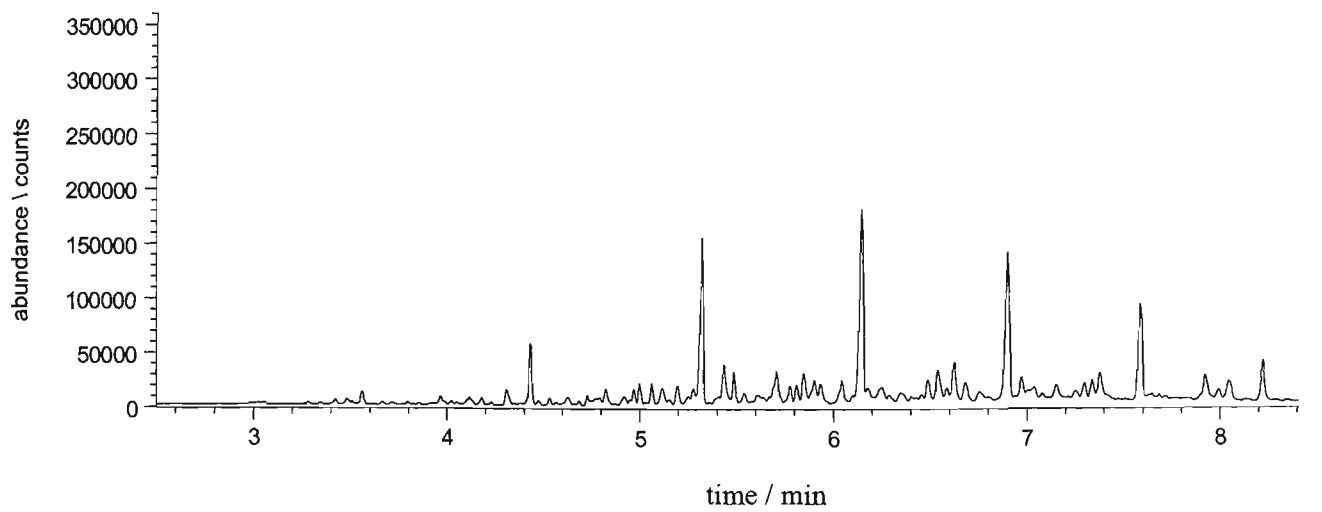

Figure 3.3: Sample chromatogram of the above soil extracted by isopropanol.

If two methods are comparable using the t-test, the F-test is applied to investigate if one method is more precise. Calculating the two sample variances the ratio should be such that F should always equal to 1. The null hypothesis adopted was that the populations from which the samples were taken are normal, and that the population variances are equal. If the null hypothesis is true, the variance ratio should be close to 1. Differences from 1 can occur due to random variation but if the difference is too great it can no longer be attributed to this cause. Therefore if the calculated value of F exceeds a certain critical value obtained from tabulated values then the null hypothesis is rejected.

Appendix 3.7.1 contains the paired t-test results between DCM and DCM/acetone. The $t_{critical}$ value is 2.04 compared to the $t_{calculated}$ value 0.8156 at $p = 0.05$. Therefore the $t_{calculated} < t_{critical}$ and the null hypothesis is retained. The DCM and DCM/acetone (1:1, v/v) solvents produce comparable TPH (C_{10}-C_{36}) concentrations. Appendix 3.7.2 contains the paired t-test results between DCM/acetone (1:1, v/v) and isopropanol. The $t_{critical}$ value is 2.04 compared to the calculated value 2.77 at $p = 0.05$. Therefore the $_{calculated} > t_{critical}$ and the null hypothesis is rejected. The DCM/acetone (1:1, v/v) and isopopanol solvents do not produce comparable TPH (C_{10}-C_{36}) concentrations. Appendix 3.7.3 contains results of the F-test applied to establish if there is an advantage of DCM over DCM/acetone (1:1, v/v) in extracting soil contaminated with TPH (C_{10}-C_{36}). The comparison of $F_{critical}$ against the $F_{calculated}$ for DCM against DCM/acetone (1:1, v/v) showed $F_{critical} = 1.93$ compared to $F_{calculated} = 1.43$ at $p = 0.05$. Therefore the TPH (C_{10}-C_{36}) concentrations obtained by DCM/acetone (1:1, v/v) appears to be more precise compared to the data achieved by using DCM alone. However, the difference is not significant. For the difference to be statistically significant the $F_{calculated}$ should be greater than $F_{critical}$.

The TPH (C_{10}-C_{36}) concentration achieved by the two solvent systems are presented in Figures 3.4 and 3.5. The comparison of DCM against DCM/acetone (1:1, v/v) was conducted

on 36 soils classified to be sand, sandy loam and clay. The soils were extracted in duplicate with each solvent and the TPH (C_{10}-C_{36}) concentrations were computed on a moisture-free basis.

The paired t-test results applied to the mean differences demonstrate that DCM and DCM/acetone (1:1, v/v) solvents do not significantly alter the extractable concentration of TPH (C_{10}-C_{36}).

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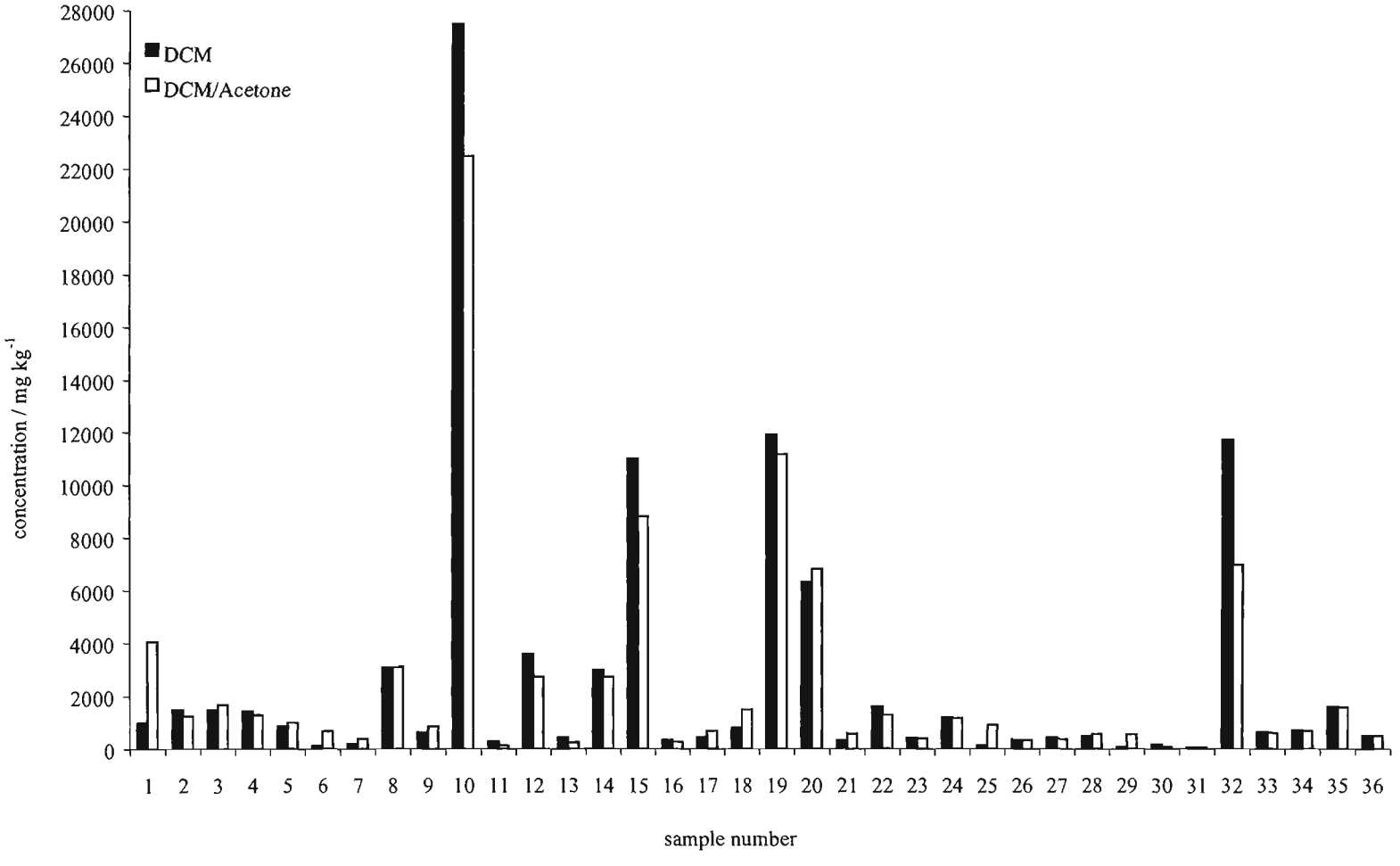

Figure 3.4: Histograms comparing TPH (C_{10}-C_{36}) concentrations obtained by DCM and DCM/acetone (1:1, v/v) extractions.

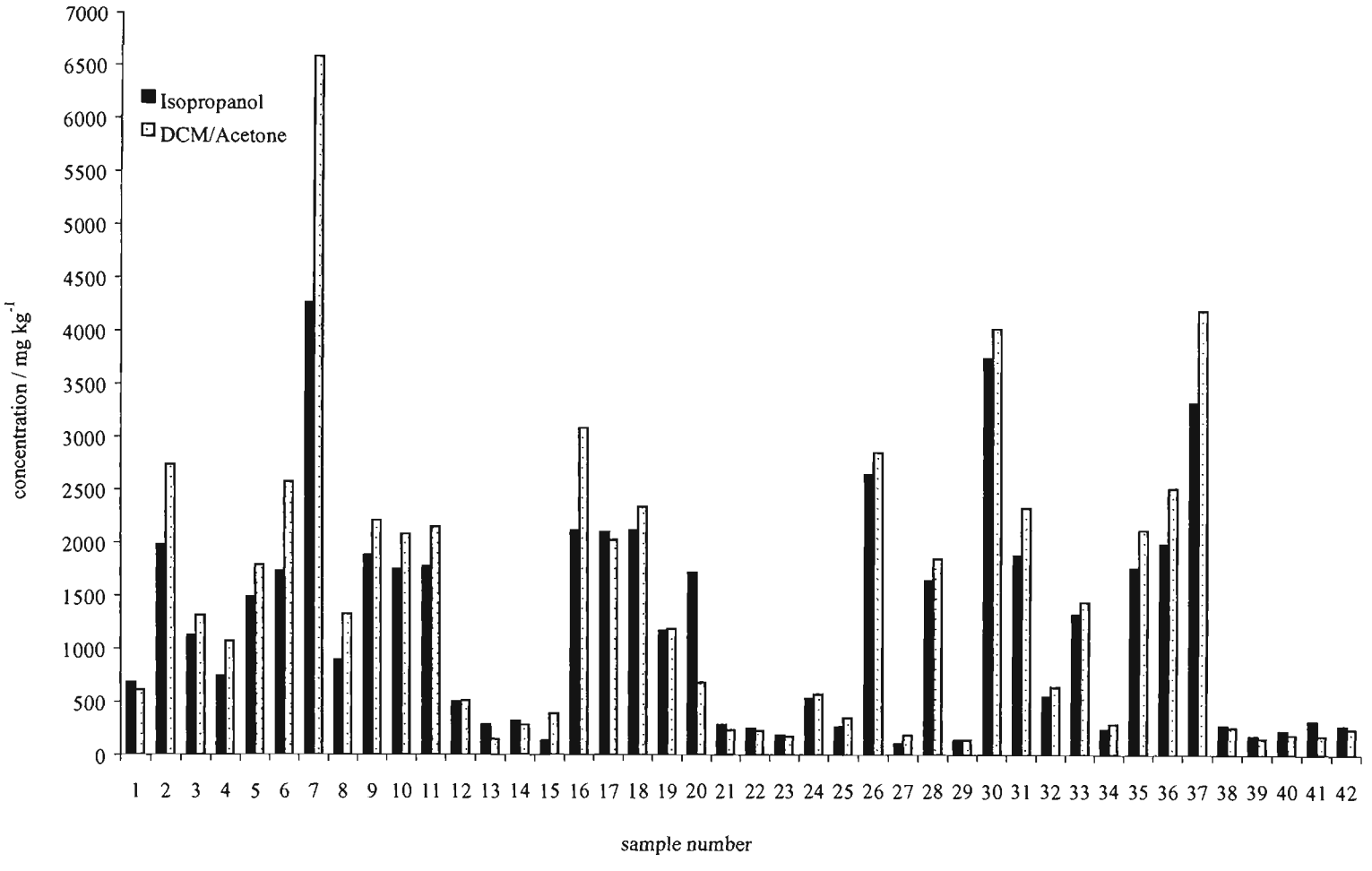

Figure 3.5: Histograms comparing TPH (C_{10}-C_{36}) concentrations obtained by isopropanol and DCM/acetone (1:1, v/v) extractions.

When the F-test was applied to compare if DCM is a better solvent than DCM/acetone (1:1, v/v) for TPH recovery, there was only a marginal bias towards the precision of DCM/acetone. This is most likely due to the ability of acetone as a polar solvent to penetrate wet soil and assist DCM to dissolve TPH.

Comparing the results of DCM and DCM/acetone, it can be concluded that at high concentrations of TPH DCM/acetone appear to give lower results. This can be caused by the limitation of solubility of TPH components in the solvent. At lower concentrations DCM/acetone give higher concentrations which is due to the availability of additional solvent. Because there can be many components including TPH, PAHs, and polar non hydrocarbon type components it is very difficult to assess if the DCM/acetone was sufficient to extract the TPH at higher concentrations.

3.5 Conclusion

The results of the 36 contaminated soil samples which included sand, sandy loam and clay demonstrates that TPH concentrations achieved from DCM/acetone (1:1, v/v) to be more precise than DCM only concentrations. However, the difference was not significant. It is therefore appropriate to use either of the DCM and DCM/acetone (1:1, v/v) for the extraction of TPH (C_{10}-C_{36}) from soil. However, including acetone with the DCM as a 1:1 (v/v) solution will enable DCM to penetrate the soil even when soils are heavily moisten.

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Chapter Four: Extraction of TPH from Clay Soils by Sonication and Soxhlet Techniques

4.1. Introduction

The third step of the analytical process is the extraction technique. Usually the extraction of TPH volatile and the semi-volatile fractions are treated differently due to variations in required extraction conditions. This chapter will examine some of the more common extraction methods used for the semi-volatile fractions. Regulatory authorities around the world use the total petroleum hydrocarbon (TPH) concentrations as an indicator for the level of soil contamination by petroleum products. Similarly in Australia, TPH analysis of soil is an integral part of the site contamination assessment[1~9]. Numerous analytical methods have been developed to obtain optimum results in response to the problem by the Australian testing laboratories[5~7]. Most of the current methods used in the TPH analysis are derived from the United States Environmental Protection Agency (USEPA)[10]. A site may require a clean-up when the concentrations of TPH present in the soil represent an unacceptable risk to human health, land use or the environment. The principles for such clean-ups are detailed in the Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites (ANZECC) and the National Environmental Protection Measures (NEPM) [1,4]. The site specific TPH requiring to be investigated are the total hydrocarbons (C_6-C_{36}), fractionated hydrocarbon groups including the volatile C_6-C_9 fraction and the semi-volatile fraction (C_{10}-C_{14}, C_{15}-C_{28} and C_{29}-C_{36})[3]. The TPH (C_6-C_{36}) is defined as the total of the above volatile and semi-volatile four fractions. The concentration of the TPH contamination in mg per kilogram of moisture free soil is used to decide whether a clean-up is required[2~7].

The semi-volatile TPH fraction in Australia is regarded as the fraction containing C_{10}-C_{36}[2~7]. However, there can be variations to this range of carbon numbers with the change in guidelines in various parts of the world. For example, in Germany this range is extended to C_{10}-C_{40}[9]. This fraction is usually extracted from soil by Soxhlet extraction[11~12] or sonication extraction[13]. Soxhlet extraction is regarded as an efficient extraction technique commonly

used in extracting semi-volatile organic compounds from soil[2,5,11~16]. The choice of extraction technique is decided on the basis of cost and time considerations. Sonication extraction is regarded as a faster technique than Soxhlet and requires less solvent and can be conducted in large batches using a small setting-up area. Therefore, in Australia, sonication extraction is more popular than the Soxhlet extraction[5]. The use of sonication and Soxhlet extractions for TPH extraction in soil is regarded as a valid technique by regulators around the world[2,4~9,16]. The National Association of Testing Authorities (NATA) of Australia accepts both techniques when methods are submitted for registration. This work is designed to determine if there are statistical variations in TPH (C_{10}-C_{36}) obtained by Soxhlet extraction and sonication extraction when homogenised samples of clay soils are split into sub-samples, extracted by the two techniques and analysed by GCFID. The results of this work will inform the user of the two methods and assist in understanding the expected variations in order to take adequate steps to minimise the impact on the results and the decisions based on them. Projects conducted on contaminated site assessments cannot proceed to the next stage until the soil assessment results are available. For example during a validation stage of a site the longer the time taken to conduct analysis the greater the rental cost for excavating equipment which is on stand by. A review conducted by the Environmental Protection Authority of Victoria, Australia (VicEPA)[5] concluded that among the responding nineteen TPH testing laboratories ten laboratories used sonication extraction and six used Soxhlet (Figure4. 1). Table 4.1 is a summary of significance of TPH components published by the AIP [3].

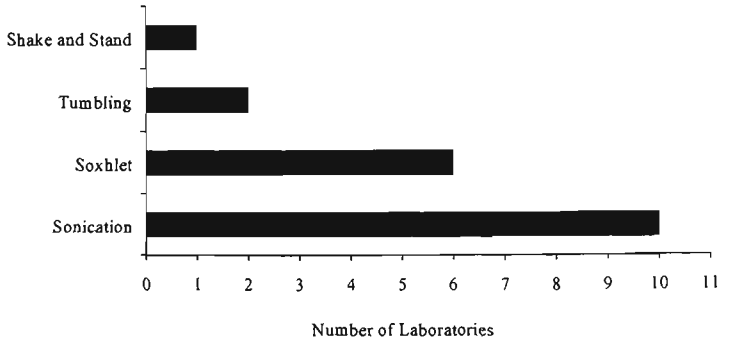


Figure 4.1: Plot of extraction technique survey.

Table 4.1: Guideline for assessing the importance of levels of soil contaminants.

Contaminant	Degree of Contamination in mg/kg			
	Very Significant	**Significant**	**Low Significance**	**Insignificant**
TPH	100,000's	10,000's	1,000's	100's
C_6-C_9	1000's	High 100's	Low 100's	<5
C_{10}-C_{14}	10,000's	1,000's	100's	10's
C_{15}-C_{28}	100,000's	10,000's	1,000's	100's
Total Aromatics	100's	High 10's	Low 10's	<5
Benzene	Low 10's	>10	<5	<1
Xylene	100's	10's	Low 10's	<1
Ethyl benzene	100's	10's	<5	<1
Total PAH	100's	Low 100's	Low 10's	<1
(Polynuclear Aromatic Hydrocarbon)				
Benz(a)pyrene	10's	>10	<1.0	<0.1

Clay soil contaminated with TPH was chosen for research because contaminated clay is regarded as the most difficult to homogenise, sub-sample and extract due to their tightly packed structures and limited permeability[17-18]. This study was conducted on clay soil collected from a contaminated site in Southern Australia. The clay content of all contaminated soils analysed for this research was greater than 50%.

The research in this chapter included the comparison of TPH concentrations achieved for fractions C_{10}-C_{14}, C_{15}-C_{28}, C_{29}-C_{36} and C_{10}-C_{36} in homogenised sub-samples of soil when extracted by sonication and Soxhlet methods and analysed by the GCFID[1,19-20]. Eighty four contaminated soil samples were collected from a discontinued refinery site to be used in this research. The range of TPH in each of the samples were unknown prior to the study and all the samples were assumed to contain TPH across the chromatographic range of C_{10}-C_{36}. The concentration of semi-volatile TPH fractions (C_{10}-C_{14}), (C_{15}-C_{28}) and (C_{29}-C_{36}) were determined by sonication and Soxhlet extractions[5,8-9].

As discussed in Chapter 3, TPH represent a lumped parameter rather than an ensemble of individual compounds and characterisation relies on the total area (detector response) of the resolved and unresolved components of petroleum mixtures[1,21]. The resolution and quantification of TPH using GC are unique and different to conventional GC procedures. The GC separations are usually designed for samples producing sharp peaks with baseline separations and resolution. For example if six pesticides are monitored in a soil extract which is free of artefacts, six compounds eluting at specific retention times with baseline separations can be achieved. However baseline separation is not usually achieved during TPH analyses due to unresolved complex material (UCM) [8]. Therefore the analyst should be able to work within this chromatographic limitation to compute the resulting TPH concentration[1,9,22-25].

4.2 Experimental

4.2.1 Soil Sampling

Soil samples were collected from an oil refinery site (manufacturing, storing and processing petrol, diesel and lubricating oils) using a hollow-stem auger drilling technique into solvent washed stainless steel cores. The soils were taken from the top 10-25 cm and the cores were sealed with Teflon™ tape. The core samples were transferred within 8 h of sampling to the laboratory at 4 °C. Each core sample was transferred into a 250 mL glass jar with Teflon ™-lined caps. These soils were homogenised[26], classified[17-18], tested for moisture[27] and sub-samples extracted by the sonication[5,6,13] and the Soxhlet extraction[11-12]. The extracts were concentrated or diluted as required and analysed by GCFID.

4.2.2 Sub-Sampling of Soil

Vigorous homogenisation techniques such as grinding and particle sizing were not applicable to wet clay requiring to be tested for TPH due to losses. Each of the soil samples were weighed into four, 10 g lots to be analysed as follows: (i) classification, (ii) moisture analysis, (iii) sonication extraction and (iv) Soxhlet extraction.

4.2.3 Apparatus

Glassware used for the study is described in Section 3.2.5. Additionally the Soxhlet extraction apparatus was assembled using 70 mL extractor tubes fitted with two neck 500 mL round bottom flasks, consisting a second side neck with a thermometer probe inlet sealed by a Teflon™ lined silicone septa. Whatman™ cellulose thimbles (25 mm ID and 80 mm length) washed with dichloromethane (DCM); volumetric flasks, pipettes and 2 mL GC vials with crimp caps (containing Teflon™ lined rubber) and a crimper was required.

4.2.4 Reagents

Many of the substances used in this study are flammable, toxic or corrosive and therefore utmost care was taken when performing experiments[28-38]. The solvents and reagents included

chromatographic grade DCM (Merck-pesticide residue grade) and Mallinckrodt, granular anhydrous sodium sulphate obtained from Crown Scientific and Millipore water further purified by passing through four cartridges of a milli-Q ultra cartridge system. The solutions for cleaning glassware included, chromic acid (prepared by saturating analytical grade potassium dichromate in analytical grade concentrated sulphuric acid and 2% (v/v) water and Pyroneg powder (2%, w/w) in water prescribed for cleaning laboratory glassware.

4.2.5 Standards

Calibration standards were prepared by using 99% pure normal alkanes purchased from Sigma, Supelco, and Ultra Scientific. They include n-C_9H_{20}, n-$C_{10}H_{22}$, n-$C_{12}H_{26}$, n-$C_{14}H_{30}$, n-$C_{16}H_{34}$, n-$C_{18}H_{38}$, n-$C_{24}H_{50}$, n-$C_{28}H_{58}$, n-$C_{30}H_{62}$, n-$C_{32}H_{66}$ and n-$C_{36}H_{74}$. These components were individually weighed and prepared in DCM as described in Section 3.2.6.1.

4.2.6 Major Equipment

Hewlett Packard (HP) 5890 Series II GCFID fitted with an SGE BPX5 (25m x 0.22 mm I.D. x 0.25 μm F.T.) column, with HP 7673A auto-sampler, FID detector and computer controlled HP Chemstation software. A steam bath suitable for holding 500 mL round bottom flasks and an ultrasonic bath (Branson 8210, 950 W and 47 ± 0.6 kHz).

4.2.7 Soxhlet Extraction

Homogenised soil was weighed into Soxhlet thimbles in 10 g lots and placed inside Soxhlet extraction tubes above the two neck round bottom flasks containing 300 mL of DCM. The entire Soxhlet assembly was placed on a boiling water bath with running water condenser. The Soxhlet extraction was carried out for 16 ± 2 h at a rate of 10 cycles/h. At the end of the extraction period the solution was decanted into a Kuderna Danish evaporator and the volume reduced to approximately 100 mL. The solution was quantitatively transferred into 100 mL volumetric flask and after the volume was adjusted to the calibration mark with DCM, shaken to obtain homogenisation prior to GCFID analyses.

4.2.8 Sonication Extraction

Further 10 g lots of homogenised soil were weighed into 250 mL glass jars and 20 mL of DCM added and sonicated for 10 min. Anhydrous sodium sulphate (10 g) was added and mixed using a rod and the mixture was further sonicated for 16 ± 0.5 h. The temperature in the ultrasonic bath was maintained at less than 10 °C to minimise any heat generation. At the end of the extraction period the solution was transferred into a 100 mL volumetric flask and the volume was made up with DCM. These solutions were analysed by GCFID. The moisture content of each of the test soils was analysed by the method specified in Section 3.2.6.4.

4.2.9 Analysis by GCFID

The GCFID was calibrated by the normal alkane mixtures of 2, 10 and 1000 mg/L as in Section 3.2.6.7. The response of the 1000 mg/L normal alkane mixture was verified using a 1000 mg/L diesel fuel standard. The experimental concentration of the diesel fuel computed by using the 1000 mg/L normal alkane mixture was 980 mg/L which differed by less than 1% of the certified concentration of the diesel standard. Therefore the normal alkane standards was used in quantifying TPH contamination in soil caused by diesel, kerosene and heavy oils. The soil extracts were analysed as batches by the GCFID. The GCFID was calibrated using three calibration standards. The 2 mg/L was chosen as the calibration check standard and analysed at intervals of one in every four injections. Figure 4.2 contains a chromatogram of a TPH calibration standard. Response between two adjacent calibration check standards were monitored to check if the injector volumes were consistent. If the response between two adjacent check standards differed more than 10%, then the samples between the adjacent check standards were reanalysed assuming errors in the auto-injections. These steps were taken to improve the quality of the data and to compensate for omitting internal standards (IS). The IS were not considered for this part of the research due to (i) GCFID not having the

capability of identifying co-eluting compounds, (ii) IS can overlap with TPH, (iii) TPH components can be present in all regions of the chromatogram (iv) compounds outside the C_{10}-C_{36} range i.e. C_{40}[9] can be too insoluble as IS (v) early eluting compounds are too volatile as IS and (vi) the front of the chromatogram just prior C_{10} may contain a mass of peaks making it impossible to identify the IS.

There were secondary reasons for omitting IS. Utmost consideration was given to minimise the analyses time to manage urgent turn-around times required for TPH assessments. During the analysis of a batch of soil extracts the following quality assurance samples were included to improve the evaluation of data. Blank samples prepared by using hydrocarbon free soil processed using the same extraction technique, reference material obtained from the National Analytical Reference Laboratories (NARL) Australia, clean soil samples spiked with known amounts of normal alkanes to check percent recoveries.

Analyses were performed on a HP 5890 GC fitted with a FID[8]. Sample volume used for the analysis was 1 μL, injection, injector temperature 325 °C, detector temperature 350 °C, head pressure 175 kPa, initial temperature 40 °C, initial time 0.8 min., ramp rate 27 °C/min up to 100° C, ramp rate (2) 35 ° C/min up to 350 ° C, and hold time 5 min. The TPH concentrations were calculated on a moisture free basis and the three fraction concentrations were compared by comparison of the concentration obtained on each fraction. Figures 4.3 (a-c) shows typical TPH profiles detected in semi-volatile hydrocarbon region containing unresolved complex material (UCM).

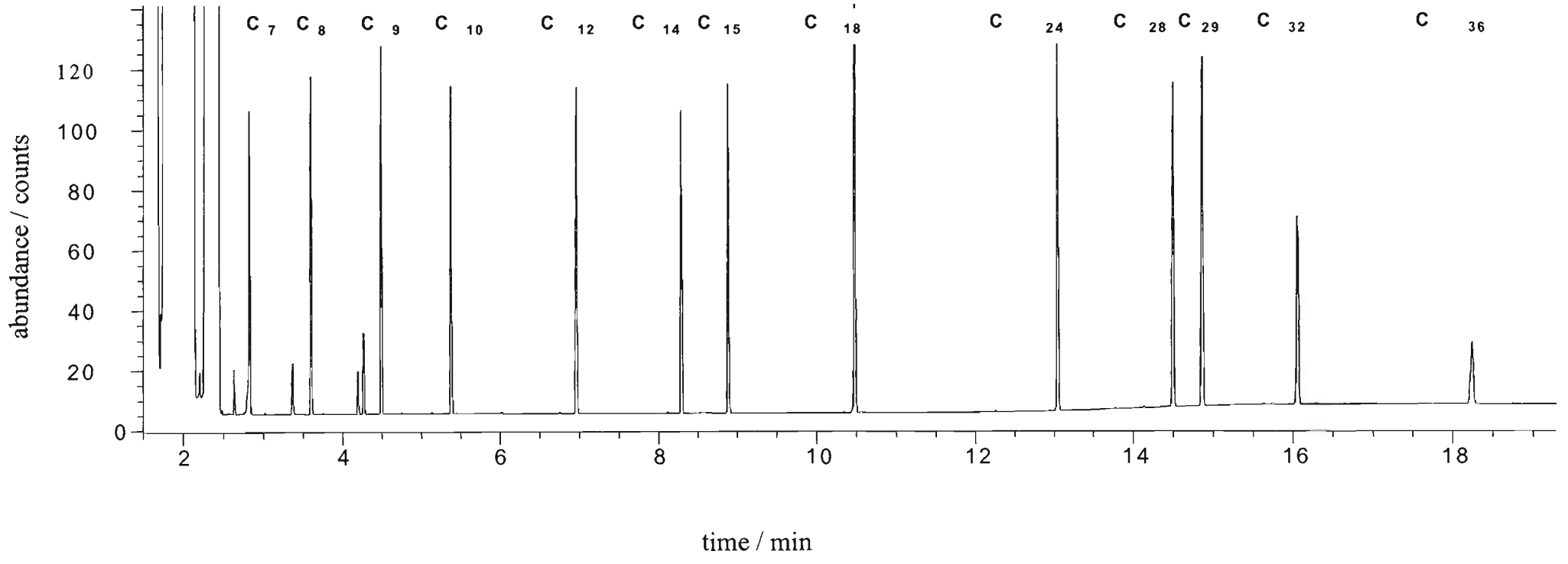
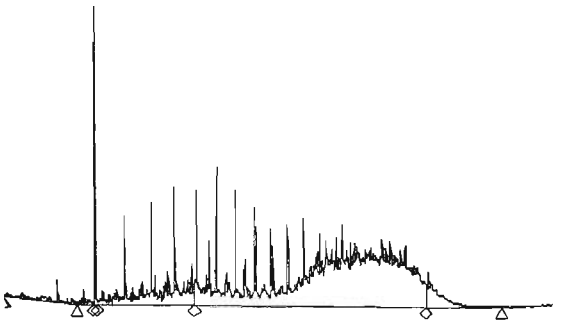


Figure 4.2: Example of TPH calibration standard.

3a)



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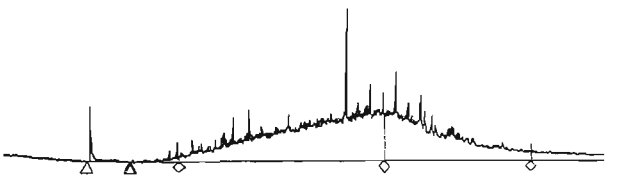

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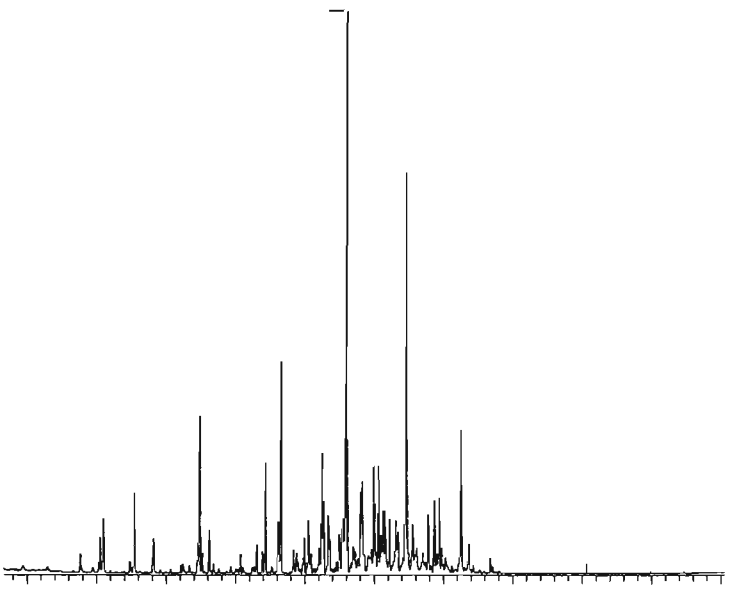

Figure 4.3 (a-c): Examples of a typical TPH sample profile at the semi-volatile range.

4.2.10 Analysis of Chromatograms

The integration event timetable was programmed to calculate the TPH fraction concentration in the C_{10}-C_{14}, C_{15}-C_{28} and C_{29}-C_{36} time ranges. Soil samples containing TPH concentrations greater than 10 mg/kg for each of the three fractions were detected by the GCFID. These concentrations were recorded for statistical tests.

4.2.11 Characterisation of Soils

Characterisation of the soils were performed by the Northcote bolus manipulation technique[17]. Presence of lime was tested by adding a few grains of soil into a 2 molar hydrochloric acid solution and checking for fissing.

4.3 Results and Discussion

The eighty four contaminated soils were subjected to the following tests. Soil type, the moisture content, presence of lime and the TPH concentrations for fractions C_{10}-C_{14}, C_{15}-C_{28}, C_{29}-C_{36} and C_{10}-C_{36}. The results of the TPH fraction concentrations were tabulated and presented in Appendix 4.6.1. The classifications and the summary of the classifications were tabulated in Appendix 4.6.2 and 4.6.3. The TPH fractions C_{10}-C_{14}, C_{15}-C_{28}, C_{29}-C_{36} were statistically tested using the t-test statistics tabulated for statistical comparison [47]. The results of the t- tests are tabulated in Appendices 4.6.4-4.6.6. The 84 contaminated soils were all clay soils. They included 66 grey/brown clays, 8 sandy clay and 10 clay loams. Figure 4.4 represents the percentage of each clay type. The percentage moisture range for the grey/brown clay were 11-29 with a mean percent of 20, sandy clay were 6.9-16.3 with a mean percent of 11.6 and clay loam 11.4-32.7 with a mean percent of 22.1. Figure 4.5 represents the percentage moisture range for each of the clay soil types. The soils contained a wide moisture range with a minimum of 6.9% and a maximum of 32.7% with a mean percent of 19.8. It is considered that the occurrence of relatively high moisture in clay soil to be common due to limited space among the soil particles for the permeation once the moisture is entrapped. Lime was present in 22% of the grey/brown clay, 11% of the grey/brown sandy clay loam and 91% of the grey/brown clay loam. Total chromatographic response was assumed to be contributed by the TPH in each of the samples. The chromatographic contribution by the reagent blank was subtracted from every chromatogram.

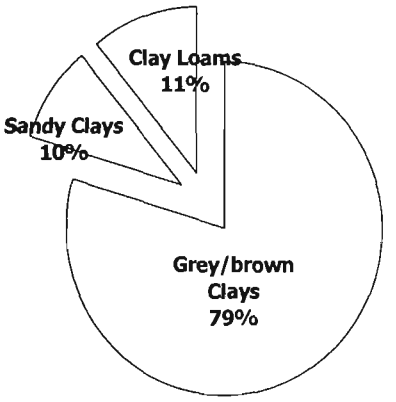

Figure 4.4: Percentage of each clay type.

The concentrations for each of the TPH fractions ranged 100-19,000 mg/kg for TPH (C_{10}-C_{14}) with a mean of 9,550 mg/kg, 120-8,100 mg/kg for TPH (C_{15}-C_{28}) with a mean of 4,110 mg/kg and 120-6,700 mg/kg for TPH (C_{29}-C_{36}) with a mean of 3,410 mg/kg respectively. The soils contained a wide TPH range with a minimum of 100 mg/kg and a maximum of 19,000 mg/kg with a mean of 9,550 mg/kg. Among the 84 tested samples of contaminated soils 21 were determined to contain similar TPH (C_{10}-C_{14}) concentrations by sonication and Soxhlet extraction techniques. The remainder was producing higher concentrations by Soxhlet extraction.

Samples containing similar concentrations of TPH by the two extraction techniques contained only 50 mg/kg of the TPH. There were only two samples with the same concentrations of TPH (C_{15}-C_{28}) fraction obtained by the two extraction techniques and the rest produced higher concentrations for Soxhlet. These two samples were further examined and one was detected at 50 mg/kg and the other at 6,700 mg/kg. There were 29 samples with similar concentrations of TPH (C_{29}-C_{36}) fraction obtained by the two extraction techniques and the rest produced higher concentrations for Soxhlet extraction. It was noted that samples containing similar concentrations by the two extraction techniques were only 50 mg/kg (which would have been the background contamination of TPH on the site and this concentration was twice the limit of detection of TPH). This variation is most likely due to the tightly compacted texture of the

clay soils, which require stronger extraction conditions to be released from the soil into the solvent prior to analysis. Figures 4.6 contains the concentration range of TPH extracted by

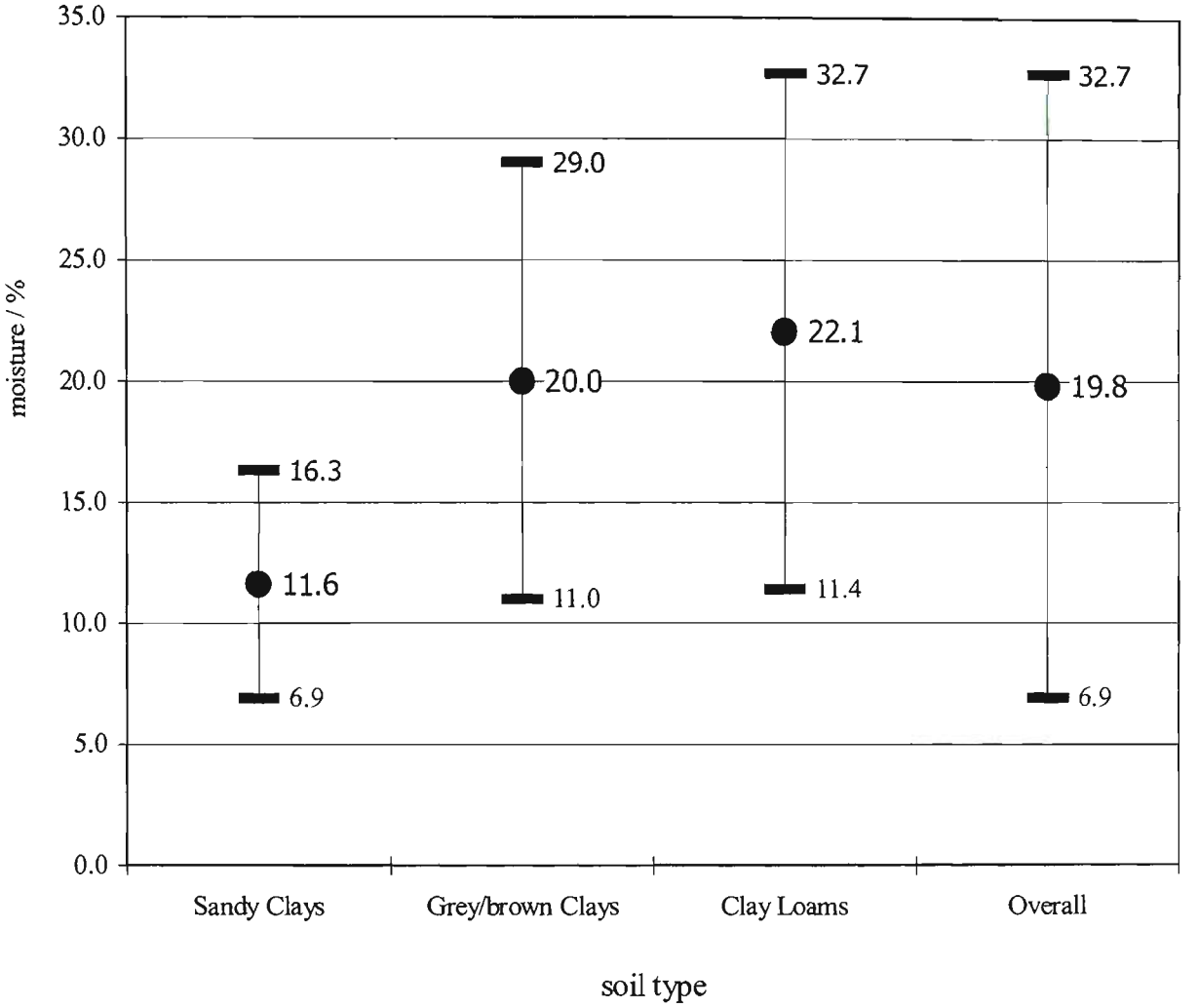

Figure 4.5: Percentage moisture range.

The TPH fraction concentrations were compared by using paired t-test. The calculated t-test results between sonication and Soxhlet extractions at 95% confidence interval are 5.28, 6.79 and 4.75 respectively. The $t_{critical}$ value is 1.96 for n-1 degrees of freedom. Therefore $t_{calculated}$ is greater than $t_{critical}$ for the three fractions, the null hypothesis is rejected and the two extractions produce statistically different concentrations with the Soxhlet being higher. Figures 4.7-4.11 shows histograms of TPH (C_{10}-C_{14}), (C_{15}-C_{28}), (C_{29}-C_{36}) and (C_{10}-C_{36}) respectively. The histograms for each of the fractions are presented in two parts to obtain

better data representation. This study concludes that clay soils contaminated by TPH C_{10}-C_{14}, C_{15}-C_{28}, C_{29}-C_{36} (i.e. C_{10}-C_{36}) generates statistically greater TPH concentrations by Soxhlet

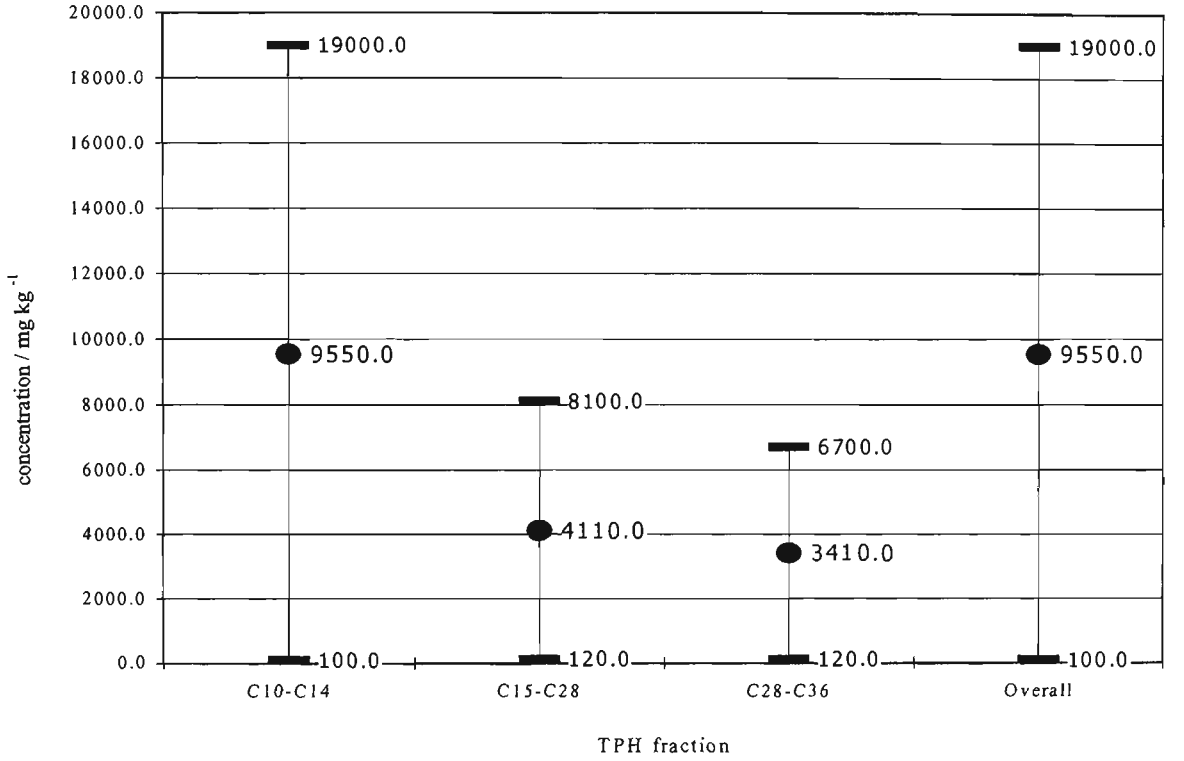

Figure 4.6: Concentration range for the TPH fractions using sonication extraction.

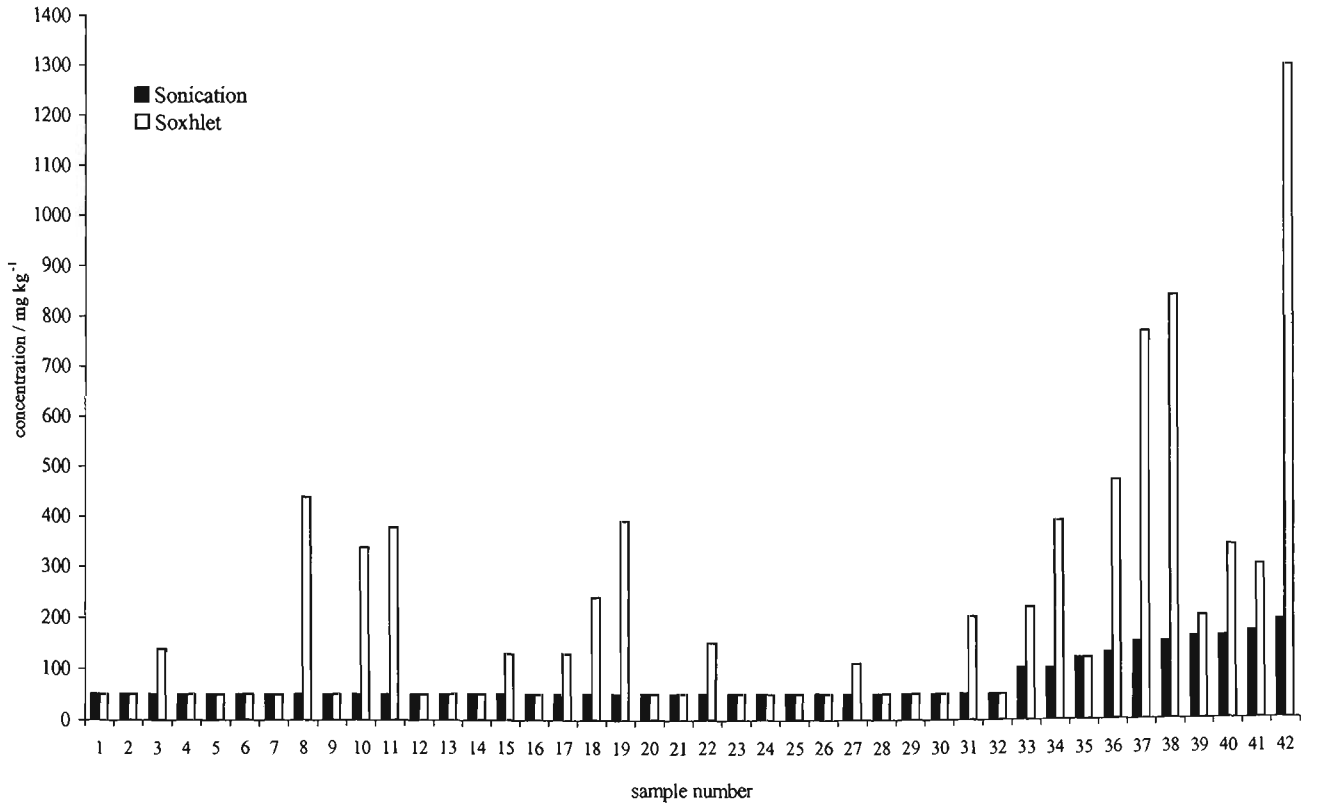

Figure 4.7a: Comparison of TPH (C_{10}-C_{14}) concentrations by sonication and Soxhlet.

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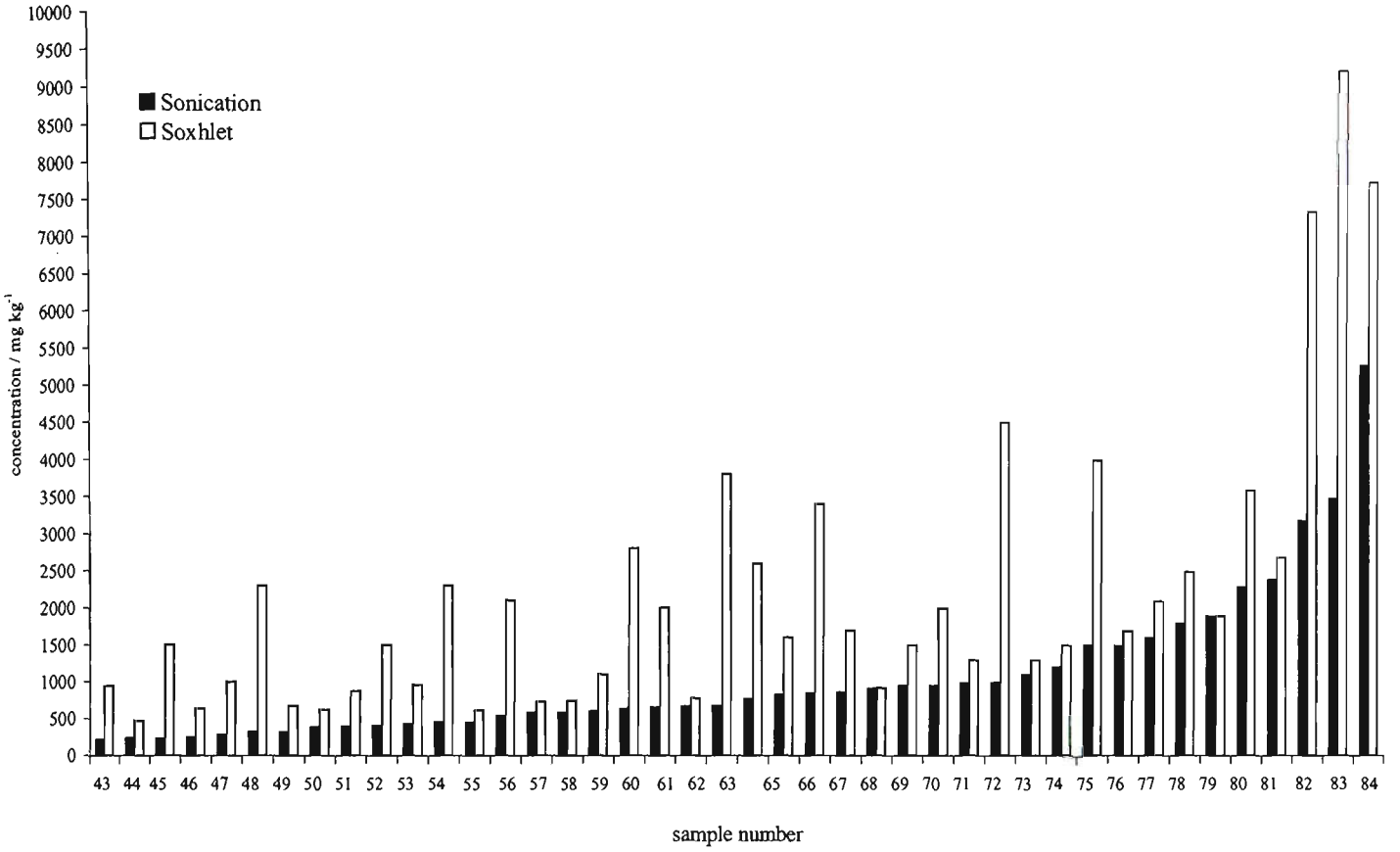

Figure 4.7b: Comparison of TPH (C_{10}-C_{14}) concentrations by sonication and Soxhlet.

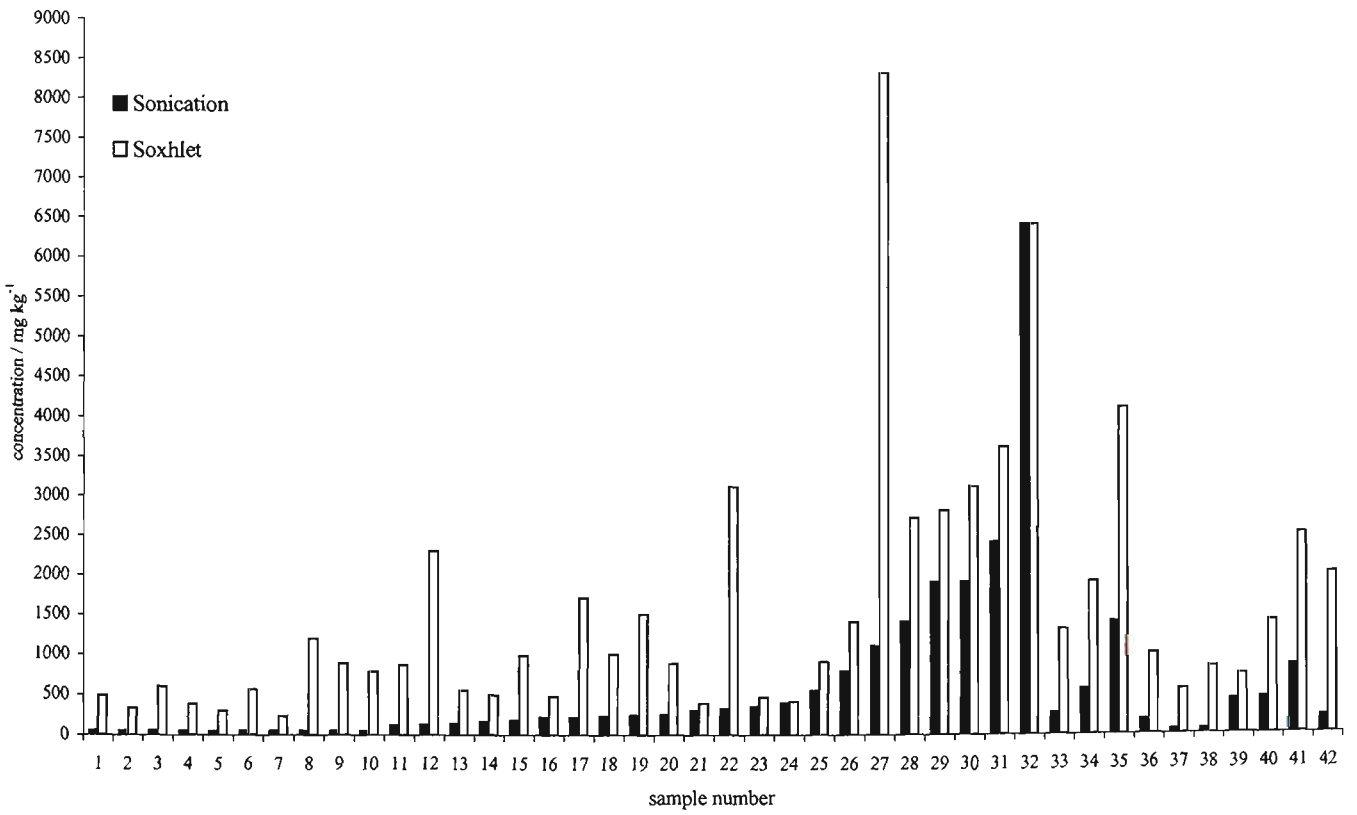

Figure 4.8a: Comparison of TPH (C_{15}-C_{28}) concentrations by sonication and Soxhlet.

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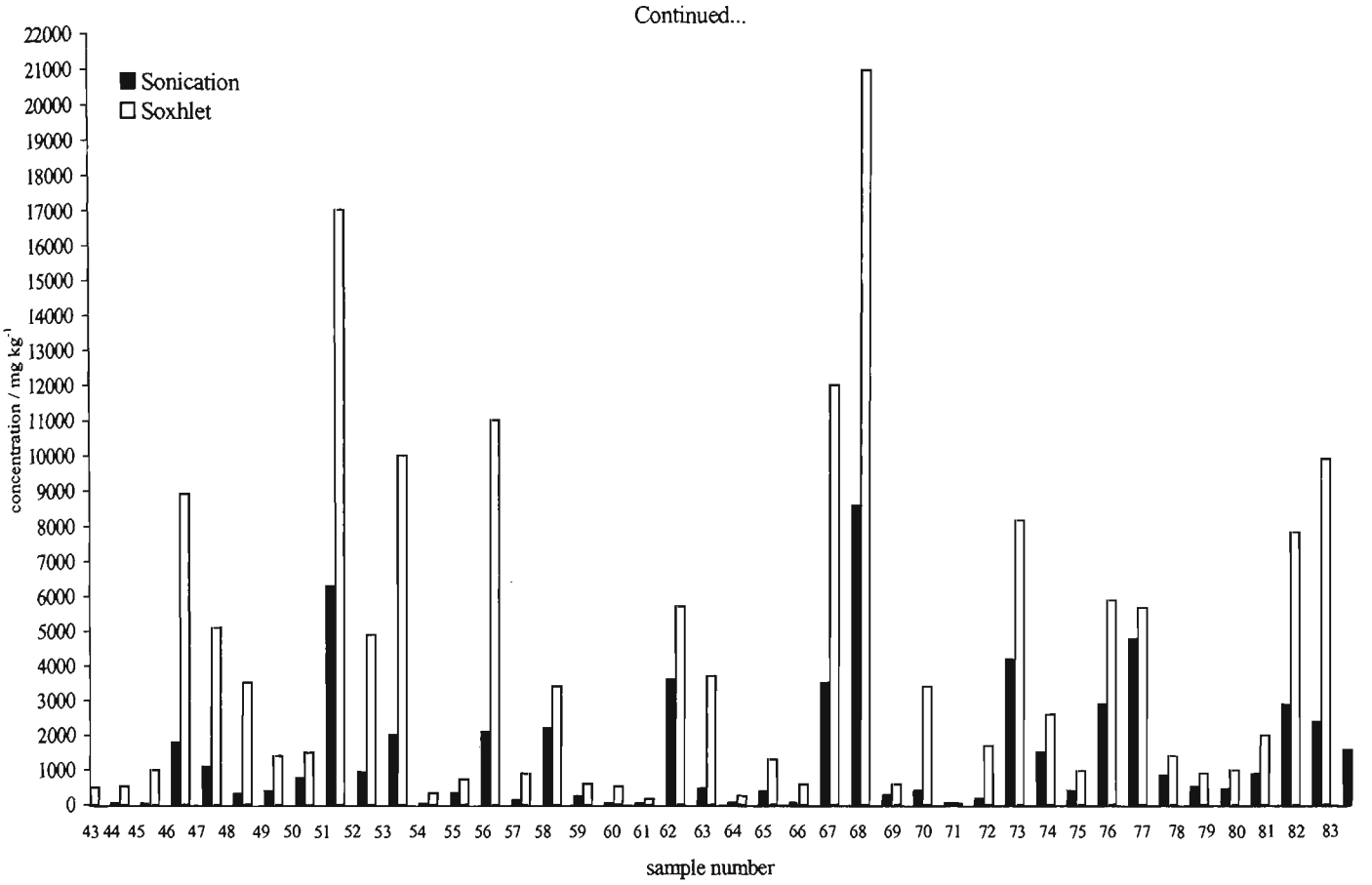

Figure 4.8b: Comparison of TPH (C_{15}-C_{28}) concentrations by sonication and Soxhlet.

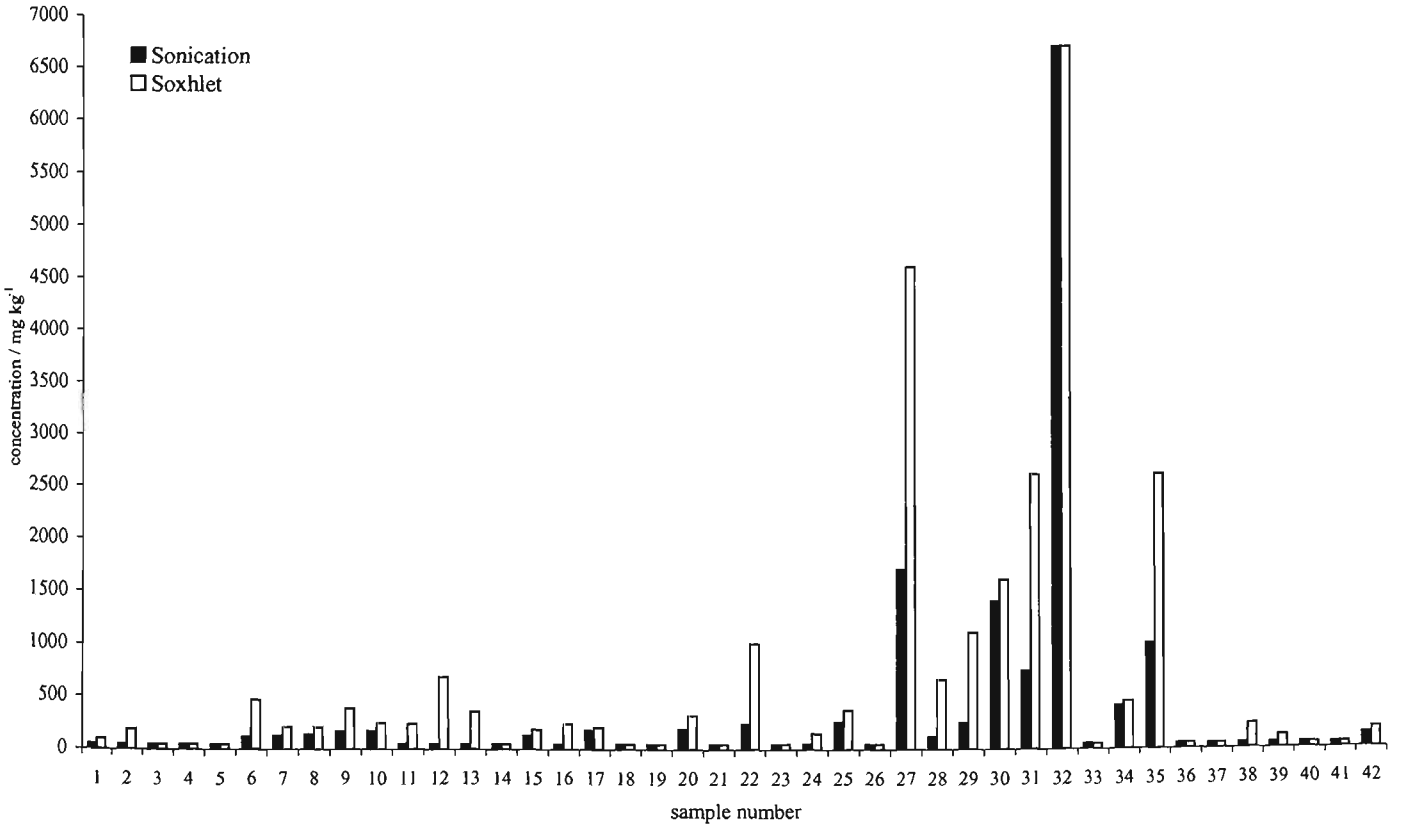

Figure 4.9a: Comparison of TPH (C_{29}–C_{36}) concentrations by sonication and Soxhlet.

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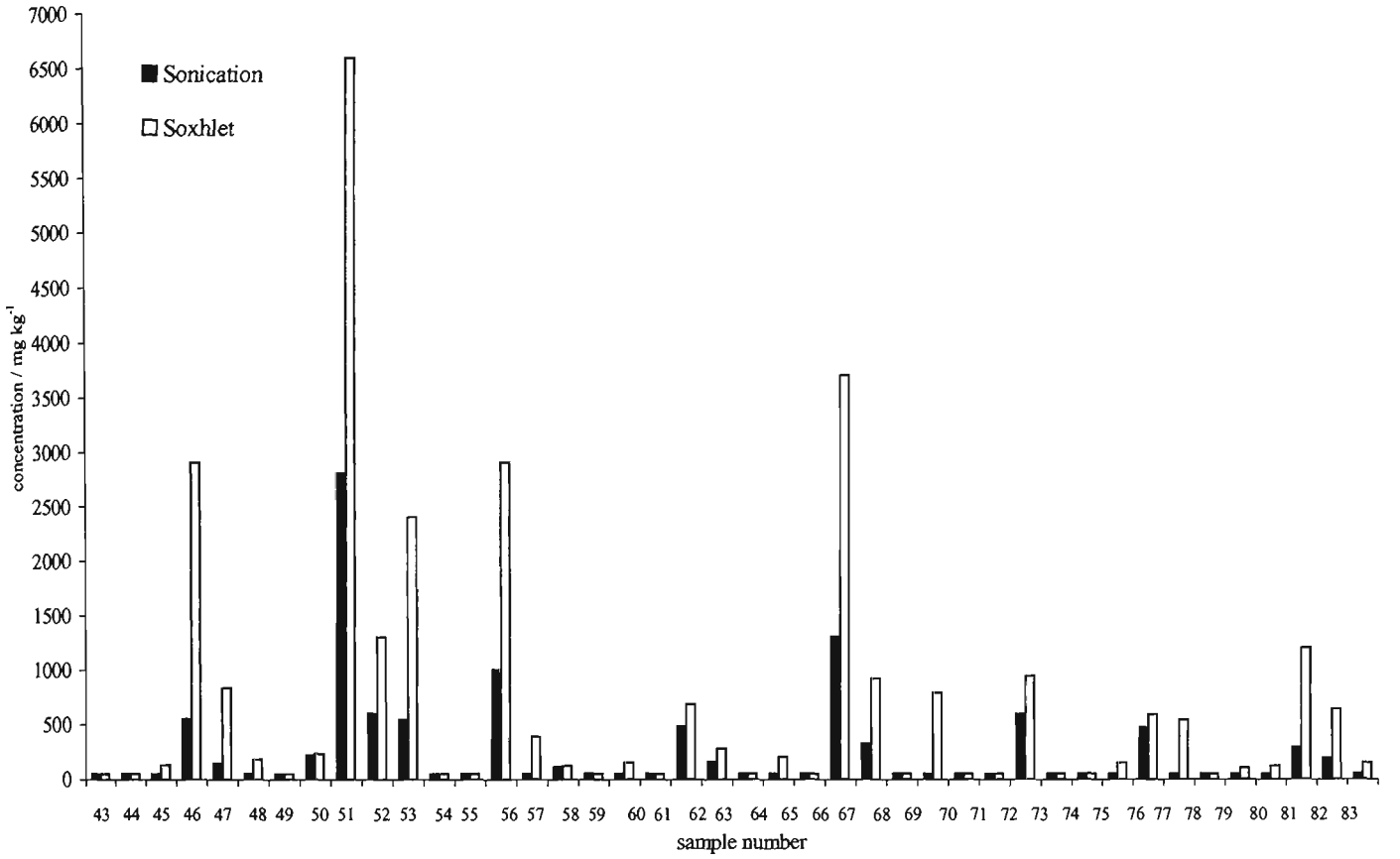

Figure 4.9b: Comparison of TPH (C_{29}–C_{36}) concentrations by sonication and Soxhlet.

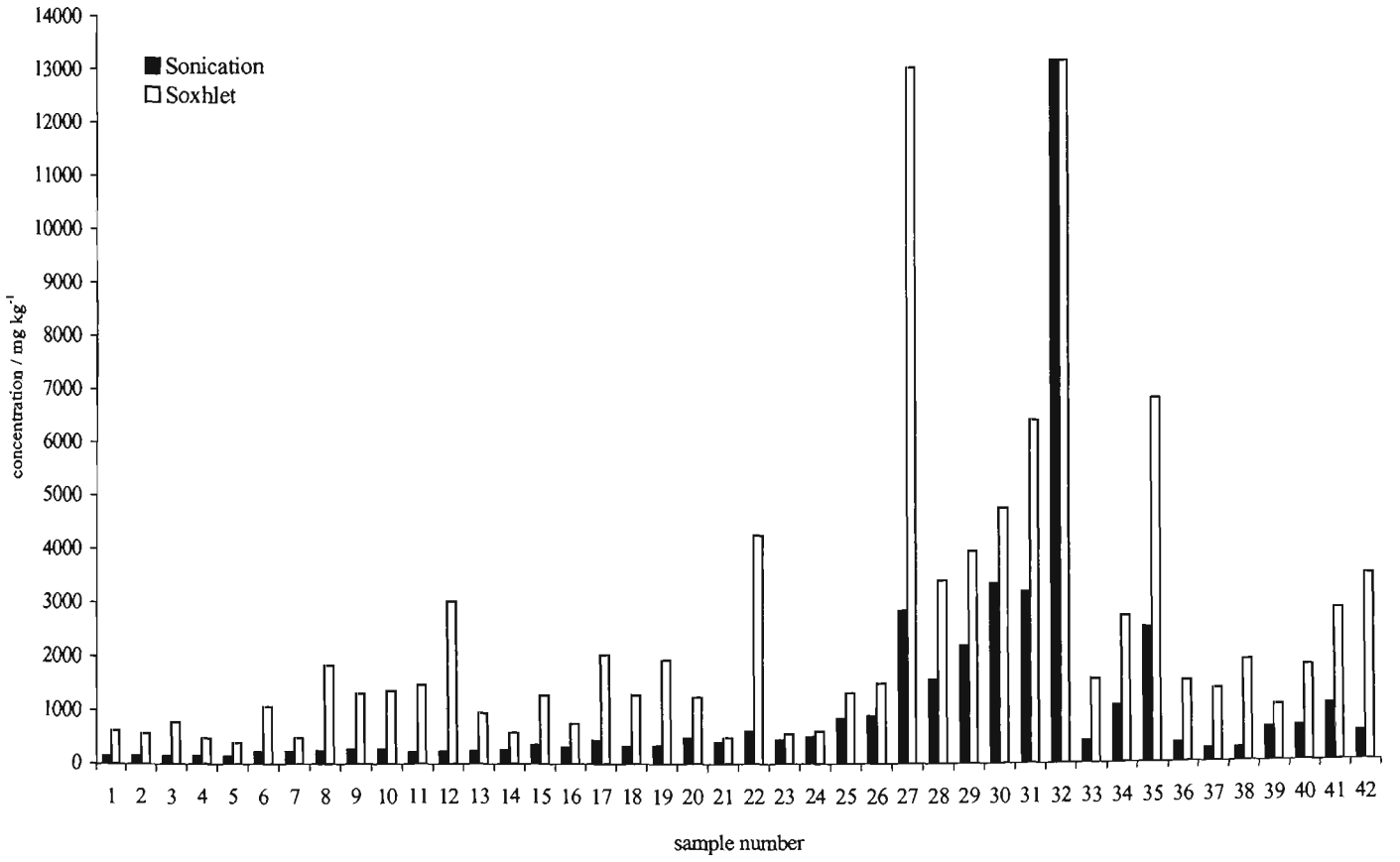

Figure 4.10a: Comparison of TPH (C_{10}–C_{36}) concentrations by sonication and Soxhlet.

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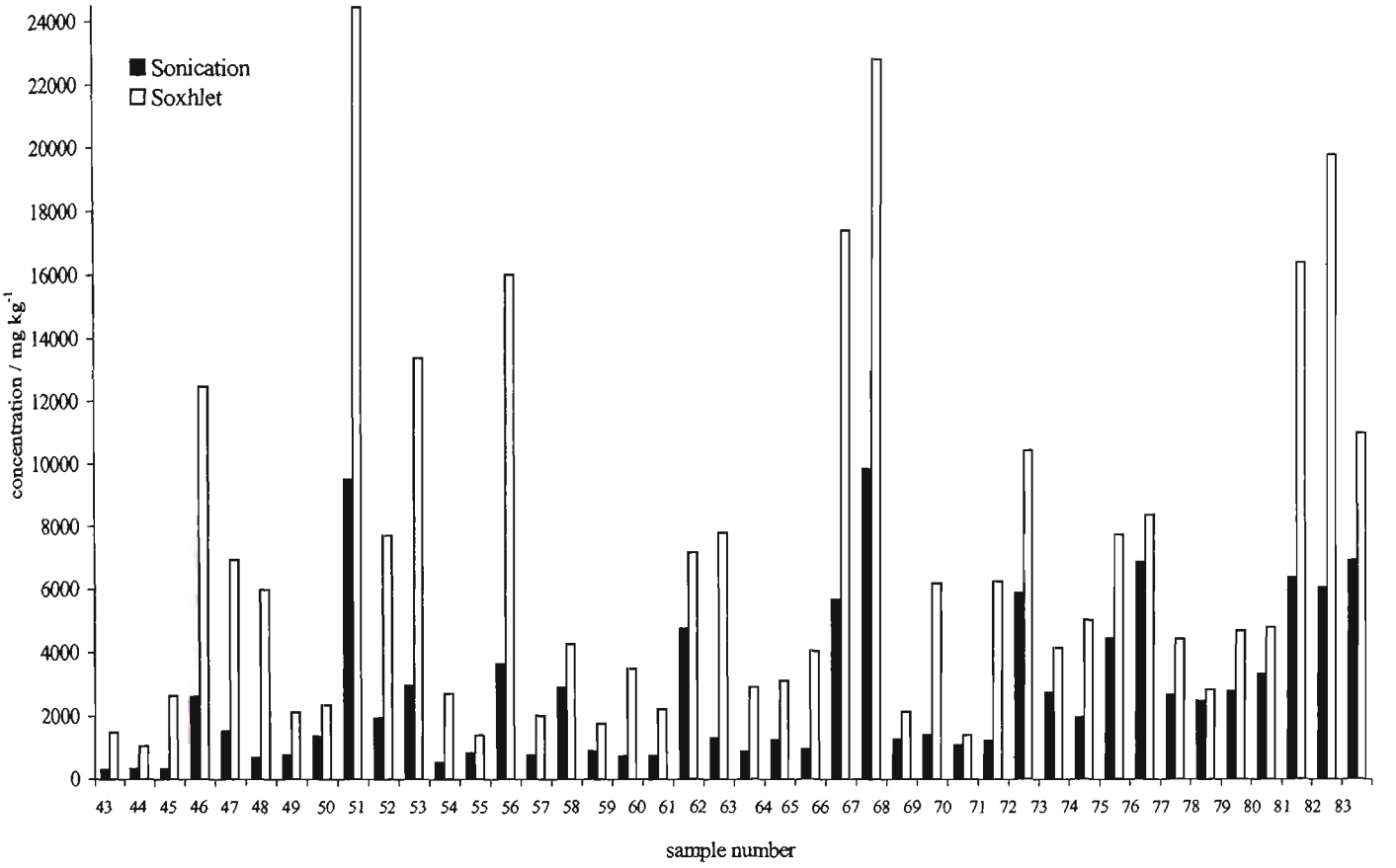

Figure 4.10b: Comparison of TPH (C_{10}–C_{36}) concentrations by sonication and Soxhlet.

Figure 4.11 contains the TPH (C_{10}-C_{36}) concentrations by Soxhlet extractions plotted against their corresponding sonication concentrations. This figure demonstrates that the data points are closely clustered around the lower left corner but towards the upper right corner of the plot they are markedly spread out. With the aid of the regression analysis facility of the Excel® 97 Worksheet a trend line is drawn to the scatter plot based on a power regression model. The trend line passes through the origin and its equation is of the form

$$y = ax^b,$$

where a and b are constants; y is the dependent variable representing the TPH concentrations by Soxlet extraction; and x is the independent variable representing the TPH concentrations by Sonication extraction. The value of a = 14.835 and that of b = 0.765. Hence

$$y = 14.835x^{0.765}.$$

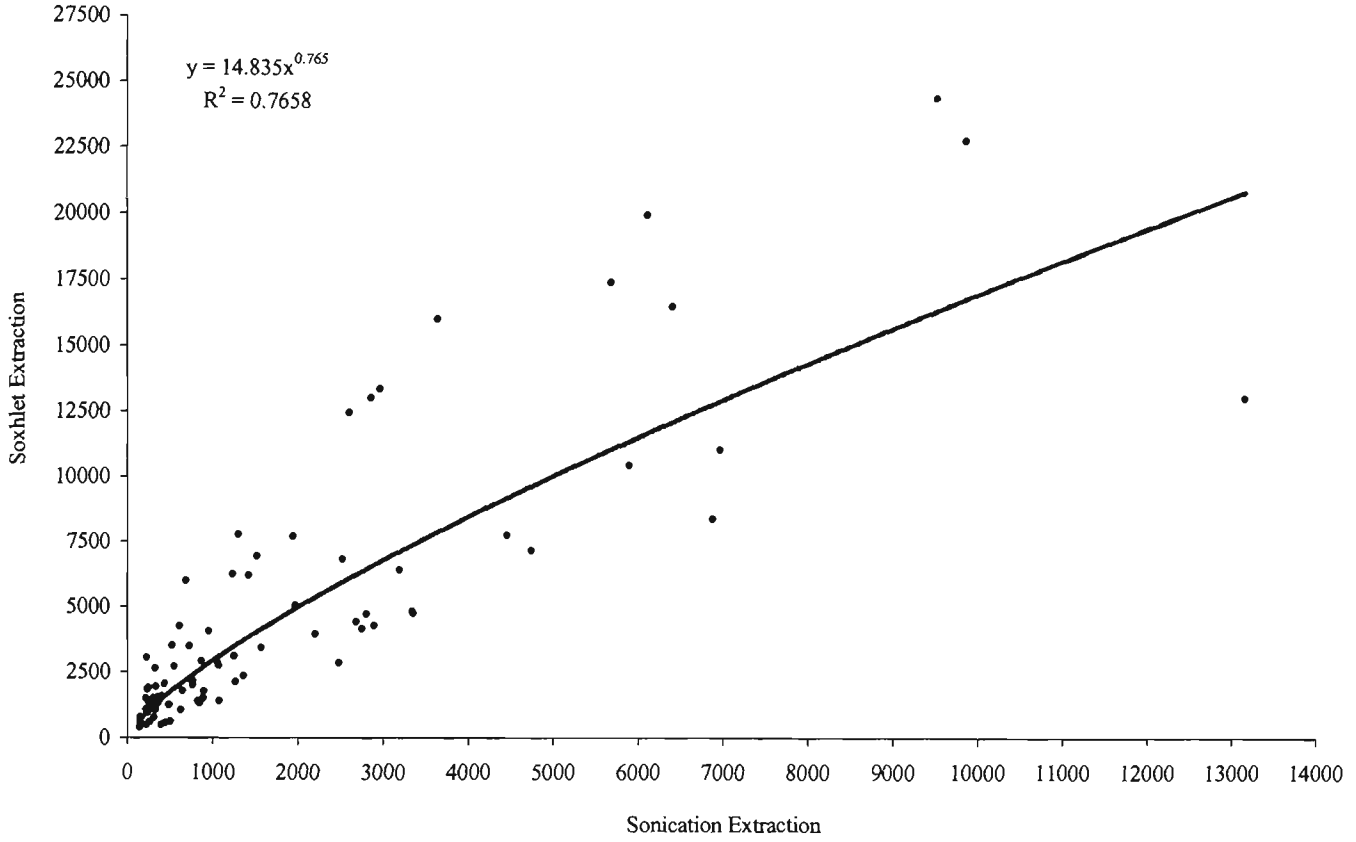

Figure 4.11: Scatterplot of TPH (C_{10}–C_{36}) concentrations by sonication and Soxhlet extractions.

A commonly used measure of the goodness of fit of a regression model is the coefficient of determination, denoted by R^2. R^2 indicates the proportion of variation in the dependant variable (the y values) which can be explained or accounted for by the regression model. The coefficient of determination for this power regression model calculated is 0.7658 (76.58%). This implies that the regression model determined for the variables of the Soxhlet extractions and the variables of sonication extractions is a good fit since 76.58% of the variations in the TPH (C_{10}-C_{36}) concentrations extracted by the Soxhlet method can be explained by the equation of the regression model.

4.4 Conclusion

This study concludes that clay soils contaminated by TPH fractions C_{10}-C_{14}, C_{15}-C_{28}, C_{29}-C_{36} and C_{10}-C_{36} will generate statistically higher concentrations when the extraction technique is by Soxhlet than by sonication under the conditions used in this trial. This variation is most

likely due to the tightly compacted texture of the clay soils compared to soils which are loosely packed such as sandy soils. It should therefore be noted that if TPH (C_{10}-C_{36}) analysis are to be conducted on soil collected from one site, it is necessary to use the same extraction technique to obtain precise concentrations. If samples were analysed by different extraction techniques then the concentration trends will not be seen due to variation in extraction efficiency. However the accuracy of the data will be biased towards Soxhlet extraction than those obtained from sonication extraction.

This finding shows a relative underestimation of the TPH concentration in contaminated soils when the soil is extracted by the sonication extraction technique and therefore since most commercial laboratories use the sonication technique for the extraction of soil they most likely will be underestimate the "true" TPH concentration. Since the TPH does not have a comprehensive definition it is difficult to propose a "true" value.

4.5 References

(1) Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites, (1992). Australian and New Zealand Environment and Conservation Council (ANZECC) and National Health and Medical Research Council (NH&MRC), Canberra, Australia.

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Chapter Five: Investigations on Extraction Conditions for TPH (C_{10}-C_{36})

5.1 Introduction

Since there are a multitude of variables which can be monitored during an extraction process this chapter examines some of these parameters. The assessments are carried out by maintaining some of the variables constant while fluctuating the others to determine if there are statistical differences in the TPH measurements. Extraction of TPH in soil is an important analytical step within any given analysis. This chapter examines some of the specific extraction conditions applied to soil for the separation of TPH. Examples of extraction methods are (i) extracting analytes into a solvent, (ii) heating the samples to vaporise the volatile fraction and (iii) purging samples with an inert gas to remove volatile components[1]. The USEPA Office of Solid Waste has published a series of methods (SW-846) which contain these extraction steps[2]. In this series there are approximately twenty methods addressing extraction and preparation of organic chemicals for analysis[3-22].

There are two groups of TPH requiring extraction from soil and are broadly classified into (a) volatile petroleum hydrocarbons containing C_6-C_9 (gasoline range) and (b) semi-volatile petroleum hydrocarbons containing C_{10}-C_{36} (diesel and lubricating oil range) [1]. Reliable analytical data for both the volatile and semi-volatile TPH contamination in soils is critical when making decisions during land transactions and site developments[23-24]. The determination of TPH can be performed using a variety of extraction, detection and quantification techniques. The commonly used extraction techniques for isolating volatile and semi-volatile TPH from contaminated soils are, (i) Soxhlet extraction (for semi-volatile TPH), (ii) extraction by soncation (volatile and semi-volatile TPH), (iii) extraction by tumbling (volatile and semi-volatile TPH), (iv) extraction by soaking (volatile and semi-volatile TPH), (v) headspace sampling (volatile TPH) and (iv) purge and trap (P&T) (volatile TPH). Soxhlet, sonication, tumbling and soaking require the use of solvents to extract the TPH from the soil. The headspace sampling technique and the P&T are specific for volatile TPH analysis[23,25-27]. GC techniques which are used in determining and quantifying TPH

require FID[25,28-33] or GC/MSD[30]. Standard reference soils or certified grade chemical standards are used in identifying and quantifying the extracted TPH. These reference materials should have known purities with a certification from the manufacturer outlining chemical concentrations. Examples of some reference materials include *n*-alkane standards such as *n*-C_{10}, fuel profile standards such as kerosene, deuterated internal standards (IS) such as d_5-chlorobenzene, deuterated surrogate standards (SS) such as d_8-toluene, monoaromatic hydrocarbons such as benzene and polycyclic aromatic hydrocarbons (PAH) such as naphthalene[25,30,34-36]. Therefore there is a multitude of options to choose from when one requires the extraction of TPH from soil. However depending on the chosen method there can be sufficient variations in TPH concentration due to variation in extraction conditions[23].

Chapter 3 of this thesis examined the effects on TPH (C_{10}-C_{36}) concentrations when three solvent systems were applied to extract soil. Chapter 4 examined the variations in recoverable TPH (C_{10}-C_{36}) from clay soil when Soxhlet and the sonication extractions were applied. Research carried out in this Chapter will be using a selected number of extraction techniques to investigate if there are optimum conditions to be used in analysing TPH contaminated soil. The research carried out in Chapter 3 has concluded that the acetone/dichloromethane (DCM) (1:1, v/v) is suitable for the extraction of TPH (C_{10}-C_{36}) and was used in this chapter.

Soils chosen from ten batches of contaminated soils are used in investigating optimum extraction conditions. Further characterisation of the soil batches are detailed within this chapter. The range of contamination in the ten batches of soil were estimated to be within 1,000-20,000 mg/kg. The research includes investigating extraction efficiencies: (a) between Soxhlet, sonication, tumbling and soaking (b) between a single and a multiple extraction (c) with variations in percent moisture (d) using variations in DCM/acetone volumes (e) using variations in DCM/acetone ratio.

Currently there are no set guidelines or agreed standard methods for the GC analysis of TPH

(C_{10}-C_{36}) contamination in soil within Australia and most other countries[28-33]. This research will be carried out to demonstrate if there can be variations in TPH (C_{10}-C_{36}) recoveries with variation in the above identified extraction conditions. The of contaminated soils were collected from independent contaminated service station sites located around Australia representing clay and sandy type soils. The soils were homogenised and classified to identify soil types[37-38] and the moisture content of each batch of soil was determined in the laboratory [39-40]. The material and methods including chemicals, reagents and calibration standards were identical to those used in Sections 3.2.4, 3.2.5, 3.2.6, 3.2.6.1-3.2.6.3.

5.2 Material and Methods

5.2.1 Preparation of Soils

Among the ten batches of contaminated soils the sandy soil types were obtained from service station sites located in the western part of the continent (i.e. Perth, Australia) and the clay soils were obtained from service station sites located in the east (i.e. Melbourne, Australia). These batches were prepared individually to obtain representative and homogenous samples as required for the testing[39-42]. The homogenisation was conducted on each of the soils by first transferring into large stainless steel trays and removing stones and plant material. The contents of each tray were then homogenised using a mortar and a pestle to obtain a fine soil mix. The homogenised soils were placed in 1 L screw-cap glass jars and stored at 4 °C to obtain sub-samples as required during the project. The research was aimed at the resultant, TPH (C_{10}-C_{36}) contamination in the soils and therefore the initial losses of hydrocarbons during homogenisation were not considered to affect the outcome. The soils were sequentially numbered using 001-010.

5.2.2 Characterisation of Soils

The characterisation of soils was based on Northcote bolus manipulation method[37] described in Chapters 3 and 4. Appendix 5.7.1 contains a summary of the soil classification process.

The colour, grain size and presence of clumps ascertained. Maximum moisture content of the soils was 22% (w/w) by weight. The moisture content was analysed using the technique detailed in Section 2.6.4[40]. The moisture content was used to convert the TPH concentration to a moisture free-basis.

5.2.3 Moisture Effects Study

The moisture effects study was conducted to evaluate if the moisture content in a contaminated soil affects the TPH (C_{10}-C_{36}) extractability. Duplicate samples of soils 003-010 (see Table 5.1) were weighed in 10 g lots and mill-Q water was added.

Table 5.1: Moisture added to soils.

Soil Sample Number	Natural Moisture (w/w)	Moisture Range Added (w/w%)
003	7.9	17, 21
004	7.2	16, 18, 20
005	6.3	15, 17, 19, 21
006	12.9	15, 17, 19, 21
007	8.9	15, 21
008	6.8	9.0, 11, 6.0, 15, 17, 19, 21
009	3.0	5.0, 7.0, 9.0, 11, 6.0, 15, 17, 19, 21
010	6.0	8.0, 10, 12, 7.0, 16, 18, 20

Samples were extracted by tumbling for 2 h with 20 mL of DCM/acetone (1:1, v/v) with 10 g of anhydrous sodium sulfate. Tumbling extraction method was chosen for this study since it is used in many commercial laboratories around Austalia as a standard extraction technique. Supernatants were transferred to GC vials and the vials were crimped and analysed by GCFID[43].

5.2.4 GCFID Analysis

This study was based on the GCFID technique described in Section 3.2.6.7. It was assumed that the total response of the GCFID measured between the retention times of the start of the *n*-C_{10} peak to the end of the *n*-C_{36} peak was due to the TPH (C_{10}-C_{36}). The measurements were taken by baseline-to-baseline integration. The responses of the solvent blank was subtracted to remove solvent interference[44]. The identification by the GCFID was carried out by comparing chromatographic profiles of petroleum products such as kerosene with the

profile of the soil extract. However, these patterns were complex due to the degradation of the petroleum products by weathering[45-47].

5.2.5. Analysis of the Chromatograms

The detection limit of the TPH (C_{10}-C_{36}) was chosen by using the sensitivity of the FID for hydrocarbons[48]. The minimum concentration of TPH (C_{10}-C_{36}) used in this study was determined to be 250 mg/kg for each contaminated soil. If any of the TPH (C_{10}-C_{36}) concentrations were less than the 250 mg/kg they were rejected and assumed to be zero in statistical applications [49-50].

5.2.6 Extraction Methods

5.2.6.1 Soxhlet Extraction

The Soxhlet extraction equipment was modified to obtain the optimum extraction time by assembling a Soxhlet system with a round-bottom flask containing two necks, the side neck used for collecting sub-samples during the extraction process. Homogenised soil (25 g) was weighed into a Soxhlet thimble and the thimble was placed in a Soxhlet extraction tube above a two-neck, round bottom flask containing 300 mL of DCM/acetone (1:1, v/v). The second side neck contained a thermometer probe holder sealed with a Teflon™-lined silicone septum, to withdraw a 100 μL aliquot from the solvent reservoir. The Soxhlet assembly was placed on a boiling water bath with a running water condenser. A 100 μL aliquot was withdrawn at timed intervals with a syringe. The intervals were chosen according to the siphoning drain times when the thimble reservoir was completely drained. The aliquot collection frequency was designed to be the highest within the first hour. The 100 μL reservoir aliquot was placed into a 200 μL limited volume insert in a 2 mL GC vial and crimped. The samples were analysed using the conditions described in Section 3.2.6.7.

5.2.6.2 Sonication Extraction

The sonication extraction was applied by weighing 10 g of homogenised soil into a 125 mL glass jar, mixing with 20 mL of DCM/acetone (1:1, v/v), and sonicating for 20 min. A 10 g

portion of anhydrous sodium sulfate was added, mixed using a glass rod, and the mixture was sonicated for a further 2 h. An aliquot of the supernatant was transferred into a GC vial and the vial crimped. The samples were analysed using the GC conditions described in Section 3.2.6.7. This method is an accredited method of the National Association of Testing Authorities (NATA) of Australia for TPH (C_{10}-C_{36}) analysis in soil.

5.2.6.3 Extraction by Tumbling

The tumbling extraction method was based on submissions made to Standards Australia Working Group EV/8/2/2, extraction of total petroleum hydrocarbons[28]. The tumbler was designed using the conditions specified in SW 846 methods 1311[51] Toxicity Characteristic of Leachable Properties (TCLP). This method is an accredited method of NATA, Australia for TPH analysis in soil. A 10 g portion of soil was weighed into a 125 mL glass jar with 10 g of anhydrous sodium sulfate and extracted with 20 mL DCM/acetone (1:1, v/v) mixture. Samples were tumbled in a mechanical tumbler end-over-end at a tumbling rate of 30 ± 2 tumbles/min. The extractions were conducted in duplicate and the tumbling times were varied from 1, 2, 5, and 18 h to obtain the optimum time. Supernatants were transferred to GC vials which were crimped and analysed using the GC conditions described in Section 3.2.6.7.

5.2.6.4 Soaking Extraction

Soaking extraction was based on a test method, which was developed at the Australian Government Analytical Laboratories[52] to analyse organochlorine pesticides in grain. Homogenised soil (10 g) was weighed into a 125 mL glass jar and 20 mL of DCM/acetone (1:1, v/v) was added followed by 10 g of anhydrous sodium sulfate. The jars were left overnight (18 h) for soaking and aliquots of the supernatant were transferred to GC vials and crimped. The samples were analysed using the GC conditions described in Section 3.2.6.7.

5.2.6.5 Single and Multiple Extractions

The following experiments were carried out to compare TPH (C_{10}-C_{36}) recoveries from soil. (i) 10 g portion of each soil was weighed into 125 mL glass jars with 10 g of anhydrous sodium sulfate and extracted by tumbling with 20 mL DCM/acetone (1:1, v/v) in duplicate for 2 h, (ii) maintaining all but the tumbling time and the solvent additions, a second lot of soil was weighed and extracted for 2 h in duplicate and a further 20 mL of DCM/acetone was added and the extraction continued for a further 2 h; this experiment consisted of a total tumbling time of 4 h and a total solvent volume of 40 mL, (iii) a third lot of soil was weighed in duplicate and extracted by maintaining all but the tumbling time and the solvent additions. The tumbling was continued for 2 h and a further 20 mL of DCM/acetone was added and the extraction continued for a further 2 h and finally a third 20 mL portion of DCM/acetone was added and the extraction continued for a further 1 h. This experiment consisted of a total tumbling time of 5 h and a total solvent volume of 60 mL. Supernatants from experiments (i), (ii) and (iii) were transferred to GC vials, crimped and analysed using the conditions described in the GC analysis in Section 3.2.6.7.

5.2.6.6 Application of the Michaelis-Menten and Wilkinson Fits

The Michaelis-Menten and Wilkinson fits were applied to the Soxhlet and tumbling concentrations obtained for each extraction to compute the optimum extraction times[49]. The time to reach optimum TPH (C_{10}-C_{36}) using the tumbling extraction was 2 h at a tumbling rate of 30 ± 2 tumbles/min. The time to reach optimum TPH (C_{10}-C_{36}) using the sonication extraction was 2 h using a Branson Ultrasonic bath (950 W) at an RF frequency of 47 kHz (± 6%). The optimum extraction time for the sonication was obtained from the validation data to be 2 h [29]. A samples of plots are presented in Appendix 5.7.2.

5.2.6.7 Effects of Moisture Content on TPH

Multiple samples of soils were weighed in 10 g portions and mill-Q water was added in increments up to 21% (w/w) from the initial natural moisture contents as indicated in Table

5.2. Samples were extracted by tumbling for 2 h with 20 mL of DCM/acetone (1:1, v/v) and 10 g of anhydrous sodium sulfate. Supernatants were transferred to GC vials and the vials were crimped and analysed using the conditions described in Section 3.2.6.7.

5.2.6.8 Solvent Volume Effects

A 10 g portion of soil was weighed into a 125 mL glass jar with 10 g of anhydrous sodium sulfate and (i) extracted by tumbling with 20mL DCM/acetone (1:1, v/v) in duplicate for 2 h, (ii) maintaining all except the solvent volume, a second lot of soils was weighed and extracted for 2 h with 40 mL of DCM/acetone (1:1, v/v), (iii) third lot of soils was also weighed and extracted by tumbling for 2 h with 60 mL of DCM/acetone (1:1, v/v). Extracts were transferred to GC vials at the end of each tumbling time setting and the vials were crimped and analysed using GC conditions described in the Section 3.2.6.7.

5.2.6.9 Solvent Ratio Effects

A 10 g portion of soil was weighed into a 125 mL glass jar with 10 g of anhydrous sodium sulfate and extracted by tumbling with 20 mL DCM/acetone (1:1, v/v) in duplicate for 2 h. The volume ratios between DCM and acetone were varied at the ratios 9:1, 7:3, 1:1 and 1:9 (v/v) and each tumbled for 2 h. Extracts were transferred into GC vials and the vials were crimped and analysed using GC conditions described in the Section 3.2.6.7.

5.3. Results

5.3.1 Results of Soil Classification

The results of the soil typing confirmed that the contaminated soils used for the study varied between sand and clay (Table 5.2). The study provided three major types of contaminated soils namely, sand, clay and fine gravel. The moisture contents of the soils varied between 3-21.3% (w/w), which were within the set limit of 22% (w/w). The summary of statistical and the measurement uncertainty formula used during this study are summarised in Appendix 5.7.3.

Table 5.2: Soil classification results.

Soil	Soil Characteristics Type	Colour	Grain Size	Moisture (w/w, %)
001	Clay Grey brown	Light brown	Fine	21.3
002	Sand, with traces of organic matter	Brown	Fine	10.3
003	Sand with traces of organic matter	Brown	Fine medium	14.9
004	Fine gravel	Olive brown	Fine-medium grained	14.2
005	Fine sand	Light grey	Fine-coarse	13.3
006	Angular fine gravel	Brownish grey	Desiccated into blocks	12.9
007	Clay mixed with organic matter	Light Grey	Fine grained	8.9
008	Sand mixed with traces of clay and organic matter	Light greyish brown	Fine-medium grained	6.8
009	Sand with traces of organic	Brown	Fine grained	3.0
010	Sand with some fine gravel and organic matter (top soil)	Dark brown	Fine-medium	5.9

5.3.2. Results of Homogeneity Study

The mean and coefficients of variation (CV) in TPH concentration using the sonication extraction technique for each of the ten contaminated soils were determined. Appendix 5.7.4 contains an example using the results for soil 003. The coefficients of variation (CV) for the ten soils (four replicate analyses) are presented in Appendix 5.7.5. The CVs for seven out of the ten soil batches, were less than 10% (w/w) and this was considered sufficiently homogeneous. The CV's for the remaining three batches of soil were somewhat higher indicating a lesser degree of homogeneity.

5.3.3 Measurement of GCFID Precision

The precision of the GCFID measurement was achieved by assessing the repeatability of multiple GCFID injections. The CV of ten injections into the GCFID from one supernatant of soil was 0.7% (w/w) (Appendix 5.7.6). The CV of four replicate extracts taken from the same soil was 8.8% (w/w). Comparison of these two CVs demonstrates that the variation due to GCFID measurement was minimal in the overall method precision. The CVs of the ten soils are presented in Appendix 5.7.5. The range of CVs on four replicate analyses was between 2.6-18% (w/w) when the soils were extracted by sonication and analysed by GCFID.

5.3.4 Results of the Four Extractions

Soxhlet extraction results were calculated as a mean value for the four TPH (C_{10}-C_{36}) concentrations obtained using 3, 4, 5 and 6 h extractions. The ten soils reached optimum extraction within 2 h. When Dixon's 'Q'[49] test was applied to the results (Appendix 5.7.7), soils 006 and 009 contained TPH (C_{10}-C_{36}) concentrations which were above the critical value of 0.831 for a sample size of four. The outliers are represented in bold typing in Appendix 5.7.7. The outliers were removed prior to further statistical analysis. Appendix 5.7.8 contains the details of the uncertainty assessment for statistical parameters specified in Appendix 5.7.3. These includes the mean, standard deviation/$\sqrt{n}$ and the t-distribution value obtained from statistical tables[22].

The Dixon's Q test was applied to the results obtained using sonication extraction (Appendix 5.7.9). Appendix 5.7.10 contains the details of the uncertainty associated with the concentration measurement. The results are depicted in Appendix 5.7.13.

The tumbling extraction reached the optimum concentration within 2 h. Therefore the mean TPH (C_{10}-C_{36}) concentrations determined by the 2, 5 and 18 h duplicate results were used as replicate analysis. The application of the Dixon's Q test (Appendix 5.7.11) to the TPH (C_{10}-C_{36}) concentrations indicates that the data were below the critical value of 0.621 (sample size of six). Appendix 5.7.12 contains the details of the uncertainty associated with the concentration measurement. The results are depicted in Appendix 5.7.13.

Dixon's Q test was not applied to these results due to the low replicate numbers tested. The statistical data including the mean, standard deviation and CV% are included in Appendix 5.7.14. Appendix 5.7.15 contains the details of the uncertainty associated with the concentration measurement. The results are depicted in Appendix 5.7.13.

5.3.5 Comparison of the Four Extraction Techniques

The soils were extracted using the Soxhlet, sonication, tumbling and overnight soaking techniques and the extracts were analysed by GCFID. The TPH (C_{10}-C_{36}) concentrations were assessed by determining the optimum extraction times. The mean concentration computed upon each extraction for each soil is included as bar charts in Appendix 5.7.13. The graphs are presented with the standard error of the concentration associated with the mean. The TPH (C_{10}-C_{36}) concentrations obtained for the ten contaminated soils ranged between 1,000-20,000 mg/kg. The comparisons of sonication with Soxhlet, tumbling with Soxhlet, tumbling with sonication are presented in Appendix 5.7.16. The concentrations obtained from the soaking extraction was not consistent due to the extreme variations in replicate analysis.

A second statistical test using statistical uncertainty (Appendix 5.7.2) is applied to decide if the difference of the mean concentrations (Δ), obtained from sonication extraction and Soxhlet extraction exceeds the statistical uncertainty, U. Therefore, if the difference of the mean concentrations (Δ) is either less or equal then any of the two extraction techniques produce statistically similar concentrations for TPH (C_{10}-C_{36}). If Δ is greater than U the extractions do not produce statistically similar concentrations. Appendix 5.7.13 include the comparison of the extraction technique for the ten contaminated soils. The error obtained for extraction by soaking is wider than the errors for the rest of the extraction techniques most likely due to the inconsistency of the technique.

5.3.6 Results of the Comparison of Single and Multiple Tumbling Extractions

Results for TPH (C_{10}-C_{36}) by the single and the multiple tumbling extractions of the soils are tabulated in Appendix 5.7.17. The standard error of the mean concentration associated with each extraction time, is presented in Appendix 5.7.18.

5.3.7 Results of the Comparison of TPH with Variable Moisture

The results of moisture variation studies are tabulated in Appendix 5.7.19. The original moisture content of each of the samples were not adjusted and the natural moisture present in each sample was used as the initial moisture reading. Therefore the moisture contents were variable depending on initial natural moisture. Some samples were tested on a wider range of moisture than others. The mean of duplicate TPH (C_{10}-C_{36}) concentrations are included in Appendix 5.7.20 with the error bars associated with the standard error from the mean concentration.

5.3.8 Concentration Effects due to Solvent Volume

The results of change in solvent volume used for the extraction of the TPH (C_{10}-C_{36}) are tabulated in Appendix 5.7.21. Soils were tested for solvent volume effects in duplicate by extracting them the using tumbling extraction method. The mean TPH (C_{10}-C_{36}) concentrations obtained are presented in Appendix 5.7.22 including the standard error associated with the mean concentration.

5.3.9 Concentrations Effect due to Change in DCM to Acetone Ratio

The TPH (C_{10}-C_{36}) concentrations obtained by computing the mean values of duplicate analyses, conducted with each solvent ratio are tabulated in Appendix 5.7.23. The results are depicted as histograms in Appendix 5.7.24. The concentrations are depicted graphically in bar charts with the standard error associated with the mean concentration as an error bar for each solvent ratio.

5.4 Discussion

The results obtained from the study are summarised in Table 5.3 and discussed below.

5.4.1 Contaminated Soil Types

The contaminated soils collected from service station sites around Australia consisted of a range of soil types of varying colours, textures, moisture contents and homogeneity. The soils

included clay soils, sandy soils with traces of organic matter, fine gravel, fine sand, angular gravel, clay mixed with organic matter, sand mixed with organic matter, sand with traces of clay and organic matter and sand with some fine gravel and organic matter. The TPH (C_{10}-C_{36}) concentrations for the ten contaminated soils ranged between 1,000-16,000 mg/kg. This study was based on the hypothesis that the TPH (C_{10}-C_{36}) to be sufficiently homogeneous in the soil if the CV% of a mean of four replicate concentrations on a given sample was less than or equal to 20. Therefore the ten soils were within the specified CV% range to be regarded as homogeneous.

Table 5.3: Summary of results on extraction conditions.

Basic Soil Type	**Clay**	**Sand**	**Fine gravel**
Batches Tested	2	6	2
Approximate Concentration Range (mg/kg)			
by Soxhlet	2,100-3,200	1,200-15,900	1,300-1,800
by Sonication	1800-4,900	1,400-16,400	1,500-1700
by Tumbling	1700-2,600	1,300-20,000	1,400-2,600
by Soaking	1700-2500	1,400-18,900	1,400-1,800
Soxhlet vs Sonication	**Not Comparable**	Comparable	Comparable
Soxhlet vs Tumbling	**Not Comparable**	Comparable	Comparable
Sonication vs Tumbling	Comparable	Comparable	Comparable
TPH Recovery in Single vs Multiple Tumbling Extraction	Comparable	Comparable	Comparable
TPH Recovery with Variable Moisture	Comparable	Comparable	Comparable
TPH Recovery with Variable DCM/acetone Volume	Comparable	Comparable	Comparable
TPH Recovery with Variable DCM/acetone Ratio	Comparable	Comparable	Comparable

Soil samples were not oven dried or ground to maintain the quality similar to those tested for TPH in contaminated site assessments. Although oven drying and grinding can provide better homogenisation in soil these procedures can also cause changes to TPH concentration, the soil structure and the extraction efficiency. Conclusions reached from such experiments will therefore most likely mis represent real situations.

The precision studies conducted on the GCFID measurements indicated that the measurement step contributed to only < 1% (w/w) variation on multiple injections. Variation of replicate analyses for the same sample, over the entire analytical process was approximately 10% (w/w). Sandy type soil textures produced relatively low (approximately 5% w/w) variation among replicate analysis than the samples with clay and mixed soil matrices. Two of the soils (007 and 008) found to contain unevenly distributed pockets of oily tar type material which made them virtually impossible to homogenise using standard techniques.

5.4.2 Extraction Technique

Four extraction techniques were investigated in this study to determine if there were statistical variations in TPH (C_{10}-C_{36}). The optimum extraction time for Soxhlet was determined by periodic sampling and determining the TPH (C_{10}-C_{36}) concentrations. The TPH (C_{10}-C_{36}) concentrations were then applied to the Wilkinson variant of the Michaelis-Menten equation. This study indicated that the ten contaminated soils reached optimum TPH (C_{10}-C_{36}) concentrations within 2 h of extraction. Therefore contrary to specifications in most Soxhlet extraction methods, extraction times of 10 h or greater are not necessary to extract TPH from soil. Nine of the ten soils were analysed in replicates of four to obtain the mean TPH (C_{10}-C_{36}) concentration by Soxhlet extraction.

The optimum time for sonication extractions was validated to be 2 h. Similar to Soxhlet extractions, each of the ten soils were extracted in replicates of four by sonication extraction. No set of data contained outliers when the Dixon's Q test was applied. This may be due it to

being a simple application, this is more robust and reproducible than the Soxhlet extraction. The optimum time for tumbling extraction determined by the periodic sampling of extracts at set time intervals and analysing for TPH (C_{10}-C_{36}) was found to be 2 h. The tumbling extraction was carried out in replicates of four for each of the ten soils. No set of data contained outliers when Dixons Q test was applied. Similar to the sonication extraction, tumbling extraction was more robust than the Soxhlet extraction.

Extraction by soaking produced large variations among replicate analysis. Therefore the technique was not applied in further studies.

5.4.3 Comparison of Extraction Efficiency

The four extraction techniques were compared by applying a range of statistics to the TPH (C_{10}-C_{36}) concentrations obtained from replicate analysis of each soil. The statistics included the mean concentration for each of the soils when extracted by each technique, the standard deviation, the CV%, error of the mean concentration per soil per extraction technique, and a test to determine if the means of two measured values disagreed significantly. The pairs of extraction techniques compared were: tumbling against sonication, tumbling against Soxhlet and sonication against Soxhlet. Extraction by soaking was not used for the comparison.

Appendix 5.7.13 represent results for each of the ten soils. The extraction techniques for each of the samples were compared by two independent statistical methods: (i) if the error bars for two or more extraction techniques fell within the same range then the techniques were regarded to be comparable to each other, (ii) if statistical uncertainty, U was greater or equal to the difference of concentrations obtained by any two methods (Δ), then the two extraction techniques were assume to produce statistically similar concentrations and if U was less than Δ then the extraction techniques produced statistically non similar concentrations.

The results of the statistical tests demonstrate that the efficiency of Soxhlet extraction compared to sonication and tumbling techniques varies significantly for soils containing clay.

However, this variation is not significant for soils containing predominantly sand and gravel. Soils 001 and 007 which contained clay gave rise to TPH (C_{10}-C_{36}) data which were significantly different for Soxhlet extraction compared to sonication or tumbling. Additionally soil 007 produced TPH (C_{10}-C_{36}) concentrations which statistically differed between sonication and tumbling. This was a clay soil mixed with organic matter compared to soil 001, which contained grey-brown clay. Soils 004 – 006 and 009 which contained sand or gravel as the major constituents, gave rise to TPH (C_{10}-C_{36}) data which were not significantly different in concentrations for Soxhlet extraction compared to the sonication and tumbling. There were no statistical differences for these soils even when sonication and tumbling extraction was applied. Soil samples 002, 003 and 008 which were sand mixed with organic matter produced statistically different TPH (C_{10}-C_{36}) between sonication and Soxhlet extraction but this difference was not produced between concentrations achieved by tumbling and Soxhlet extraction. The TPH (C_{10}-C_{36}) concentrations for soils 002 and 003 were not statistically different however soil 008 was shown to be statistically different. Soil 010, was a sandy soil containing fine gravel and some organic matter similar to topsoil. This soil produced no significant differences between sonication and Soxhlet extraction, tumbling and Soxhlet and tumbling and sonication.

The variation between sonication and tumbling extractions was minimum but the sonication results were substantially greater for samples 007 and 008. The tumbling technique produced a marginally higher concentration for sample 010.

At least 50% of the soils tested by Soxhlet and sonication extractions produced significant statistical differences. Soils 001, 002 and 003 produced statistically lower TPH (C_{10}-C_{36}) concentrations for the sonication extraction than the Soxhlet extraction. These three soils contained clay and sand mixed with organic material. Soils 007 and 008 produced statistically lower TPH (C_{10}-C_{36}) concentrations for the Soxhlet extraction than the sonication extraction. These two soils were clay mixed with organic matter and sand mixed with organic

matter. Assuming that the Soxhlet extraction is the most vigorous technique among the four techniques assessed, it is possible that during the Soxhlet extraction process there are some losses of the TPH (C_{10}-C_{36}) fraction compared to the sonication extraction technique for these two soils. Also it is possible that there could have been localised high concentrations (i.e. small pockets of TPH) which did not homogenise due to the uneven distribution and therefore were undetected during the homogeneity testing. However it was clear that the clay soils produced higher TPH (C_{10}-C_{36}) concentrations by Soxhlet extraction than the other soil types except for the sonication extraction concentration for soil 007. This relationship was confirmed in Chapter 4 of this thesis.

The Soxhlet and the tumbling extraction technique comparisons show a substantial statistical difference for clay soils but do not show significant differences for other soil types. Seven of the ten soils compared by the two techniques produced comparable TPH (C_{10}-C_{36}) concentrations. The exceptions were samples 001 and 007 which were clay soil and TPH (C_{10}-C_{36}) concentrations on them for Soxhlet extraction, were marginally higher except for sample 010. This can also be caused by losses of volatile end of the semi-volatile components during the Soxhlet extraction process.

Extraction by soaking produced inconsistent replicate concentrations therefore the uncertainty was not determined. However, the comparison of the techniques for each sample indicated that the soaking extraction compare well with the other techniques on average for most samples. The soaking extraction technique is cheap due to a minimal use of complex extraction apparatus and energy.

Although the Soxhlet extraction technique is regarded as more effective in removing TPH (C_{10}-C_{36}) there can be losses during the extraction process due to the heating step. Additionally the setting–up and maintaining the analyses of large batches is not convenient. Sonication and tumbling extractions require moderate extraction times and losses due to

heating are minimal for these techniques. If ice blocks are used in the ultrasonic bath evaporation and related losses can be further controlled. Soaking extraction is more time consuming than the other three techniques. However it appears that the use of sonication and tumbling extractions will most likely produce lower TPH (C_{10}-C_{36}) concentrations in clay soils due to variations in extraction efficiency.

5.4.4 Single Against Multiple Extraction

Each soil sample was extracted by tumbling at three time intervals with the addition of solvent. Results of the studies conducted in duplicate are presented in Appendix 5.7.18. The error associated with the mean concentration of TPH (C_{10}-C_{36}) at each time interval was calculated and included as error bars for nine of the soils. The variation in concentrations for 2, 4, 5 h was assessed by comparing the ranges of error bars between the three histograms presented in each graph. The error bars overlapped for all except sample 003 (2 h extraction was outside the range). Therefore increasing the extraction time did not significantly effect the TPH (C_{10}-C_{36}) concentration.

5.4.5 Moisture Effects on TPH Concentration

Each soil sample was spiked with clean water at 3% (w/w) increments up to a maximum of 21% (w/w). Results for this study are presented in Appendix 5.7.20. The error of the mean concentration for the duplicate TPH (C_{10}-C_{36}) at each percent moisture level was calculated and presented as error bars in the histogram. The error bars were of similar range with the possible exception of sample 003 and sample 007. It was noted that sample 003 was the least homogeneous among the tested samples and sample 007 was found to contain pockets of TPH at variable concentrations. Therefore the variation in percent moisture within a sample (up to 21% (w/w)) appears to have little effect on the extractable TPH (C_{10}-C_{36}) concentrations in soil at least in the 1,00-20,000 mg/kg TPH.

5.4.6 Solvent Volume Effect on TPH Concentration

Each soil sample was extracted by tumbling with 100, 80, 60, 40 and 20 mL of DCM/acetone (1:1, v/v) to investigate if the solvent volume will effect the TPH (C_{10}-C_{36}) concentration. The results are presented in Appendix 5.7.22. The error associated with the mean concentration of TPH (C_{10}-C_{36}) for each extraction volume was calculated and presented as an error bar in the histogram. These error bars were of a similar range. However, no increments in extraction efficiency was observed for large volumes of extraction solvent.

5.4.7 DCM to Acetone Ratio Effect on TPH Concentration

Results of these studies conducted in duplicates are presented in Appendix 5.7.24. The results are comparable for the DCM/acetone mixtures of 1:9, 1:1, 7:3 and 9:1 (v/v) and so no significant statistical variations were observed with variations in solvent ratio.

5.5 Conclusion

The efficiency of the Soxhlet, sonication and tumbling extraction techniques varied with the variation in soil type and the volatility of the hydrocarbons present. For many of the soils, tumbling and sonication provided a comparable extraction efficiency to the Soxhlet technique and may be a more convenient procedure as long as there limitations are recognised. The heating process during Soxhlet extraction can contribute to losses of volatile components within the TPH (C_{10}-C_{36}) range. To obtain reliable concentrations of TPH (C_{10}-C_{36}) from clay soils it is important to use Soxhlet extraction since it appears to be a more efficient technique and the work carried out in Chapter 4 validates this conclusion. Additionally for soils containing TPHs with relatively high molecular weights (i.e. > C_{20}) and concentrations greater than 20,000 mg/kg, Soxhlet extraction is efficient compared to sonication and tumbling. This may be due to the heating step and the replacement of fresh solvent at each extraction cycle. Soaking extraction is recommended only for "one-off" analyses, which require only a screening or samples which does not require urgent analysis. For studies requiring continuos monitoring of TPH (C_{10}-C_{36}) it is highly recommended to apply only one extraction technique to avoid variations generated by changing of the techniques. If sonication or tumbling

extraction is chosen, it is preferable to analyse a selected number of samples, namely those with greater than 1,000 mg/kg TPH (C_{10}-C_{36}) by Soxhlet extraction to examine if the variations in achieved (C_{10}-C_{36}) concentrations are substantial. These results will indicate the variation between the technique. If the soils are of a similar type and the TPH components (profiles) are the same in all samples the relationship of concentrations obtained by the two extraction techniques can be depicted as a scatter plot with a linear relationship. This relationship will enable to convert concentrations achieved by one technique to the predicted concentrations from the other. For extraction by tumbling, sonication and Soxhlet, 2 h was found to be sufficient to achieve an optimum TPH (C_{10}-C_{36}) concentration [43].

With the possible exception of soils 003 (sand with traces of organic matter) and 007 (clay with organic matter), moisture content up to 21% (w/w) had little influence on the extraction of TPH (C_{10}-C_{36}). This study concludes that moisture contents up to 20% (w/w) do not influence the TPH (C_{10}-C_{36}) concentration. For the concentration range of 1,000-20,000 mg/kg, no increase in extraction efficiency was observed for solvent volume increments between 20-100 mL. It was noted during this study that the homogenisation of contaminated soils, especially those containing pockets of TPH either in the form of a grease type material or in the form of tar-balls of approximately 50-100 micron diameter was almost impossible.

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Chapter Six: Comparative Analysis of TPH by GCFID and GCMSD

6.1 Introduction

This chapter is designed to assess the detection techniques commonly used for TPH volatile and semi-volatile measurements. The measurements of TPH obtained by the two detectors will be statistically tested to determine if there are differences in the measurements. The chemical composition of petroleum products such as petrol, kerosene and diesel is complex and these contaminants can undergo transformation in soil. Detection and measurement methods which are highly specific are necessary to achieve identification of these products. Gas chromatography (GC) with flame ionisation detection (FID) and GC with mass selective detection (GCMSD) are two such methods which are used in total petroleum hydrocarbon (TPH) analysis[1-5]. TPH (C_{10}-C_{36}) is commonly defined in Australia as the total area between the start of the *n*-C_{10} peak and the end of *n*-C_{36} peak, calculated by integrating baseline-to-baseline and incorporating all components[6]. A drawback of this approach is the fact that non-hydrocarbons responsive to GCFID can also be present in this range. Although there are numerous methods proposed for the separation of petroleum hydrocarbons from non-hydrocarbons they are not comprehensive[7-9]. Thus chromatographic material such as silica, alumina and Florisil™, used for the removal of polar compounds in solvent cleanups, may also adsorb complex polynuclear aromatic hydrocarbons (PAHs) and influence the TPH content. Furthermore, non-polar chlorinated compounds can evade the separation process. By using a GCMSD library database and obtaining the ion profiles of the peaks, the major non-hydrocarbons can be identified and excluded from the TPH calculation. Figure 6.1 shows the GCFID profiles of: (a) a polychlorinated biphenyl (PCB) mixture and (b) a standard diesel fuel on a BP 5, 30 m column. The two profiles are within the TPH (C_{10}-C_{36}) range and may be mistaken for hydrocarbons unless the ion profiles are assessed (Figure 6.1).

Two approaches have been considered in this thesis, one for volatile TPH (C_6-C_9) and the other for semi-volatile TPH (C_{10}-C_{36}). The first approach is sampling TPH (C_6-C_9) by purge and trap (P&T), diverting the injection into two separate columns, one column being attached

to an FID and the other to a MSD (Figure 6.2). Both detectors are calibrated with the same standards. The concentrations obtained by the two detectors may then be statistically compared.

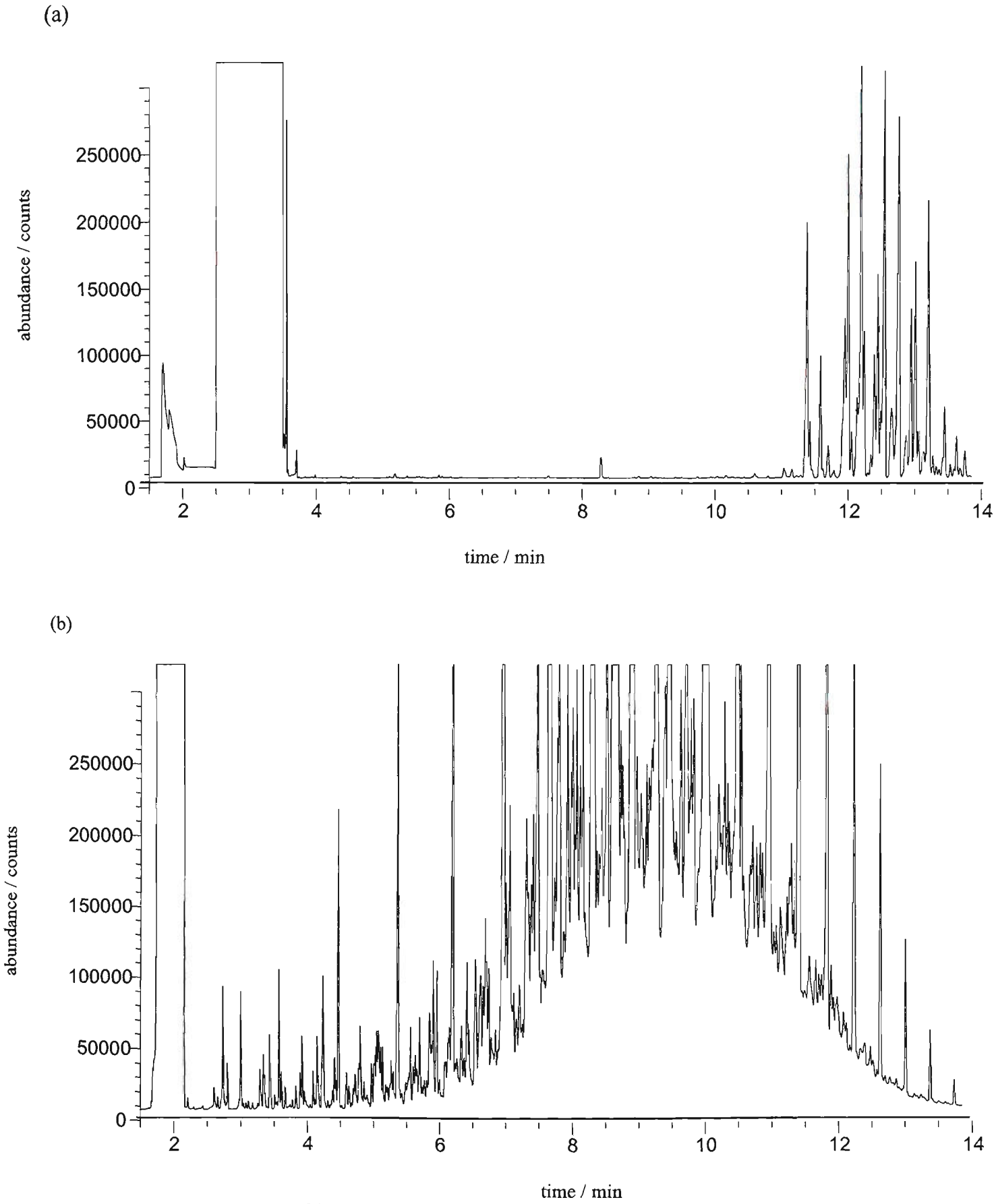

Figure 6.1: (a) GCFID profile of Arochlor 1262 (b) GCFID profile of diesel.

The second approach is a single extract of contaminated soil is divided into two sub-samples which are separately analysed for TPH (C_{10}-C_{36}) by GCFID and GCMSD.

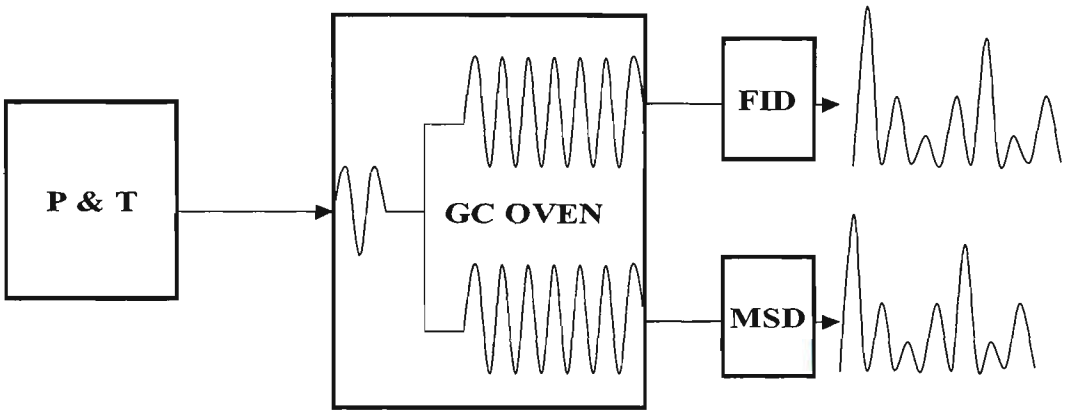

Figure 6.2: Instrumental design for diverting samples into the GCFID and the GCMSD.

6.2 TPH Analysis by GCFID

Martin and James[10] introduced GC for the analyses of organic chemicals in 1952 and this technique is currently used in many countries for TPH analysis in soil[11-14]. The FID of a GCFID senses the presence of a component different to the carrier gas and converts the information to an electrical signal[15-17]. The major components of the GCFID include a carrier gas supply and controls, an injector system for the introduction of samples, a chromatographic column and oven, the FID, an amplifier, signal processing and control electronics, computer-linked data processing software and a printer to generate reports. The response characteristics of a FID include sensitivity, selectivity and dynamic range. The linear dynamic range is 10^7 [6-17]. This detector has a broad range of selectivity for material that ionises in an air/hydrogen flame. The purpose of the detector is to monitor the carrier gas as it emerges from the column and generate a signal in response to variations in the components. The FID is the most widely used technique for the detection of organic compounds, including TPHs. The FID employs a flame produced by the combustion of hydrogen and air. The detector responds to an increase in ion concentration in the flame during the elution of hydrocarbons. A collector with a polarising voltage is applied near the flame, which attracts the hydrocarbon

ions and, in turn, produces an electrical response. This response is proportional to the amount of hydrocarbon in the flame at a given time. The FID temperature must to be kept above 100 °C to prevent condensation even when testing is not being carried out[16]. Condensation may reduce sensitivity and promote corrosion if chlorinated solvents such as dichloromethane (DCM) are used. FID is extensively used in TPH analysis due to its high sensitivity to hydrocarbons. Some important properties of an FID include it's high sensitivity to most organic compounds which can be volatilised, it's non-response to water, carbon dioxide and most carrier gas impurities, it's minimum effects on the baseline with fluctuations in temperature, carrier gas flow-rate and pressure, and it's linearity over a wide sample concentration range[15]. The major disadvantage is the non-selective nature of the detector especially in TPH (C_6-C_9) and TPH (C_{10}-C_{36}) analysis from soil extracts. A TPH chromatogram may contain over 100 peaks including hydrocarbons and non-hydrocarbons together with unresolved complex material (UCM). However, the FID does not have the capacity to discriminate or identify the differences in many compounds.

Technically the FID consists of a minute hydrogen-air flame burning at a small metal jet, with an electrode located above the flame to collect the ions formed from the molecules. The flame process is complex and direct ionisation is only a small contribution to the overall ionisation process[17]. In the flame, organic molecules undergo a series of reactions including thermal fragmentation, chemical ionisation, ionic and free radical reactions to produce charged species. When TPH enters the flame the thermal energy causes cracking and stripping of protons and terminal groups[17]. A pure hydrogen and air flame is designed to contain radical and excited species of hydrogen, oxygen and hydroxyl ions. When hydrocarbons are present in the flame, ionisation occurs with the amount being proportional to the number of molecules. The main flame process involves formation of $CH^{\cdot}$ radicals from the TPH molecules, which immediately react with oxygen radicals as follows:

$$-CH^{\cdot} + O^{\cdot} \rightarrow -CHO^{+} + e^{-}$$

The chemical nature of organic molecules influences the flame response and is corrected by the use of the "effective carbon number contribution"[15]. The ions travel to the collector electrode which is maintained at a negative potential with respect to the jet flame and an electrical current is generated. The sensitivity is in the range of 0.015 coulombs/g of carbon with a linear dynamic range of 10^7. The overall response varies slightly for a given type of compound and the carbon number. The signal is amplified and conditioned by an electrometer over 0-10 mV enabling a computer interface to easily produce the chromatogram and data. Figure 6.3 shows the typical components of a GC system.

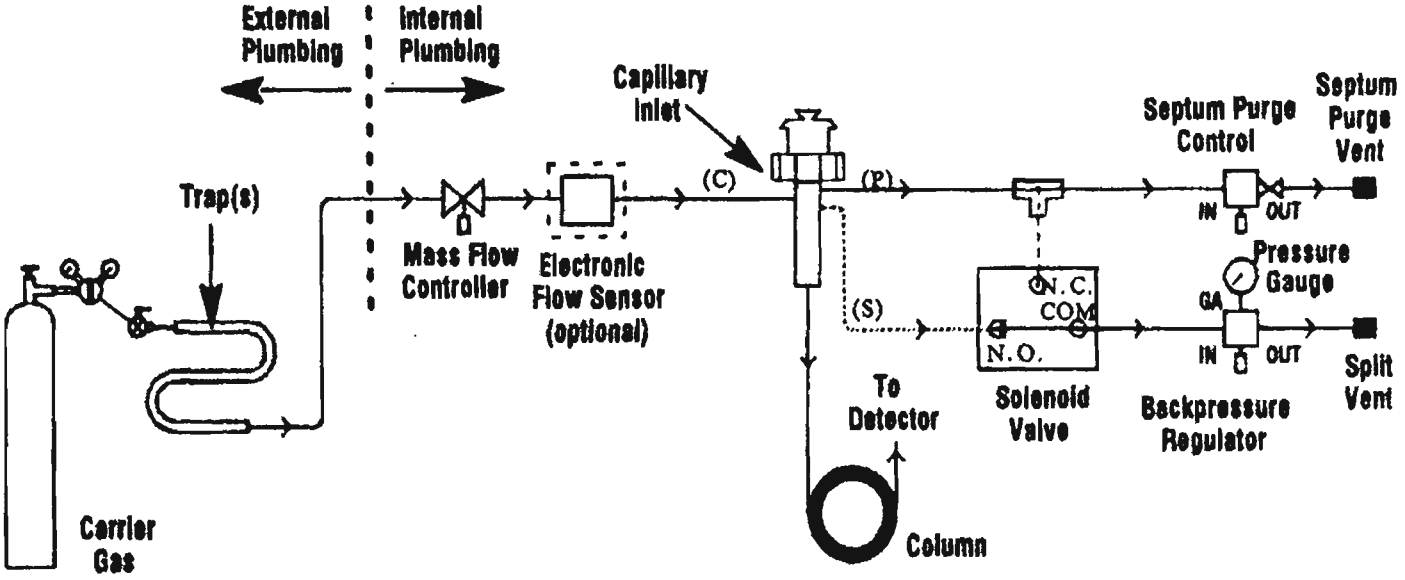

Figure 6.3: Components of a GC system (by courtesy of Hewlett Packard Australia).

6.2.1 Carrier Gas

The carrier gas is the mobile phase of the column used in transporting sample components through the column to the detector[18]. The individual partition and adsorption properties of the components, including the solvent and the TPH in the sample determines the rate that they move through the system. Helium is chosen as the carrier gas for TPH analysis due to it's smaller diffusion coefficient, relatively low molecular weight and the inert nature of the gas. The ancillary gases required for the FID are air and hydrogen. These gases are supplied from high-pressure gas cylinders, which are stored at pressures of up to 3000 psi. The quality of the gases used are 99.99% pure helium; air containing 78.1% nitrogen, 20.9% oxygen and

0.9% argon; and 99.98% pure hydrogen. These gases are further purified by passing them through a series of traps including a molecular sieve, charcoal and silica gel. Even small changes in carrier gas flow-rate can affect the separation of the components. Pressure regulators and flow-rate controllers are built into the carrier gas lines at the cylinder and the instrument to obtain a pulse-free and pre-set pressure and flow-rate. The flow control is used to counteract the changes in flow-rate. During temperature programming at constant pressure the flow-rate can change due to the increase in viscosity with increasing temperature. The flow controller maintains the flow-rate accurately over the full operating temperature range.

6.2.2 Sample Inlet System

The introduction of a sample into the GC is the first stage in the TPH analysis. Samples are introduced as liquids into the GC through an injector port. A self-sealing septum to retain the high pressure of the carrier gas is used with liquid samples. The resealing capability of the septum depends on the temperature, flexibility of the silicon rubber seal, sharpness of the syringe needle and design of the injector. The septum holder is designed by including a needle guide to reduce mechanical damage. The temperature used for the injector block for TPH (C_{10}-C_{36}) analysis is typically around 300 °C. To minimise the effects of: (i) septum degradation and the loss of low molecular weight hydrocarbons due to septum bleeding and (ii) baseline drift, the correct septa need to be used. To avoid cross contamination the inner surface of the silicon septum is coated with 0.26 mm thick PTFE liner. Septum purge is used to flush the surface of the septum with 2-3 mL/min of carrier gas to reduce artifacts due to septum effects. Septa are changed daily. The samples are introduced to the GC by an auto-injector. The entire process of sample transfer, sample injection, collection of chromatographic data and calculation of results are handled by microcomputer-controlled instruments. Liquid samples are placed in 2 mL GC glass vials with PTFE-coated silicon septa. These samples are loaded as batches of up to 100 vials, which are sequentially transferred to the sampling position. Samples are taken into an automated syringe with a

number of flushing and washing steps to avoid cross contamination. A liquid sample of 2 μL from each vial is transferred into the injection port. The sample is flushed out towards the column inside the injector port by the helium carrier gas. The TPH (C_6-C_9) fraction is analysed by extracting the soil with a solvent and transferring a portion of the solvent extract into a purge vessel containing a known volume of water. The volatile TPH in the solution is purged using ultra high purity helium gas and trapped in an adsorbent material. The sorbent is heated to release the volatile compounds, and a carrier gas sweeps the compounds into a GC[19-20].

6.2.3 Columns

Gloay [18] first invented capillary column gas chromatography in 1959. This highly efficient technique comprises a column which is made out of a long length of tubing whose inner wall is coated with a thin layer of stationary phase. To apply capillary GC techniques to TPH analysis requires knowledge of the boiling point range, vapour phase characteristics, number of components (if possible); polar and non-polar characteristics, film thickness of the stationary phase in the capillary column, type of stationary phase and optimum carrier gas velocity. The optimisation of the temperature program as well as testing and calibrating the system using a standard mixture representing TPH is also required.

The columns appropriate for the GCFID analysis of TPH (C_{10}-C_{36}) are BPX-5, DB-5, Rtx-5, CP-Sil 8CB, SPB-5, HP-5, ultra-2 and PTE-5[18] which are all commercially available. The stationary phase consists of 5% diphenyl-95% polysilphenylene-siloxane mixture which is non-polar, has low bleed and can handle high temperatures of up to 370 °C. High-temperature characteristics are essential for eluting high molecular weight hydrocarbons containing up to 36 carbon atoms. The stationary phase is chemically bonded to the column wall and laid as a film. Columns with high thermal stability were used for efficiently separating hydrocarbons ranging from 6 to 36 carbon atoms.

6.2.4 Setting-Up for TPH Analysis

Within the column, a temperature gradient is required to separate the TPH compounds[6,21-23]. The temperature parameters to be considered include the injector temperature, the temperature setting for the FID, an initial temperature for the oven, a hold time for the initial oven temperature, temperature increments at a predetermined rate, further temperature increments if required and a hold time at the maximum temperature. The injection is in splitless mode and the purge inside the injection chamber is activated at a predetermined time. The column head pressure is set at 150 kPa and prior to each injection the needle is automatically washed with high purity DCM from two vials. These vials are placed in where the needle is washed with each of the solvents vials five times. Measuring the C_{36}/C_{18} peak area ratio monitors loss of response and cross contamination. If the response ratio falls below 0.4, the injection liner is changed and the accumulated particulate matter and fragments of septum rubber are removed from the injection eyelet. When such changes are implemented the C_{36}/C_{18} ratio improves to approximately 70%. If the above servicing did not improve the quality of the response the removal of at least 0.2 m from the head of the analytical column would be required. Detector linearity is monitored by the analysis of a range of diesel standards. At the start of each day, the oven temperature is typically maintained at 315 °C for at least 1 h to clean the column. To maintain a steady baseline during temperature programming the column compensation function available in the HP 5890 Series II system is used.

6.3 TPH Analysis by GCMSD

Detectors responding to most material eluting from the column are called universal detectors. Total ion monitoring of GC coupled to mass selective detection (MSD) can be classified as an universal detector[24-26]. The GCMSD used for the analysis of TPH (C_{10}-C_{36}) in this study was a HP 5890 Series II system with a HP 5971 MS and a HP 7673 auto injector. The GCMSD has been used in the analysis of complex hydrocarbon mixtures from petroleum fractions since the 1960[24]. This process was further developed to obtain well-defined and reproducible

mass spectra for complex molecules in later years. Due to the inroads made on improved digital and analogue electronics, personal computer systems and instrument design, gas chromatography is available that incorporates compact integrated MSDs is currently available. The control software and databases, incorporating libraries of reference spectra, run on fast personal computer work stations allowing sample mixtures containing common organic analytes to be separated and identified on a routine basis. Chromatography is primarily a separation technique measuring the amount of analyte eluted from the chromatographic system. The GCMSD is a reliable detector for the confirmation of TPH in environmental samples given the complexity of chromatograms obtained from soil extracts. The application of GCFID for reporting the presence of "real" TPH is only possible if samples are known to contain only hydrocarbons or if all peaks are assumed to be TPH equivalents. Environmental samples such as soil collected from contaminated sites, may potentially contain large amounts of non-hydrocarbon material, which requires confirmation. This can be achieved by GCMSD analysis where the non-hydrocarbons can be distinguished from the hydrocarbons using a spectral library. If a non-hydrocarbon co-elutes with a hydrocarbon, a unique ion from either component can be used in determining the specific contribution by each compound.

Electron impact (EI) is a process used for ion source production in GCMSD. The pressure is maintained at below 10^{-3} torr[24-26]. The sample inlet system is designed to release the analytes into the central region of the source at a carefully controlled rate, depending on the analyte and its physical properties. A short length of heated, silanised silica or stainless-steel capillary tubing is used to transfer the eluant directly to the ion source. A library database containing standard (i.e. Wiley Library™ of the HP Chemstation) 70 eV EI spectra for 275,000 compounds is available to identify unknown peaks. The EI ion source is efficient, stable and produces ions with a narrow kinetic energy spread. The mass spectra obtained from the EI ion source are specific and characteristic of the molecular composition of the

TPH[24-26]. The fragmentation processes produces ions whose relative abundance ratio reflects the chemical composition of the sample. Electrons emitted at a hot filament are accelerated and the resulting electron beam is directed from the ion chamber to the collector anode. The interaction between the electron beam and the organic molecules (M) result in an energy transfer of over 20 eV which is sufficient to ionise most molecules. In many cases the molecular ion is unstable and subsequently undergoes fragmentation to form smaller ions. This process is presented as follows:

$$M + e \rightarrow M^{+} \text{(molecular ion)} + 2e \rightarrow A^{+} + B^{+} + C^{+} + \text{etc. (primary fragmentation ions)}$$

The resulting positive ions move from the ionisation area through the slits and an ion lens system into the mass analyser. The degree of fragmentation, and the spectral fingerprint or pattern is dependent on the energy of the bombarding electron beam. Ion currents are maximum for electron energies in the range 50-80 eV, and most reference spectra are obtained at 70 eV. The EI source requires a pressure of less than 10^{-3} torr to avoid unwanted ion molecule collisions, and a pumping system of 30-100 L/s with vacuum conductance permits 5-10 mL/min of vapour to be introduced into the source.

The quadruple mass analyser consists of a set of four rods of circular or hyperbolic cross section in a quadrant formation mounted parallel to the z-axis. Opposite rods are electrically connected to an applied voltage which consists of a direct current (d.c.) with 1-2 MHz reference frequency (r.f.) component creating an oscillating field between the rods. When an ion moves into the quadrupole field it starts to oscillate in the x,y-directions between the rods. If the mass of the ion is such that these oscillations are stable then the ion is moved through the analyser to the electron multiplier. Ions of other mass to charge values undergo unstable oscillations of increasing amplitude until they move out of the quadrupole field. Since there is no force along the z-axis of the rods an ion accelerating potential of only 20-30 V is

required. Scanning is achieved by varying the magnitude of the d.c. and r.f. voltages whilst maintaining a constant r.f. : d.c. to produce a linear mass spectrum.

6.3.1 Interfacing GC and MSD

The separated components of TPH emerging from a GC column are present in picogram amounts in the carrier gas stream. If the column eluant is to be coupled to a MSD the volume flow-rate of carrier gas needs to be minimised for a given separation to achieve high sensitivities in the ion source and to reduce pumping requirements. The GC parameters are selected to obtain symmetrical sharp peaks that elute in a minimum carrier gas volume with the best peak height to width ratio that can be achieved. If the components are not separated properly, the co-eluting peaks will not produce pure mass spectra which can be compared clearly with the reference spectra library. In order to achieve the best spectra the following factors are considered: the carrier gas chosen is ultra high pure helium with a purity of 99.999%; the carrier gas needs to be inert and easily removed at the interface; the carrier gas should not interfere with the spectra or the total ion current; the column stationary phase should not bleed; the stationary phase should operate within the specified temperature range; the split ratio should be optimised and the injections should be carried out by an auto injector to deliver the sample onto the first few plates of the column without overloading. Caution should be taken to maintain symmetrical, sharp and well resolved peaks and to obtain the highest concentration of component molecules in the carrier gas. Temperature programming should be used to maintain a satisfactory peak profile throughout the analysis so that later eluting peaks are not broad and the GC system should be set up to obtain minimum peak volume of the emerging peaks. The temperature parameters for the injector and oven are similar to the GCFID used for the separation of the TPH compounds. A temperature for the detector interface of the MSD (which the GC column meets the MSD) is required. Figure 6.4 contains the basic structure of a GCMSD system.

The injection is split and the purge is set at 0.0 min and the column head pressure is 100 kPa. Prior to each injection the needle is automatically washed high purity solvent. These vials containing the solvent are placed in positions where the needle is washed with each of the solvents vials five times. The capillary column used in the GCMSD is a low-bleeding column. The stationary phase consists of 5% diphenyl-95%-dimethylpolysiloxane. Data are acquired from the MSD using the scan mode, the solvent delay set for 2 min, the monitored mass range is 30-350 atomic mass units (amu), the scan threshold is 400 with a rate of 1.9 scan/s. A range of selected ion mass to charge ratios (m/z) are used in confirming the petroleum hydrocarbon components on a sample tested for TPH. [3]

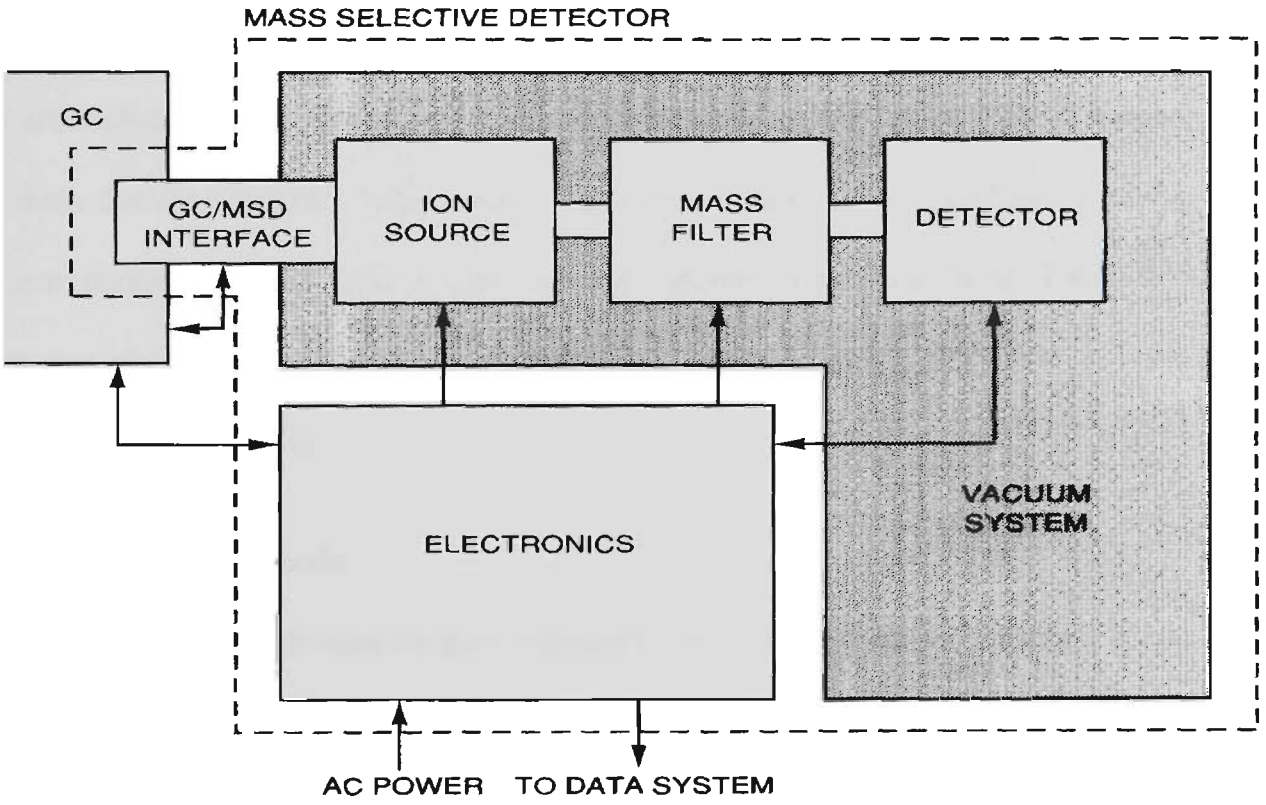

Figure 6.4: Components of GCMSD system (by courtesy of Hewlett Packard Australia).

6.4 Analysis of Volatile TPH (C_6-C_9)

6.4.1 Preamble

The study was conducted to obtain the concentration of TPH (C_6-C_9) from spiked samples with known amounts of unleaded petrol and analysed by GCFID and GCMSD[6,27-30]. Sampling for TPH (C_6-C_9) is by P&T to obtain reliable data with minimum losses and

maximum sensitivity[31]. Various laboratories use either the GCFID or the GCMSD for detecting TPH (C_6-C_9)[32-33]. GCFID is regarded as a cheaper and a more robust technique than the GCMSD. Compared to a GCFID the GCMSD requires greater capital outlay, advanced operator training and higher maintenance cost. Very little research has been carried out on methods using P&T for the analysis of TPH (C_6-C_9)[34]. This study is aimed at investigating the statistical variation between the concentration determined by the two different detector systems using a single GC injection, split and transferred into two columns and detected by the FID and the MSD. It is anticipated that the results of this study will assist interpreting analytical data on samples tested by either of the two detectors.

6.4.2 Materials and Methods

Reagents are methanol (Merc brand, HPLC grade) and granular anhydrous sodium sulphate obtained from Crown Scientific (Melbourne). Millipore water, further purified by passing through four cartridges of a milli-Q ultra cartridge system, was used in all P&T work. Glassware was cleaned as described in Chapter 3.2.5. P&T sampling vials (44 mL) were purchased from SGE Australia.

6.4.3 Preparation of Standards

The same standards have been used for the comparative FID and MSD measurements. These are as follows:

The benzene, toluene, ethylbenzene and xylenes (BTEX) calibration and retention time standard

This standard was purchased from Supelco, Australia, Pty Ltd. as a stock solution of 2000 mg/L for each component.

The n-alkane calibration and retention time identification standard

A stock alkane mixture containing *n*-C_6, *n*-C_8 and *n*-C_{10} hydrocarbons, each present at 5000 mg/L, was prepared using 99% pure individual standards (Supelco, Australia Pty

Ltd.). This was prepared by diluting 50 mg of each hydrocarbon to 10 mL of methanol.

The mixed BTEX/n-alkane (working) standard

A mixed standard of combined BTEX/*n*-C_6, *n*-C_8 and *n*-C_{10} was prepared by first creating a stock solution by combining 500 µL of (ii) and 350 µL of (i) and making up to 25 mL of methanol. The solution was transferred to a septum-sealed, screw-cap vial for storage at –20 °C. The concentrations in this stock solution were 100 mg/L in n-alkane (each) and 28 mg/L in BTEX (each). A calibration standard solution was prepared from the above stock by diluting 40 µL to 44 mL (P&T vial) with organic-free water. This solution then contained each *n*-alkane at 91 µg/L and each BTEX at 26 µg/L. This standard was used for the calibration of the detectors and defining the TPH (C_6-C_9) range. The calibrations for the comparative analysis were carried out using (a) the response of n-C_8.only (b) the total response of BTEX from the mixed standard only and (c) the sum of the responses of BTEX + n-C_8, only. The n-C_6 and n-C_{10} were only used as retention time indicators.

(iv) Surrogate standard (SS) - to monitor P&T efficiency

A prescribed USEPA method 8260 [18] surrogate standard was purchased from Supelco, Australia Pty Ltd. This stock contained a mixture of dibromofluoromethane, d_8 - toluene and 4-bromofluorobenzene, each at 2000 mg/L.

Internal standard (IS) – to monitor injection efficiency and reproducibility

A prescribed USEPA 8260 IS solution was purchased from Supelco, Australia, Pty Ltd. and contained pentafluorobenzene, difluorobenzene, d_5-chlorobenzene and d_4 - 1,4-dichlorobenzene, each at 2000 mg/L.

The combined SS/IS standard

The SS/IS working standard was prepared by diluting 500 µL of (iv) and 250 µL of (v) to a final volume of 25 mL of methanol. This working solution contained 20 mg/L

of the SS and 40 mg/L of the IS. 1 µL of the SS/IS was automatically added to all samples by the auto-sampler before the samples were purged.

Gasoline Range Organic (GRO) standard

This was purchased from Chemservice (Melbourne) and contained 2-methylpentane (at 1500 mg/L), 2,2,4-trimethylpentane (1500 mg/L), toluene (1500 mg/L), 1,2,4-trimethylbenzene (1000 mg/L), m-xylene (1000 mg/L), o-xylene (1000 mg/L), n-heptane (500 mg/L), benzene (500 mg/L) and ethylbenzene (500 mg/L). A working standard was prepared by diluting the purchased stock solution 1 in 10 in methanol. 20 µL of the mix was then added into a P&T vial (44 mL) fitted with milli-Q water. This standard has been employed to monitor instrument performance.

The unleaded petrol spiking standard

This standard was prepared by dissolving 0.1 g (cold) of unleaded petrol in 20 mL of methanol and making this up to 100 mL. The volumetric flask was capped and inverted to mix. This solution contained unleaded petrol at a concentration of 1000 mg/L and was used to prepare the spiked samples by dilution (section 6.4.5).

6.4.4 Apparatus for the Comparative TPH (C_6-C_9) Analysis

The general approach for these experiments has been detailed to in the section 6.1 and a schematic diagram of the instrumental set-up is shown in Figure 6.2. A Vocarb trap (Supelco-Shimadzu, Melbourne) for trapping purged volatile components was used in conjunction with an OI brand P&T analyser unit distributed by Shimadzu, Melbourne). The GC instrument was a Hewlett Packard (HP) 5890(II)/5972 (coupled to both an MSD and a FID) as shown in Figure 6.2. Two HP-624 columns 0.25 mm (ID) x 1.8 µm (film thickness) were connected to the two detectors. To compensate for the vacuum on the MSD which decreased retention time, a 30 m column was connected to MSD and a 24 m column connected to the FID. All analyses were carried out in the split mode at 10 mL/min.

6.4.5 Experimental

The parameters used in acquiring data were as follows: The OI brand P&T was programmed to purge for 8 min at 40 mL/min, desorb at 245 °C for 4 min, and bake at 250 °C for 8 min. The temperature of the transfer line and valve oven were set to 100 °C. The volume of water transferred from the sample to the sparge tube was set at 5 mL. Injector temperature 180 °C, split vent flow 15 mL/min at 140 kPa. Both columns were HP-624, 0.25 mm I.D. with head pressures of 80 kPa during trap purge; temperature program for the column at a initial temperature of: 35 °C for 4 min, ramp 10 °C/min to 250 °C, hold for 2 min. The MSD transfer line temperature 245 °C, MSD on full scan 35-280 amu with a threshold of 400. The MSD was tuned using maximum sensitivity auto-tune and a solvent delay of 1.2 min.

6.4.6 Preparation of Spike Samples

Unleaded petrol, which is used here to represent a typical TPH (C_6-C_9) analyte, was added at a concentration of 240 µg/L into milli-Q water. After spiking, 44 mL each P&T vial was capped and inverted 3 times to homogenise. Seven replicate analyses and seven blanks were prepared.

6.4.7 Measurement of TPH (C_6-C_9)

Prior to the measurement of TPH (C_6-C_9) in the samples, the following standardisation procedure was carried out, both on the spiked samples and the blank (seven replicates in each case):

The SS/IS working standard (6.4.3 (vi)) was automatically applied to all spiked samples, blanks and calibration standards. Figure 6.5 depicts a total ion chromatogram of a representative sample with the SS/IS standard added.

The calibration standard (6.4.3 (iii)) was used to estimate the start and end points of TPH (C_6-C_9). Figure 6.6 depicts the mass spectrum profile of benzene, a BTEX component of the standard. All peaks appearing in the chromatogram of the spiked sample between the

beginning of the benzene peak of and the end of the n-C_{10} peak were integrated baseline-to-baseline with the HP Chemstation software and the response due to the TPH (C_6-C_9) in the spiked sample was calculated by subtracting the total area of the SS/IS computed from the blank. To convert the TPH (C_6-C_9) response in the spiked sample to a concentration, the n-C_8, the BTEX and the BTEX + n-C_8 (manually) integrated standard peaks were employed.

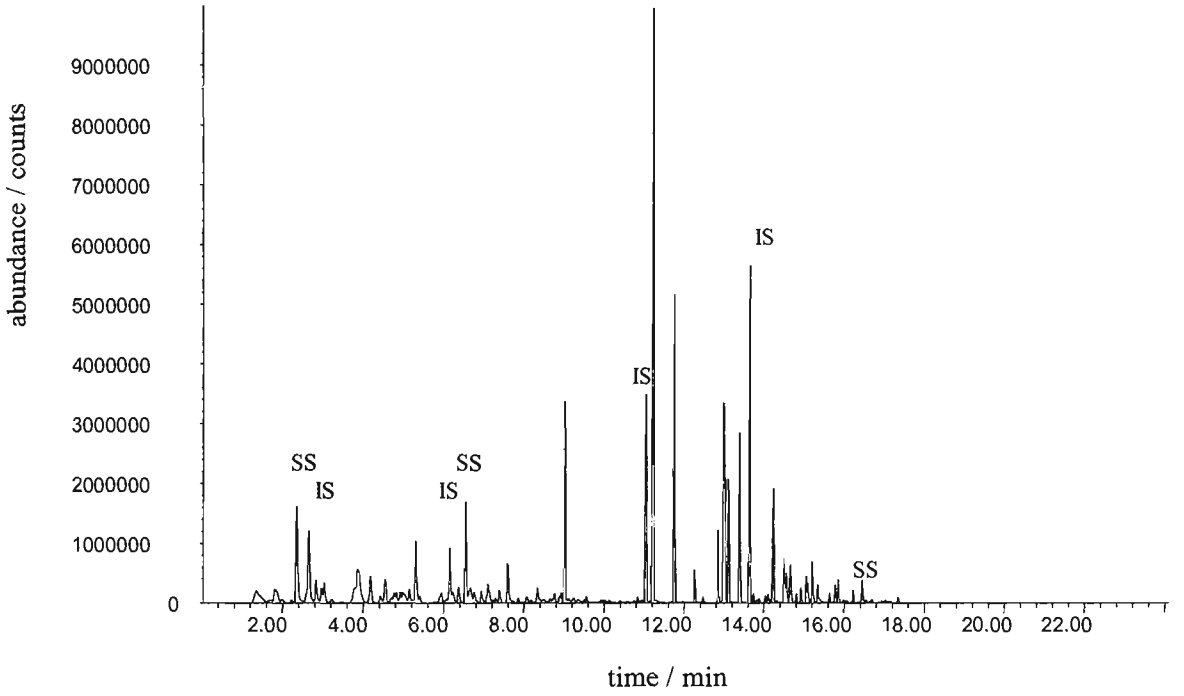

Figure 6.5: Typical total ion chromatogram of a representative unleaded petrol sample with the SS/IS.

6.4.8 Results

The results of the experiments are given in Table 6.1 and depicted in Figure 6.7. The calibration standards n-C_8, BTEX and BTEX + n-C_8 were used for the comparison of GCFID and GCMSD measurements. This study also investigated the most appropriate standard of the three to use. All statistical tests employed show that there was no significant difference at $p = 0.05$ between the measured TPH (C_6-C_9) concentrations when n-C_8 was used as the calibration standard. However, a significant difference is seen between the results obtained by the two detectors when BTEX or BTEX + n-C_8 are used as calibration standards. Therefore n-C_8 as the calibration standard produced TPH (C_6-C_9) concentrations which are

comparable to the two detectors. Furthermore, the n-C_8 standard is demonstrated to be the most appropriate with respect to reproducing the expected concentration (horizontal broken line in Figure 6.7 at 240 μg/L).

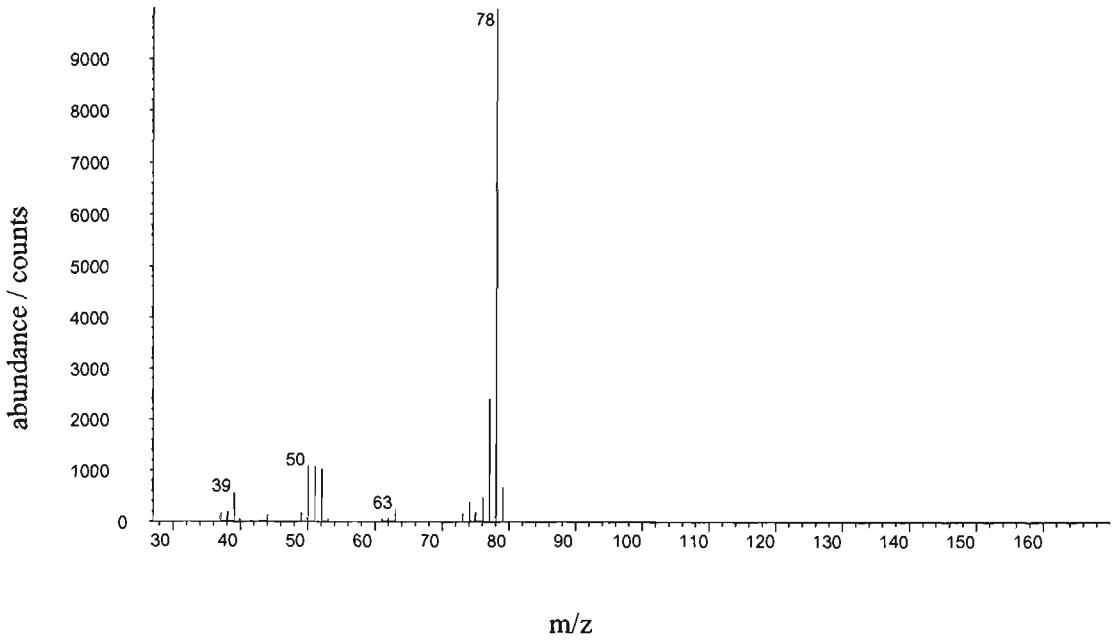

Figure 6.6: Sample mass spectrum of benzene.

6.4.9 Discussion

In order to carry out a comparative analysis of TPH (C_6-C_9) by GCFID and GCMSD, water samples spiked with unleaded petrol were analysed using three different calibration standard responses, namely, n-C_8, BTEX and BTEX + n-C_8 (Section 6.4.3). The outcome of these experiments is presented in Figure 6.7 and Table 6.1. It is clear that use of n-C_8 standard (both for FID and MSD) is superior to the use of BTEX or BTEX+ n-C_8 for achieving accuracy of measurement.

This may be attributed to the n-C_8 being more representative of the unleaded petrol in terms of detector response. The use of the latter standards, does not only give rise to an underestimation of the true level of TPH but there is also a significant difference between the values depending on weather FID or MSD are used. Again this can be attributed to a difference in response to a given standard, this time between the detectors. In this regard, it may be pointed out that the difference between the response to aliphatic and aromatic

compounds is more pronounced for MSD than for FID. For example, the FID responses to 1 ng of benzene and 1 ng of n-C_6 are relatively similar at 206 and 222 counts respectively. However, the MSD responses were 450 and 309 counts respectively, which represented a significant difference. Therefore, all of the above needs to be taken into account when selecting an appropriate standard and detector for TPH (C_6-C_9) analysis. By selecting an appropriate standard, the analysis can be carried out either by FID or MSD with accurate and comparable results. Failure to do this may lead to outcomes that are neither accurate nor comparable with respect to both detectors.

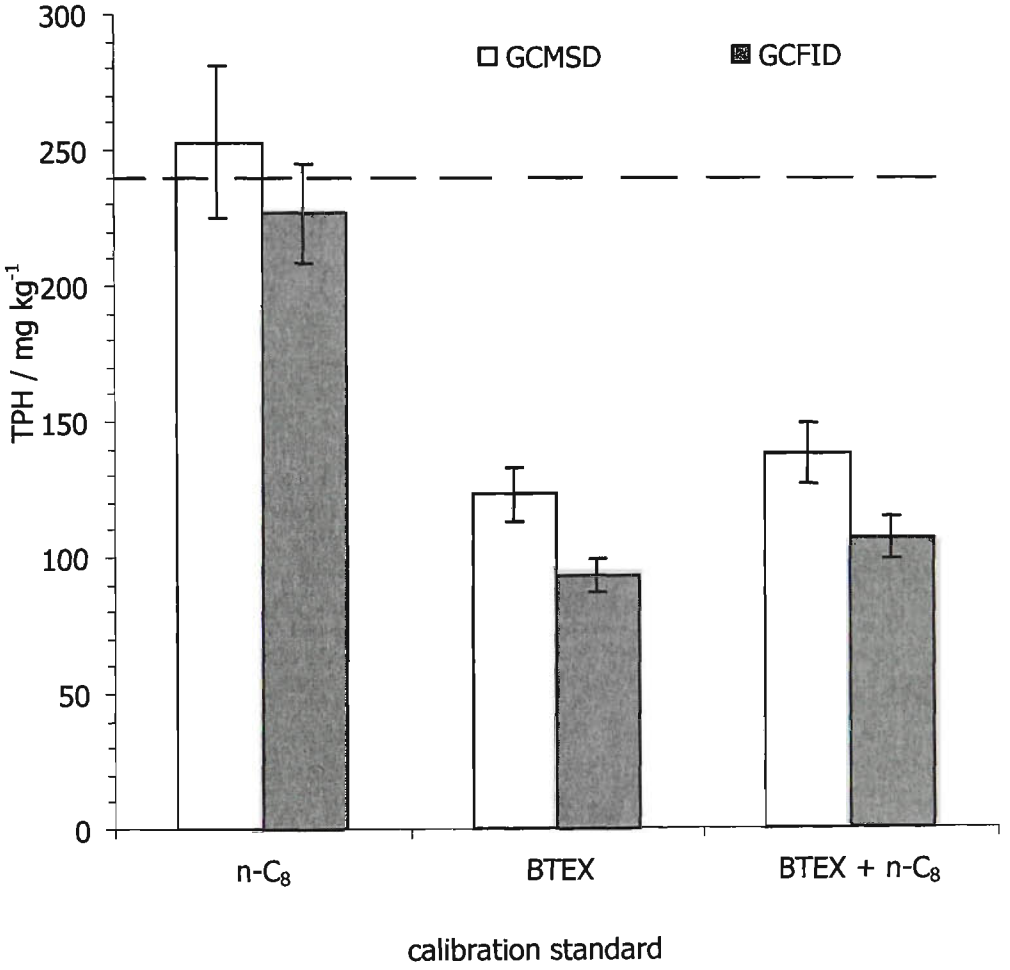

Figure 6.7: Comparative TPH (C_6-C_9) mean concentrations and confidence intervals (95%, n=7) from spiked unleaded petrol samples.

This finding is reflected in analogous investigations on TPH (C10-C36) samples. This work is described in the following sections.

Table 6.1: Comparative TPH (C_6-C_9) Concentrations from Spiked Unleaded Samples ((a) n-C_8, (b) BTEX and (c) BTEX+n-C_8).

	Sample	1	2	3	4	5	6	7	Mean	SD	t-Test [35] (two tailed) p=0.05	Uncertainty (U) [36] Against the Magnitude of the Difference (Δ)
A	TPH (C_6-C_9) Using GCMSD/ n-C_8	226	290	286	255	257	248	208	253	30	t = 1.92 tcrit = 2.23 tcrit > t null hypothesis held the difference between two results not significant	Δ = 25, U = 28, Δ < U Comparable
	TPH (C_6-C_9) Using GCFID/ n-C_8	223	228	256	229	244	198	213	227	19		
B	TPH (C_6-C_9) Using GCMSD/BTEX	107	135	135	118	121	130	112	123	11	t = 6.23 tcrit = 2.26 t > tcrit null hypothesis rejected the difference between two results significant	Δ = 22, U = 14, Δ > U Not comparable
	TPH (C_6-C_9) Using GCFID/BTEX	90	91	103	92	98	85	92	93	6		
C	TPH (C_6-C_9) Using GCMSD/BTEX+ n-C_8	120	152	151	133	136	127	147	138	12	t = 5.31 tcrit = 2.17 t > tcrit null hypothesis rejected the difference between two results significant	Δ = 31, U = 12, Δ > U Not Comparable
	TPH (C_6-C_9) Using GCFID/BTEX+ n-C_8	105	107	121	108	115	93	100	107	9		

6.5 Analysis of Semi-Volatile TPH (C_{10}-C_{36})

6.5.1 Preamble

This study was conducted to determine the concentration of TPH (C_{10}-C_{36}) from soil extracts analysed by GCFID and GCMSD. GCFID is used extensively in Australia for the detection and quantification of TPH (C_{10}-C_{36})[5]. However GCFID will not identify petroleum hydrocarbon components. Often TPH (C_{10}-C_{36}) is analysed by GCFID to minimise cost and to simplify the analysis. When component identification is required GCMSD has to be used. This study was carried out to determine if there are significant variations between TPH (C_{10}-C_{36}) concentrations determined by GCFID compared to GCMSD.

6.5.2 Sample Preparation

For this investigation, 24 samples of sandy loam contaminated with TPH (C_{10}-C_{36}) were collected in 250 mL glass jars. The glass jars, which were filled to the top with these samples, were opened and the top 2 cm of soil from each jar was discarded. The samples were then homogenised by transferring each of them into a stainless steel tray and mixing with a mortar and pestle. Each homogenised sample was then split into two sub-samples, one for moisture analysis and the other for the GCFID and GCMSD analysis. Moisture analyses was carried out using the method described in Chapter 3.2.6.4.

6.5.3 Materials and Methods

The reagents are acetone (Omnisolve, EM Science, Australia), DCM (EM Science) and sodium sulphate, (anhydrous granular Mallinkrodt, Australia). Standards covering the C_{10}-C_{36} range were prepared using analytical reagent grade hydrocarbons (Supelco, Australia Pty. Ltd.) and included n-C_{10}, n-C_{12}, n-C_{14}, n-C_{16}, n-C_{18}, n-C_{24}, n-C_{28}, n-C_{32} and n-C_{36}.

6.5.4 Preparation of Standards

The working standards are tabulated on Table 6.3. A stock solution (Std 1) of the n-alkanes: C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{24}, C_{28}, C_{32} and C_{36} was prepared by accurately weighing (~1 g) of each into 50 mL of DCM and diluting to 100 mL with DCM (volumetric flask).

Table 6.2: Dilution of stock standard.

Std	Standard	Individual hydrocarbon (mg/L)	C_{10}-C_{36} (mg/L)
Std 1	Stock Solution	10,000	90,000
Std 2	Spike	1,000	9,000
Std 3	Recovery	25	225
Std 4	Intermediate	10	90
Std 5	GC Working Injection	2	22.5

This stock solution contained individual hydrocarbons at 10,000 mg/L (TPH (C_{10}-C_{36}) concentration of 90,000 mg/L). This stock solution was serially diluted with DCM to prepare the working standards.

6.5.5 Apparatus for the Comparative TPH (C_{10}-C_{36}) Analysis

The instrumentation included (i) gas chromatograph-HP 5890 Series II with an auto-sampler and a FID, (ii) gas chromatograph-HP 5890 with a HP 5970 MSD and (iii) HP Chemstation software.

6.5.6 Experimental

A mixture of 1:1(v/v) DCM/acetone was prepared and 20 mL was added to jars containing 10 g of the homogenised soil. The jars were placed in an ultrasonic bath and sonicated for 1 h while maintaining the temperature below 25 °C. Each extract was dried over anhydrous sodium sulphate. The sample was placed in an ultrasonic bath for a further 30 min. The soil was then allowed to settle and the supernatant was checked for suspended particulate or floating insoluble material, which requires centrifuging to separate. The supernatant was

centrifuged at 13,000 rpm for 5 min if required. A portion of the clear supernatant was transferred to a 2 mL glass crimp-top GC vial and analysed by GCFID and GCMSD.

The sample extracts were analysed on a HP Series II GC fitted with an SGE BPX5 (25 m length, 22 mm I.D. and 0.25 μm F.T.) column, a HP7673A auto sampler and FID. The following GC conditions were used: sample volume 2 μL, injector temperature 325 °C, detector temperature 350 °C, head pressure 175 kPa, temperature program with an initial temperature 40 °C, initial time 0.8 min., temperature rate (1) 27 °C/min up to 100 °C, temperature rate (2) 35 °C/min up to 350 °C, hold time 5 min. Integration of the chromatograms was performed with the proprietary HP Chemstation data analysis software. The TPH (C_{10}-C_{36}) concentration was computed by integrating the response by defining the baseline over a distance. The concentration was proportional to the sum of the areas between the start of the n-C_{10} peak and the end of the n-C_{36} peak. Only the soil extracts containing TPH (C_{10}-C_{36}) at or above 100 mg/kg were calculated for this study. The GCFID was calibrated using the GC working standard (Std 5).

Sample extracts analysed by the GCFID were re-analysed on a HP 5890 GC fitted with an HP5-MS (25 m length, 0.22 mm I.D. and 0.25 μm F.T.) column and a HP 7673A auto-sampler coupled to a HP 5970 MSD. The sample volume used was 2 μL, injector temperature 280 °C, detector temperature 290 °C, head pressure 30 kPa, temperature program with an initial temperature 35 °C, initial time 7.0 min., temperature rate 15 °C/min up to 320 °C and hold time 10 min. The data were acquired from the MSD using the following conditions: mode scan, detector was turned on at 2.0 min, low mass 30 amu, high mass 300 amu and scan threshold 400 amu. Integration of the chromatograms was performed with the HP Chemstation software. The integration event timetable was programmed to calculate the sum of area between the start of the n-C_{10} peak and the end of the n-C_{36} peak. Only the soil extracts containing TPH (C_{10}-C_{36}) at or above 100 mg/kg were calculated.

6.5.7 Preparation of Spike Samples

The analysis was carried out as described in Section 3.2.6.6 with monitoring to see if there were response variations in standards. The checking for response variations was carried out by using a GC working standard (Std 5) in one in every four analyses. A reagent blank containing the solvent and drying agent, a soil blank containing clean sandy loam the solvent and the drying agent, and a recovery sample were analysed to obtain the percent recovery of TPH (C_{10}-C_{36}) and to check for cross-contamination. The recovery sample was prepared by adding a clean sandy loam to the TPH spike standard to obtain a 450 mg/kg sample of TPH (C_{10}-C_{36}). The spiking was carried out using a sandy loam (10.0 g) and spiking 500 μL of Std 2 by injecting the solution just below the surface of the soil from the side of the jar. The percentage recovery was calculated by direct comparison of the response obtained for the spiked sample chromatogram with that for the recovery standard (Std 3) chromatogram. These recoveries were between 95-100% and are considered to be satisfactory.

6.5.8 Calculations

A GC calibration factor was calculated to correct for moisture content (% moisture), sample extraction volume and sample mass:

$$\text{Calibration Factor} = \frac{100}{[100 - (\%\ \text{moist})]} \times \frac{\text{Extraction Volume}}{\text{Sample Mass}}$$

The TPH (C_{10}-C_{36}) concentration for each sample was directly obtained from the calibration when the sample volume was 0.020 L and the sample mass was 0.01 kg.

6.5.9 Results

The TPH (C_{10}-C_{36}) concentration for each sample was read directly from the calibration table. TPH (C_{10}-C_{36}) concentrations were obtained for each sample using GCFID and the GCMSD. The results are shown in Figure 6.8 and suggest that in the majority of samples the TPH (C_{10}-C_{36}) concentration obtained by the GCFID is greater than the concentration obtained by

GCMSD. This has been confirmed by statistical testing and is discussed (sections 6.5.10 and 6.8.1).

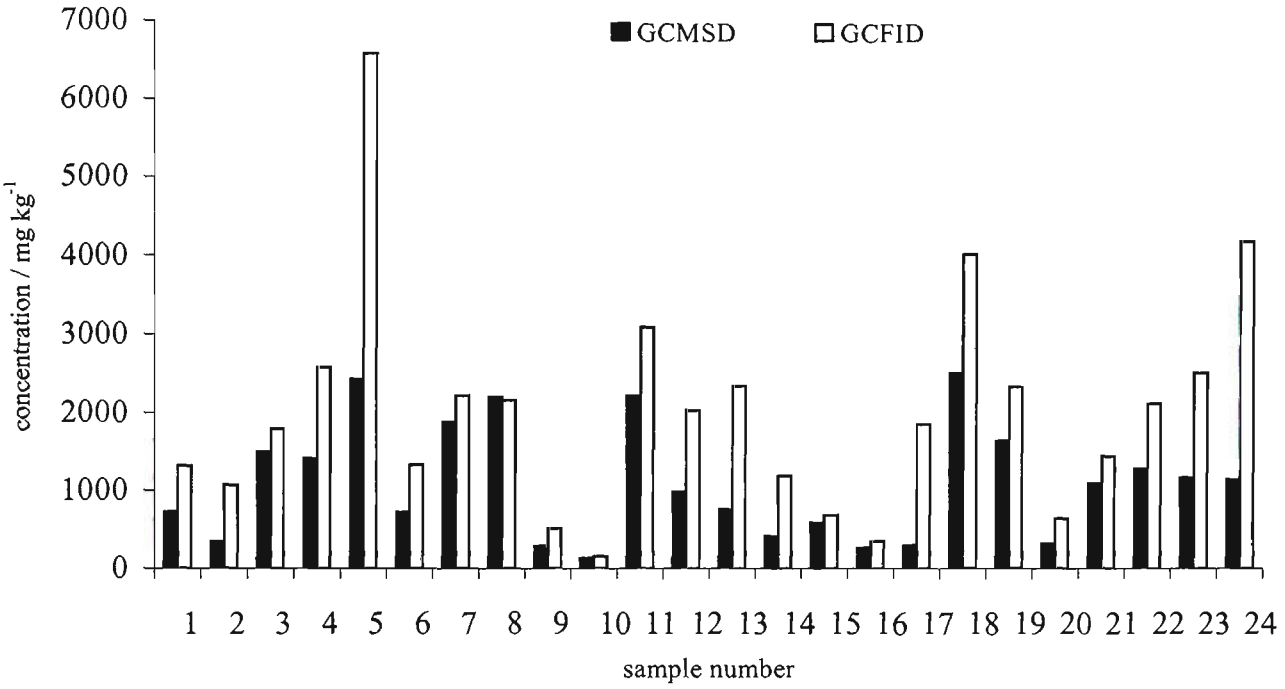

Figure 6.8: Comparative TPH (C_{10}-C_{36}) concentrations using GCFID versus GCMSD.

6.5.10 Discussion

Twenty four contaminated sandy loam extracts were each homogenised, extracted and subjected to comparative TPH (C_{10}-C_{36}) analysis using GCFID and GCMSD. The results in Figure 6.8 suggest that the GCFID analyses produce higher TPH (C_{10}-C_{36}) values than the corresponding GCMSD analyses. A subsequent ANOVA analysis (Appendix 6.1) confirms that the two detectors produce statistical variations in TPH concentrations for a given sample. This is probably a reflection of the different responses of the two detectors to various chemical compounds present in the TPH samples. To illustrate this point, the FID response to n-C_6 was found to be relatively similar to the C_6 aromatic analogue, benzene (see section 6.8.1) but the MSD response between these two analytes was substantially different. Indeed, the TPH (C_{10}-C_{36}) fractions in the soil extracts were identified by the GCMSD library to

contain numerous classes of hydrocarbon with complex structures, including polynuclear aromatic hydrocarbons (PAHs). Therefore the FID, due to it's relatively linear response to hydrocarbon concentration rather than to carbon number or molecular structure, produces a better estimate of TPH concentration with a less complex choice of standards.

One can argue that, in order to overcome the difference in response between the FID and MSD, as many representative components of the sample as possible should be used in the calibration. However, this is complicated by a lack of knowledge of the sample history given that TPH (C_{10}-C_{36}) is subjected to weathering and chemical transformation. A suggested approach is to use a combination of FID and MSD with due consideration of the limitations involved. Thus GCFID is more suitable for determining concentrations and the GCMSD complements this by identifying non-hydrocarbon components. Such compounds can then be excluded from the GCFID quantification.

6.6 Conclusion

Two studies were conducted to determine if there are variations of results when TPH is analysed using GCFID and GCMSD. The first study included the analysis of TPH (C_6-C_9) by P&T/GCFID and GCMSD on spiked water with known concentrations of unleaded petrol. The analysis was conducted using three sets of calibration standards. The three sets included n-C_8, BTEX, and BTEX + n-C_8. Only n-C_8 produced TPH (C_6-C_9) concentrations which are comparable by the two detector systems and closer to the spiked concentration of unleaded petrol. Therefore it is essential to select the proper standard to obtain comparable TPH (C_6-C_9) concentrations.

The second study involved a comparison of the TPH (C_{10}-C_{36}) concentrations from contaminated sandy loam soil using GCFID and GCMSD was conducted. A total of 24 contaminated soil samples were analysed for TPH (C_{10}-C_{36}) using the two detectors. The percent moisture of each sample was determined prior to extraction with DCM/acetone (1:1).

The data obtained from each detector was statistically tested to determine trends that may exist in the TPH (C_{10}-C_{36}) concentrations. The data analysis showed the GCMSD concentrations were consistently lower than the GCFID concentrations when n-alkane mixtures were used as calibration standards. Therefore, the use of appropriate standards together with a suitable detector system is critical for TPH (C_{10}-C_{36}) analysis. The quantification is more reliable with the GCFID even when less complex standards are used and the identification of the components in a soil extract can be achieved only by the GCMSD.

6.7 References

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Chapter Seven: Comparative Analysis of BTEX from Contaminated Soils by Three Standard Methods

7.1 Introduction

This chapter is designed to investigate three common methods used in determining BTEX which is an integral part of the volatile TPH fraction. The C_6-C_9 TPH range (so-called volatile hydrocarbons) is a specific range which requires monitoring due to the relatively higher solubility, toxicity and volatility of individual components such as benzene[1-11]. The most significant components within this range are benzene, toluene, ethyl benzene and the xylene isomers. These components are collectively referred to as BTEX. BTEX is the most abundant component in petrol and therefore a very common contaminant in the industrialised world. BTEX in contaminated soil has implications with respect to toxicity to humans and animals. In this regard, their solubility in water promotes faster migration[12-18]. When soil is contaminated by petrol, the contamination may reach ground water through seepage[2-3]. Testing for BTEX in soil is a requirement implemented by authorities in most industrialised countries [4-6]. Apart from BTEX there are other aromatic hydrocarbons present in petrol in the C_6-C_9 range. These include compounds such as *1*-methyl-*2*-ethylbenzene, *1*-methyl-*4*-ethylbenzene and *2,3*-trimethylbenzene[1,6]. However, BTEX is chosen as the major indicator required for the measurement of volatile hydrocarbon contamination, especially for sites contaminated by petrol. Sections 1.2 – 1.4 describes the properties of BTEX in petrol.

Analysis of BTEX requires particular care and the application of complex methods due to the volatility of the components and the legislated requirement to detect sub-parts per million concentrations in soil[2-3]. Environmental agencies around the world, with a view to improving soil quality and the health of their citizens, have implemented guidelines to manage soil contaminated by BTEX[19-23]. The methods used for BTEX analysis should be robust and produce reliable estimates. Utmost care needs to be taken to minimise losses during sampling, transportation and handling, and the homogenising and preparative stages. The choice of analytical method and operator experience can also influence the reliability of BTEX analysis. However, even highly skilled analysts will not be able to obtain reliable

results if the chosen method is not appropriate. Three analytical methods commonly used for BTEX analysis in contaminated soils are as follows:

(i) Purge and trap (P&T) sampling and analysis by gas chromatograph, coupled to a mass selective detector (GCMSD). In this method, the soil is extracted with methanol, the volatile components are purged out of solution using helium and trapped and concentrated on an inert material. These are then de-sorbed by heating prior to transfer into the GCMSD. The P&T/GCMSD method is based on the United States Environmental Protection Agency (USEPA) SW846 series method 8260 B [24]

(ii) Headspace sampling where a sample of soil is heated to approximately 90 °C to form a vapour of the volatile components which is then analysed by GCMSD. The headspace analysis method is based on SW846 series methods 3810 and 5021[25-26]

(iii) Analysis of soil extracts by gas chromatography with flame ionisation detection (GCFID). The GCFID analysis method is based on SW846 series methods 3550 B and 8000 B [27-28]. In this method, the soil is extracted with dichloromethane (DCM), the volatile components are analysed by the GCFID.

All three methods are used in laboratories around the world. This study was conducted to compare BTEX concentrations obtained by these three methods when contaminated soils are analysed.

In order to meet the objective of the study which included the assessment of three methods it was conducted in two parts. The first part consisted of analysing 109 contaminated soil samples collected from petrol station sites suspected to contain BTEX. The soils were classified according to soil type using the Northcote bolus manipulation technique [29] and tested for total organic carbon (TOC)[30], moisture content [31] and pH [32]. Soils were analysed for BTEX by the three above methods and the resulting concentrations were statistically tested to establish if different results were obtained depending on the method employed[33].

The second part of the study use bulk samples of clean soil spiked with eight different concentrations of unleaded petrol and each sample was analysed in triplicate by the three methods. The mean concentrations obtained by each of the three methods was assessed to determine trends where bias towards a particular method might be indicated. The relative differences between the spiked and the recovered concentrations from each method were assessed to establish which method produces the optimum recovery.

7.2 Materials And Methods

The 109 contaminated soil samples were collected from twelve service station sites around Australia and analysed for BTEX by the methanol extraction and P&T/GCMSD, DCM extraction/GCFID and headspace/GCMSD methods. The soils were chosen from both clay and sandy soil sites to include extremes in soil type. Clay soils were regarded as soils which retain contamination due to the limited permeability of the structure and the sandy soils are regarded as soils which do not retain all contamination due to high permeability of the soil structure[34]. To minimise losses of BTEX through volatilisation, soils were refrigerated at or below 4 °C from the time of arrival in the laboratory to the weighing and extracting stages [35]. The study did not examine procedures involved in field sampling and the aim was limited to investigating laboratory methods. Homogenisation and weighing was conducted while samples were maintained at or below 4 °C.

7.2.1 Reagents

The reagents used were Methanol (Merck-HPLC grade), DCM and acetone, (Merck-pesticide residue grade), granular anhydrous sodium sulfate and calcium chloride (Crown Scientific). Millipore water, further purified by passing through four cartridges of a milli-Q ultra cartridge system, was used in all P&T work. The glassware cleaning solutions included chromic acid and Pyroneg™ powder (2%, w/w) in water. The pH meter calibration solutions included

buffer standards of pH 4, 7 and 10. For the TOC analysis a sucrose calibration standard was prepared by using AR grade anhydrous sucrose and AR grade sulfuric acid.

7.2.2 Apparatus

Glassware was soaked overnight in 2% (w/w) Proneg™ solution, rinsed with water, soaked for 2 h in a 2% (w/w) chromic solution and washed with water, rinsed with acetone and air dried. It included 125 mL glass jars with screw-cap lids fitted with Teflon ™ liners, 1 L glass jars with screw-cap lids fitted with Teflon™ liners, glass rods with rounded edges, 6 mm diameter, Pasteur pipettes, 15 cm length P&T vials (44 mL glass) and syringes (e.g. 25-500 µL), calibrated prior to measurements. Clean stainless steel spatulas were used for sample transfer, glass volumetric flasks at various volumes and glass pipettes ranging from 0.5-20 mL at various volumes were calibrated prior to measurements. Glass GC vials (2 mL) with crimp caps (containing Teflon™ lined) and a crimper were used. The 20 mL glass containers designed for headspace sampling (Hewlett Packard (HP) cat. No. 9301-0716), septa to fit headspace vial (HP cat. No. 9301-0719) and aluminium seals to crimp the septa (HP cat. No. 9301-0721) were purchased. A hand crimper was used to seal the soils inside the headspace vials. A Branson 8210, 950 W (47 ± 0.6 kHz) ultrasonic bath was used for extraction. The extractions were conducted at the maximum power setting. A MSE, Microcentaur centrifuge and a Retex Instruments vortex mixer were also required for separating particulate material from the extract. A pH meter and a TOC analyser were also used in these tests.

7.2.3 Analysis by P&T/GCMSD

Analysis by P&T/GCMSD was conducted using a Tekmar ALS 2016/ Tekmar LSC 2000 P&T sampler with sixteen 5 mL sparge tubes and VOCCARB 3000 (Supelco Inc. 2-1006) trap. The P&T was operated at a purge pressure of 270 kPa with ultra high purity helium and at a purge flow of 40 mL/min. The purge was activated for 8 min and the dry purge for 1 min. The desorb preheat was set to 245 °C, desorbed for 4 min at 250 °C and the trap was baked for 8 min at 270 °C.

The GCMSD system included a HP 5890 GC interfaced to a HP 5971 MSD. The operating conditions for the GCMSD were injector at 220 °C, interface temperature at 250 °C, inlet split at 20:1. The oven temperature program included an initial temperature of 35 °C (hold 4 min), at a rate of 10 °C/min to 240 °C and a final hold time of 0.5 min. The chromatographic column was a HP 624, 25 m long, 0.22 mm internal diameter and 1.12 μm film thickness. Figure 7.1 depicts a typical P&T unit.

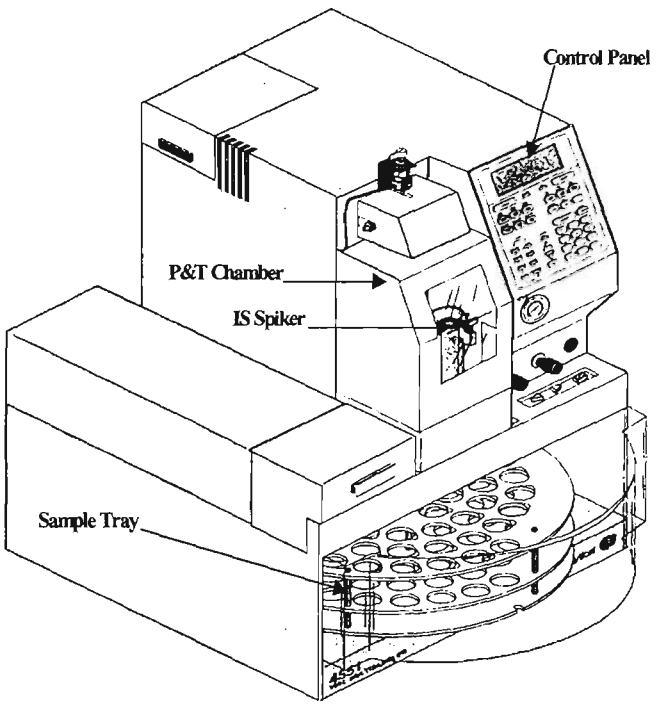

Figure 7.1: Example of a purge and trap unit (courtesy of OI Analytical).

7.2.4 Analysis by GCFID

Analysis by GCFID was conducted using HP 5890 GC with a model 7673 A auto sampler, a split/splitless injector and helium carrier gas. The operating conditions of the FID were: initial temperature at 40 °C held for 0.5 min, temperature programmed at rate (i) 27 °C/min to 100 °C, (ii) at 35 °C/min to 350 °C and a final hold time of 5 min. The injector temperature was 320 °C, injection volume 2 μL and detector temperature 355 °C. The chromatographic column was a BPX 5 (SGE Scientific), length 25 m, 0.22 mm internal diameter and 0.25 μm film thickness.

7.2.5 Analysis by Headspace/GCMSD

Analysis by headspace/GCMSD was conducted using a Perkin-Elmer HS 40 headspace analyser with an auto sampler capable of holding 40 samples, a 13 sample sub-rack with a built-in auto-shaker and a heater and timer to maintain each sample at 90 °C for 30 min to generate headspace vapours. The sample volume was set at 2 mL of vapour. The column interface was polyamide-coated fused silica capillary tubing, approximately 1 m long, 0.22 mm internal diameter and 0.33 mm external diameter. The temperature of the interfacing column between the headspace analyser and the GC was 180 °C.

The GCMSD was a HP 5890 GC interfaced with a HP 5970 MSD. The GC column was a HP 5, MS, 30 m long with 0.25 mm internal diameter 0.25 μm film thickness. The oven temperature was programmed at initial temperature at 40 °C, a hold time of 7 min, and a temperature gradient of 10 °C/min to 180 °C and a further hold time of 5 min. Samples were split at 27:1. Figure 7.2 shows the HS 40 headspace analyser coupled to a HP 5890 GC system.

7.2.6 Standard Solutions

7.2.6.1 P&T/GCMSD Standards

A stock solution of certified grade BTEX standard containing 5000 mg/L each of the components in methanol was purchased from Ultrascientific. Calibration standards at 5, 10, 20, 40 and 60 mg/L were prepared by diluting 5, 10, 20, 40 and 60 μL aliquots into the 5 mL Tekmar sampling chamber.

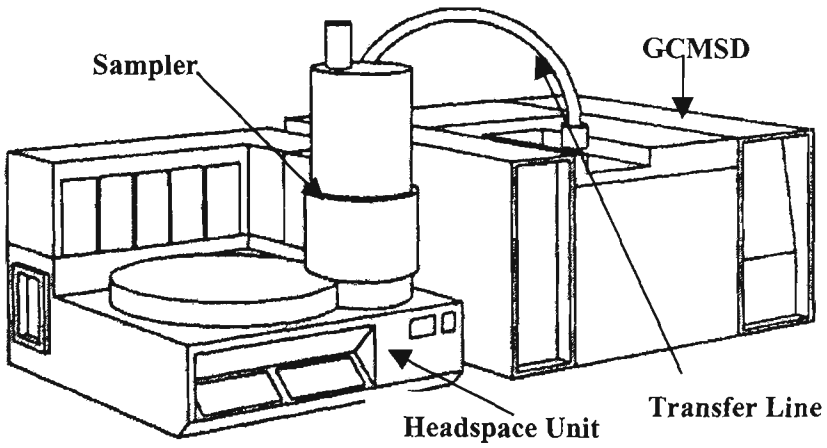

Figure 7.2: Example of a headspace (HS 40) coupled to a HP 5890 GC system (courtesy of Perkin-Elmer Australia and Hewlett-Packard Australia).

Internal standards (IS) were used to correct for injection volumes in case the injector malfunctioned. Certified grade IS were purchased from Ultrascientific. They included toluene-d_8, *4*-bromofluorobenzene and dibromofluoromethane, each at 2000 mg/L in methanol. Solutions were prepared by diluting a 500 µL sample into 200 mL flasks with methanol. These solutions contained each IS at 5 mg/L.

7.2.6.2 GCFID Standards

A stock solution was prepared using analytical reagent grade BTEX (Supelco) by weighing 10 g of each component into 100 mL standard flasks and diluting with DCM. These solutions contained 10,000 mg/L of each BTEX component. A mixed, dilute standard was prepared by adding 1 mL the stock solution to a 50 mL standard flask at 2000 mg/L for each component in DCM. A further two dilutions were prepared by : (i) diluting with DCM, 5 mL of the above mix into a 100 mL standard flask (This solution contained 100 mg/L of each BTEX component) and (ii) diluting a 2 mL solution from (i) into a 100 mL standard flask (This solution contained 2 mg/L of each BTEX component).

7.2.6.3 Headspace/GCMSD Standards

The calibration standards were prepared using procedures similar to those for the FID studies. However, methanol was used in place of DCM and an additional standard containing 1000

mg/L of each BTEX component was prepared in addition to the 100 mg/L and the 2 mg/L mixtures. Surrogate standards (SS) were analysed as a part of the calibration process to minimise errors due to headspace vapour generation. If the surrogate material was not recovered to at least 100 ± 20% then the samples were re-analysed. The compounds used as surrogate standards were chosen from components which were not expected to be found in soil. In most cases these components were radioisotope analogues of the test material. For example, toluene-d_8 was used as an SS in the radio isotope analogue of toluene. Certified grade SS standards were purchased from Ultrascientific. They included each component at 2000 mg/L in methanol. The components were dibromofluoromethane, toluene-d_8 and 4-bromofluorobenzene. A 10 µL mixed SS solution was added into every sample to monitor the extraction and the analysis. These components were used for monitoring and for correcting the efficiency of the headspace generation and injection volume.

7.2.7 Sampling and Analysis by P&T/GCMSD

The top 2 cm of soil was discarded to remove the interfacing layer that can undergo varying degrees of loss. Once the top layer was removed the soil in the jar was quickly stirred with a metal spatula and an 8 g sub-sample was removed and placed in 40 mL glass vial. Sub-samples for headspace/GCMSD and the GCFID were also taken at the same time. The complete sub-sampling process was performed as rapidly as possible to ensure minimum evaporation. All sub-samples were subjected to P&T/GCMSD analysis by calibrating with external standards. Sub-sampling for all tests was carried out as close to the same time as possible to minimise sample handling and losses.

Lumps in soil samples were rapidly broken using a clean glass rod while submerged in methanol. The soil was ultrasonically extracted for 30 min using 20 mL of methanol. The ultrasonic bath was cooled to at least to 10 °C using synthetic ice packs. Extracts containing particulate or floating insoluble material were centrifuged (13,000 rpm for 5 min). A quantity of methanol (between 10-1000 µL depending on the contamination) was added to 39 mL of

milli-Q water, the IS spiked added, and volume adjusted to 40 mL. The samples were then ready for analysis by P&T/GCMSD. A clean soil was analysed as a blank to determine if there was any interference. A multi-point calibration table was prepared using 5.0, 10, 20, 40 and 60 μg/L BTEX components.

7.2.8 Sampling and Analysis by GCFID

Sub-samples were weighed in 10 g lots into 40 mL P&T vials with 20 mL of DCM and placed inside an ultrasonic bath for 30 min. The ultrasonic bath was maintained at or below 10 °C to minimise any losses of BTEX and the soil samples were extracted at the highest sonicator setting (950 W) to dissolve BTEX in DCM. Approximately 10 g of anhydrous sodium sulfate was added to the container and sonicated for a further 10 minutes whilst it was drying with sodium sulfate. The soil was allowed to separate and settle. Extracts containing particulate or floating insoluble material were centrifuged (13,000 rpm for 5 min). A clean soil was analysed as a blank to determine if there was any interference. A multi-point calibration table was prepared using 2.0, 5.0, 25, 50 and 100 μg/L BTEX components.

7.2.9 Sampling and Analysis by Headspace/GCMSD

Sub-samples were weighed in 5 g lots into 20 mL headspace vials with 5 mL of a saturated calcium chloride solution and 10 μL of the 2000 mg/L SS added to each sample. The vials were capped and crimped immediately and placed in the ultrasonic bath for 30 min to homogenise and prepare for incubation at 90 °C. Sub-samples were subjected to headspace GCMSD analysis using an external standard calibration.

7.2.10 Identification Techniques

The GCFID measurements were taken by analysing the BTEX calibration standards and recording the retention time of each of the BTEX components eluting from the column. The soil extracts were analysed and the peaks eluting at the same retention windows to those as the calibration standards were identified and determined as BTEX. The quantification of each

BTEX component was conducted by the peak area ratios between the soil extract and the calibration standard multiplied by the concentration of the standard. These concentration measurements were obtained directly from the calibration table constructed using HP Chemstation software. The GCMSD measurements were taken for the headspace sampling method and the P&T sampling method from the GCMSD. These measurements included the peak areas of each BTEX component in the calibration standard and the peak area of components eluting at the same retention window as the soil extracts. These chromatograms are referred to as total ion chromatograms (TIC). The comparison of retention times is similar to the GCFID analysis. The mass spectrum of each of the BTEX components were checked for additional confirmation using ion fragments. The fragmented ions were referenced using the GCMSD library. The ions used in confirming each of the BTEX components and the IS are presented in Table 7.1.

Table 7.1: Confirmation ions for BTEX and IS.

Component	Confirmation Ions
Benzene	78, 51, 63, 74
Toluene	91, 65, 63, 51
Ethyl benzene	91, 106, 77, 65, 51
m-Xylene	91, 106, 79, 77, 65, 51
p-Xylene	91, 106, 79, 77, 65, 51
o-Xylene	91, 106, 79, 77, 65, 51
Dibromofluoromethane	113, 111, 192, 190
Toluene-d_8	98, 100, 70, 42, 80
4-Bromofluorobenzene	176, 174, 95, 75, 50, 151, 101, 85

Figure 7.3 shows a total ion chromatogram of a BTEX with IS and SS obtained from the GCMSD.

A second study was conducted on BTEX-free soil, spiked with a known amount of unleaded petrol, using the 3 methods. A quantity of loam with approximate clay content of 30% (w/w) was acquired from a local nursery and dried over night. The soil was sieved to retain all material between 300-550 microns. A sub-sample was solvent extracted and analysed using

GCFID. The results of the analysis indicated that the bulk soil was free of TPH and BTEX. Eight 1.2 kg portions of this soil were weighed into 1 L round bottom flasks and 120 mL of milli-Q water was added to each flask to give a soil moisture content of approximately 10%. The soils were mixed by manually shaking the flasks and connecting them to a modified rotary evaporator and rotating for 3 h. The contents of the flasks were allowed to settle over night and moisture contents were determined and found to be 9.6-8.5%. The flasks were stored in a refrigerator at or below 4 °C.

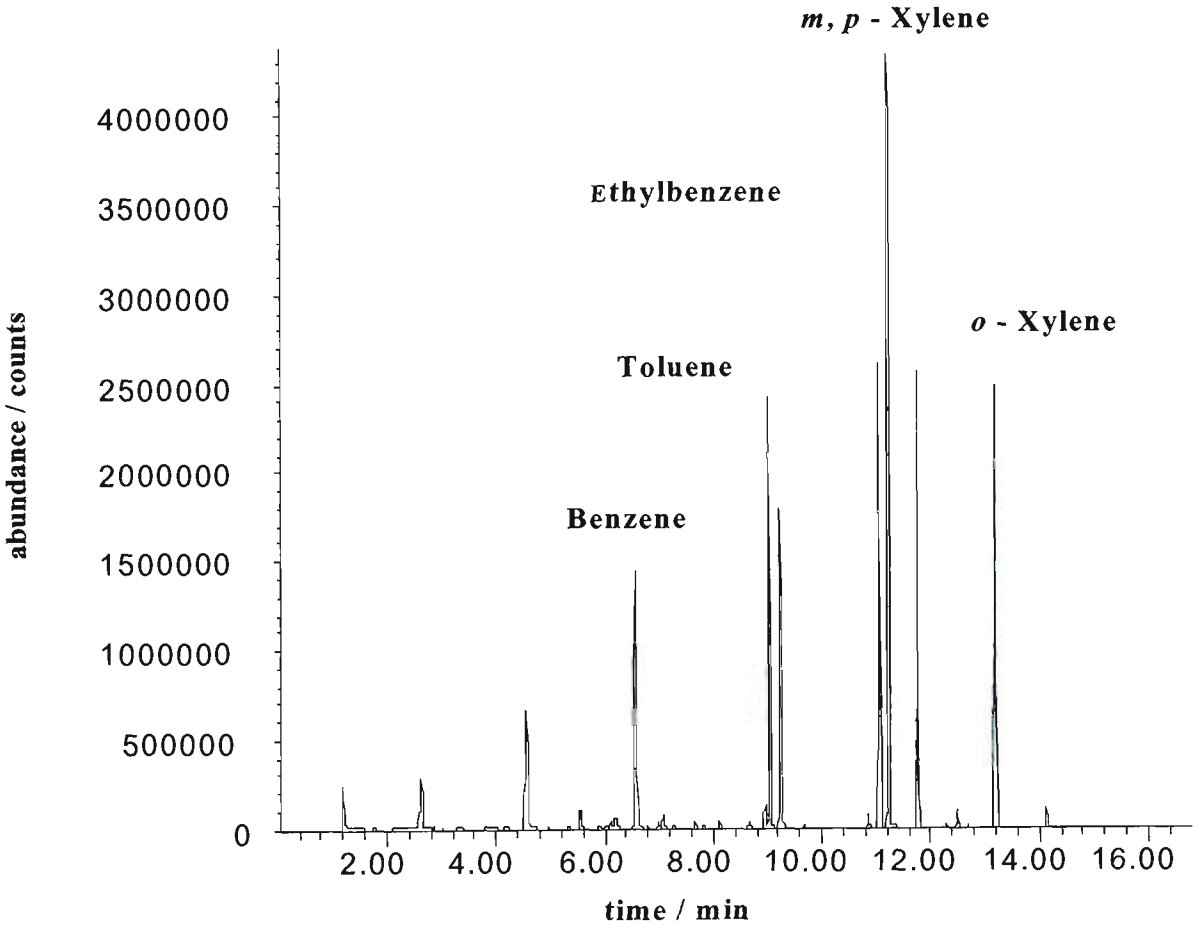

Figure 7.3: Total ion chromatogram of BTEX representing each component.

7.2.11 Study on Spiked Soil

Petrol sold as unleaded was purchased from a local service station and spiked at 30, 65, 80, 90, 100, 150, 180 and 200 mg/kg concentrations into the 8 homogenised soils. The spiking was conducted by cooling the unleaded petrol to approximately 4 °C, transferring with a glass

syringe and accurately weighing into each 1 L flask containing clean soil. The weights of spikes were 36, 96, 108, 120, 180, 216 and 240 mg respectively. After spiking with the unleaded petrol, the flasks were immediately closed and manually shaken for 30 min while being partially immersed in an ice water bath (4 °C).

The spiked soil was sub-sampled for the three methods using 10 g samples. During the process a 10 g sub-sample was taken and tested for moisture content and compared with the moisture content of the initial bulk sample to assess the homogeneity. The variation in moisture content was less than 5% (w/w) among the 8 bulk samples. A variation of 10% by weight in the moisture content was regarded as acceptable for this study.

7.2.12 Moisture Content and pH Determination

The moisture content was analysed as described in Section 3.2.6.4[31]. The pH was determined for each of the 109 soils by allowing them to dry in air over night and grinding each to form a fine powder[32,37]. A 10 g sample of the soil was weighed into a 100 mL glass jar with a screw cap and 50 mL of milli-Q water was added and tumbled for 1 h. Samples were removed from the tumbler and analysed within 1 min before the solution settled. If the samples had settled before the analysis they were shaken and analysed using a pH meter. The pH measurements were required to determine which samples contained extreme values to minimise adverse effects on the instrumentation and to implement procedures to minimise danger during handling. Knowing the pH values of the soils can assist the interpretation of results if anomalies are encountered.

7.2.13 TOC Analysis

The TOC was determined for each of the 109 soils. A series of sucrose standards were prepared by using 2.9686 g of sucrose in 250 mL milli-Q water in a standard flask. A series of dilutions were prepared by dispensing 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, and 10.0 mL of the standard into 250 mL Erlenmeyer flasks. These solutions were evaporated by placing them in

an oven at or just below 65 °C and cooling to ambient temperature. The soil samples were air dried overnight and ground to form a fine powder. Soil was weighed into a 250 mL Erlenmeyer flask (0.2-1.5 g) and 10 mL of 0.5 M sodium dichromate was added with gentle swirling to ensure soil particles were wet. The samples were held for 10 min with occasional swirling and 20 mL of concentrated sulfuric acid was carefully added. Samples were held for a further 30 min with gentle swirling then 170 mL of milli-Q water was added, mixed and allowed to cool and settle. Samples that were cloudy were centrifuged for 15 min to obtain clear solutions for analysis. Absorbance of the supernatant at 600 nm was determined (with water as blank). A standard curve was constructed by plotting absorbance of the standard sucrose assay against the known carbon content. For example 0.0594 g of sucrose contains 25 mg of carbon. The TOC values were assessed to identify if there were soil samples containing extremely high gasoline concentrations before conducting analyses such as the headspace GCMSD which could be dangerous due to the possibility of explosion.

7.2.14 Spot testing for Lime Content

The presence for lime was assessed for each of the 109 soils by adding a few grains of soil into 50 mL of 1 M HCl in a 100 mL glass beaker and any bubbles generated by the reaction between carbonate and the hydrochloric acid observed. The reaction showed a few bubbles, slow effervescence, rapid effervescence or vigorous frothing according to the carbonate concentration. The lime content was tested to confirm the higher pH readings.

7.3 Results and Discussion

7.3.1 Comparison Study on Soil Contaminated by BTEX

Soil samples were prepared for analysis by the three methods using the same preparation procedure. The extraction and the detection process for the three methods were significantly different. Tables 7.2, 7.3 and 7.4 summarise the characteristics of the methods based on discussions with experts and on various laboratory experiences with the methods [19-23].

The 109 soils were classified and it was found that 52 samples contained clay and 57 samples contained sandy soil representing twelve individual service station sites across Australia. The moisture content for the clay soil samples ranged from 3.4% to 33.2% (w/w) with average moisture content of 16.4% (w/w).

Lime was detected in 45 of the clay soils and 7 had a pH of less than 7.0. The pH values ranged between 5.0 to 9.6 with an average of 8.1. The TOC of the clay soils ranged between 0.01% (w/w) and 9.9% (w/w) with an average TOC of 2.1% (w/w). When the total BTEX concentrations were examined among the 52 clay soils, 43 soils were determined to contain BTEX by P&T/GCMSD and in 9 soils, total BTEX was not detected by any of the three methods. The total BTEX concentrations obtained for the clay soils by the three methods are presented in Figures 7.4-7.6. The lowest detectable concentration of total BTEX by each of the three methods was estimated as 0.5 mg/kg. Among the 43 clay soils containing BTEX by P&T/GCMSD, only 27 soils were positive to BTEX when analysed by DCM extraction/GCFID and only 19 soils contained BTEX when analysed by headspace/GCMSD. Soils found to contain BTEX at concentrations close to 1 mg/kg by P&T/GCMSD were not detected by the other two methods. This result indicates that P&T/GCMSD is more sensitive for BTEX than the other two methods. One soil sample containing approximately 650 mg/kg total BTEX by the P&T/GCMSD method was not detected to contain BTEX by the other two methods. This sample was further examined and found to contain a mixed matrix including stones, building material and rubble and was regarded as totally inhomogeneous.

When the total BTEX concentrations were examined among the 57 sandy soils, all were determined to contain total BTEX by P&T/GCMSD. Only four soils produced lower total BTEX concentrations by P&T/GCMSD method compared to the concentrations obtained by the other two methods. The remaining 53 soils produced higher concentrations of BTEX by P&T/GCMSD compared to the concentrations obtained by the other two methods for the same soils. These comparisons are presented in Figures 7.7-7.10. The moisture in the sandy

soils ranged between 0.8% (w/w) and 33.2% (w/w) with an average of 16.4% (w/w). Lime was detected in 50 of the sandy soils and 7 were with a pH < 7. The pH ranged between 3.8 and 10 with an average pH of 7.76. The TOC of the sandy soils ranged between 0.03% (w/w) and 8.9% (w/w) with an average of 3.1% (w/w). Among the 57 sandy soil samples 37 samples contained total BTEX by DCM extraction/GCID and 25 by headspace/GCMSD. Soils with total BTEX concentrations approaching 1 mg/kg only produced detection by the P&T/GCMSD.

Table 7.2: Comparison of methods.

Criteria	P&T GCMSD Methanol Extraction	GCFID DCM extraction	GCMSD Headspace
Economy	***	*(1)	**
Sensitivity for BTEX	***(2)	***(3)	*** (3),(4)
Complexity of analysis	***	*	**
Suitability for BTEX	***	***	***(5)
Freedom from cross contamination, interferences and losses during extraction	***(6)	* (7)	*(8)
Operator skill dependent	***	*	***

Key : * comparatively the least , ** comparatively moderate, *** comparatively high

(1) Toxicity of DCM is a concern

(2) BTEX may saturate in methanol when soils are heavily contaminated and therefore effect the measurement

(3) Moisture content may affect results

(4) Dependent on calibration range the instrument is set up for, there are limited options available for dilutions and concentrations

(5) May require considerable modifications of methodology which may not be economical for routine analysis, suitable for material which may contaminate instruments such as waxes, oils, food which requires testing for volatile contaminants

(6) Prone to the trap being contaminated by material from soil extracts

(7) Volatile contaminants can be lost during extraction and analysis

(8) Inside the headspace generating container there can be competition between other vapours, if present

Table 7.3: Advantages and disadvantages of the three extraction techniques.

	P&T/GCMSD (Methanol)	GCFID (DCM)	Headspace/GCMSD
Advantages	Not influenced by moisture content. Methanol has relatively low toxicity. Good sensitivity during P&T extraction and GCMSD confirmation.	Non-flammable. DCM has high extraction capacity relative to methanol.	No solvent used. Ease of sample preparation and ability to use GCMSD for confirmation.
Disadvantages	Methanol is a polar extractant with a limited solubility for BTEX. Relatively complex and expensive equipment.	Influenced by moisture content. DCM is highly toxic. DCM is a non-selective extractant and GCFID confirmation is only by retention time comparisons, which is insufficient.	Matrix effects can cause variations in the vapour composition. BTEX can be adsorbed into soil at varying degrees with variation in soil type. Reliant on headspace generation. Headspace sampler calibration highly dependent on material present in headspace sample, volume of sample and sampling time. Limited options for dilution or concentration. Relatively expensive equipment requirements. May require frequent modification to methodology to obtain reliable quantification.

Table 7.4: Advantages and Disadvantages of the Measurement Techniques.

	GCFID	GCMSD
Advantages	Relatively inexpensive. Easy to operate and maintain.	Confirmation built-in and Sensitivity can be improved through Selected Ion Monitoring (SIM). Can easily confirm BTEX from complex chromatograms.
Disadvantages	Requires confirmatory analysis. Relatively low sensitivity. Non-BTEX components can cause false positives.	Relatively expensive. High degree of technical skill required operating. High maintenance schedule and expensive repairs.

The comparison of concentrations by each method on a given soil sample demonstrates that, similar to the clay soils, the total BTEX was detected in most soils by the P&T/GCMSD followed by the DCM extraction/GCFID and least by headspace/GCMSD. These results suggest that the probability of detecting total BTEX for either clay or sandy soils are greater by P&T/GCMSD compared to DCM extraction/GCFID and headspace/GCMSD.

Most of the samples (clay and sand) determined by the P&T/GCMSD contained highest concentrations compared to the same samples analysed by GCFID. The same samples analysed by headspace/GCMSD were determined to be the lowest concentrations compared to the concentrations determined by the other two methods. The three sets of concentrations were statistically compared by the two-way ANOVA statistic. The two factors used for the ANOVA statistic were the samples and the methods. Since the 109 samples were analysed without replicates the "ANOVA two factor without replication test" was applied (Appendix 7.5.2). The interpretation of the statistic was that if samples were represented in rows in the Table of Appendix 7.5.1 and the test methods represented in columns there are significant differences between both the samples in rows (representing total BTEX concentration) and the columns (representing the three methods). Therefore the ANOVA statistics confirms that there are significant differences between the concentrations achieved for a soil when the three methods are used (Appendix 7.5.3). The histograms in Figures 7.4-7.10 graphically show that the BTEX concentrations achieved by the P&T/GCMSD are relatively higher than those achieved by the other two methods.

A higher proportion of sandy soils contained detectable total BTEX than clay soils and the concentration of total BTEX in sandy soils was greater than in clay soils. The method, which had the least sensitivity in detecting total BTEX, was the headspace/GCMSD especially when applied to clay soils. The results of this study were quite different to the published work carried out by Voice and Kolb (1993) who compared recoveries obtained for BTEX from spiked soil[38]. Their conclusion was that the recoveries for soils were better from the

headspace method than the P&T method. However, it should be noted that their study was limited only to clean soil spiked with BTEX and this could explain the apparent discrepancies between the two studies.

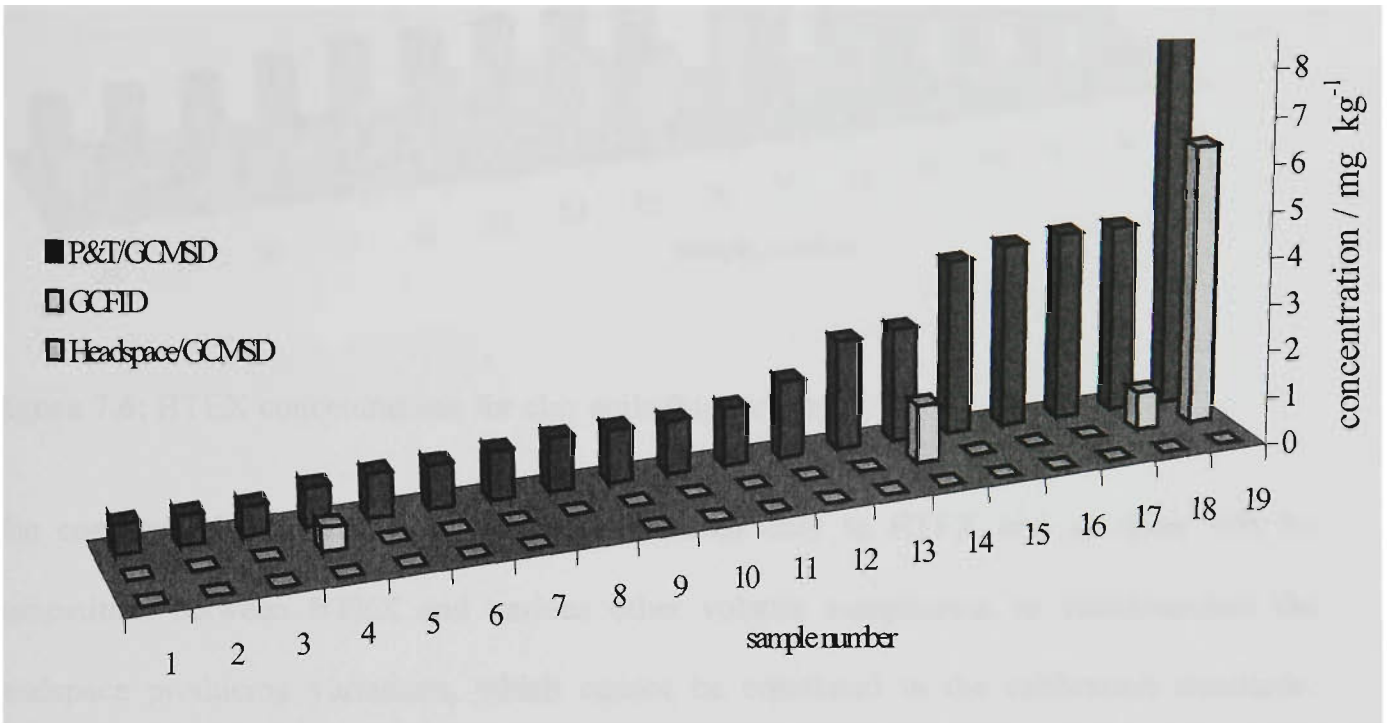

Figure 7.4: BTEX concentrations for clay soils (lower range).

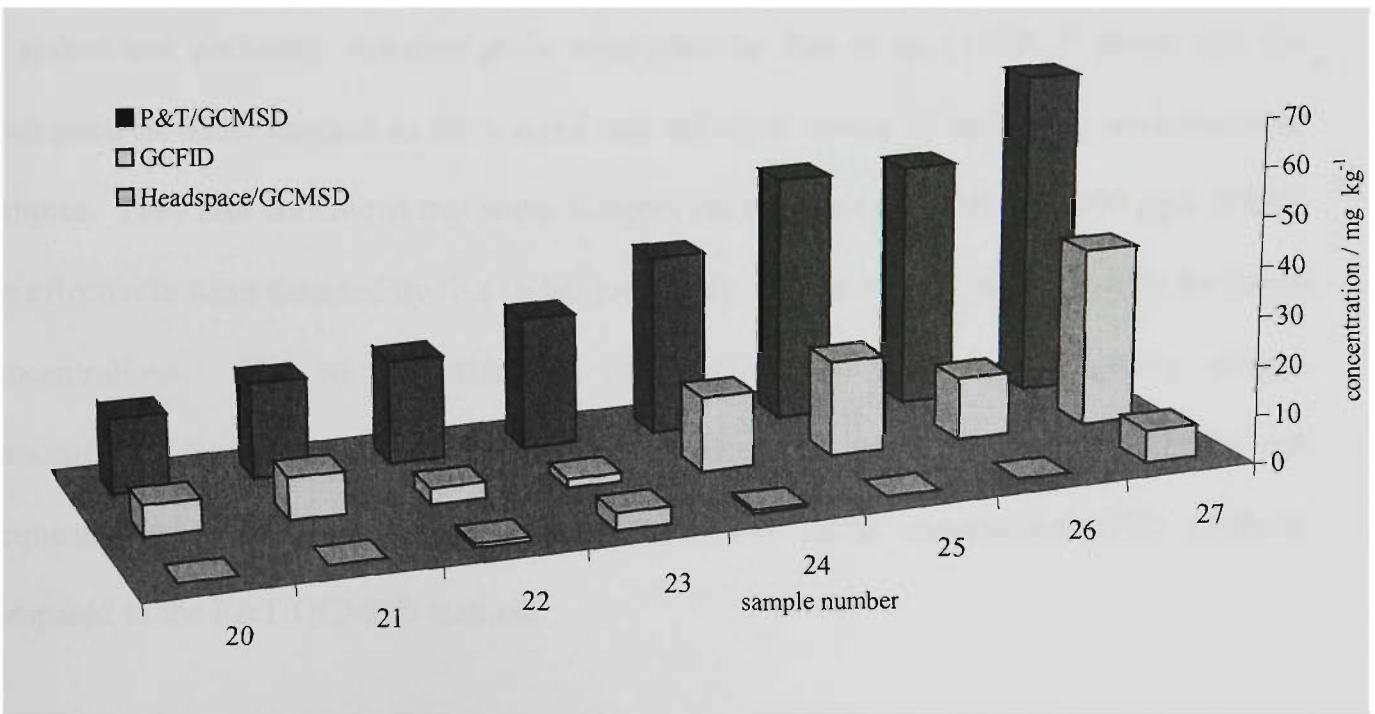

Figure 7.5: BTEX concentrations for clay soils (medium range).

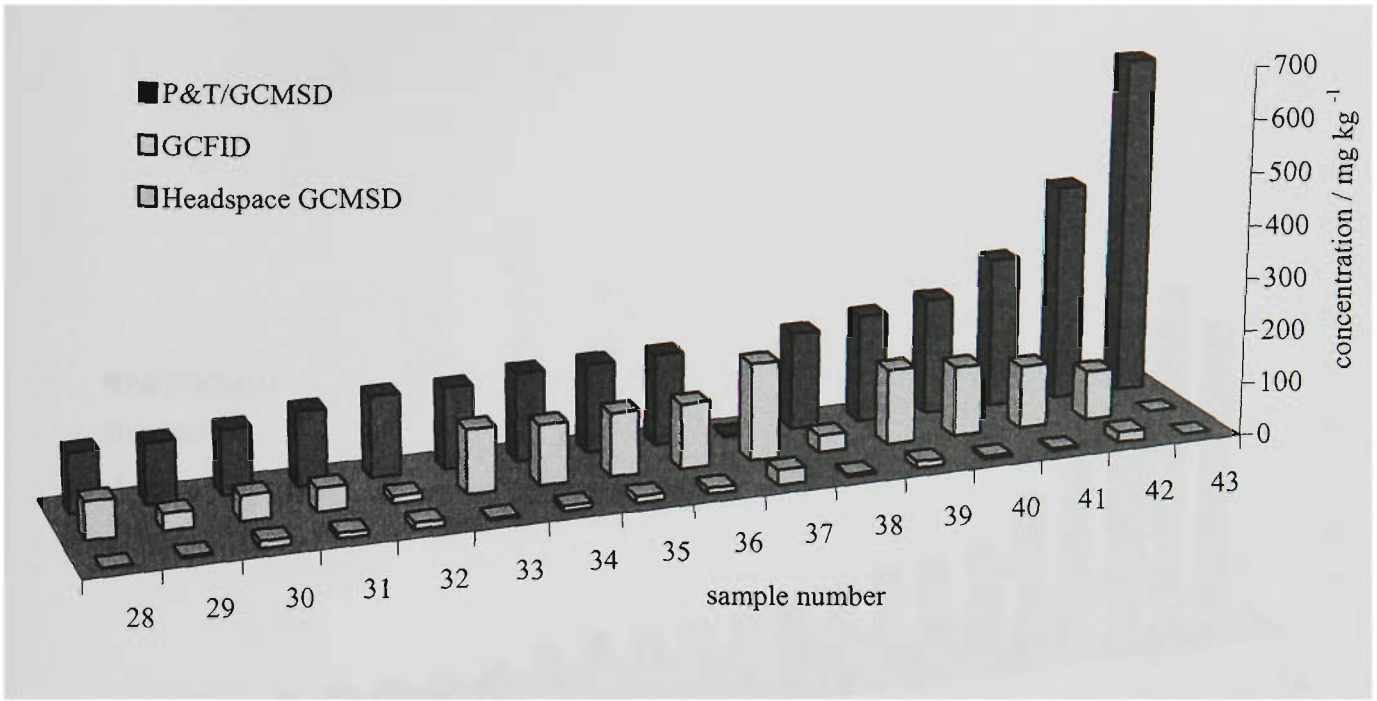

Figure 7.6: BTEX concentrations for clay soils (higher range).

The contamination in real soils cannot be limited only to BTEX and so there will be competition between BTEX and various other volatile components to accommodate the headspace producing variations, which cannot be correlated to the calibration standards. Additionally, interactions between actual soils and the contaminants can cause various environmental transformations and these behave differently to the spiked soils. Also the spiking technique may play an important roll in the studies. Spiked bulk samples are different to spiked test portions. Another study conducted by Roe et al. (1989) [11] found that the headspace/GCMSD method to be a rapid and effective means of analysing environmental samples. They also concluded that water samples containing a range of 1-15,000 µg/L BTEX are effectively were detected by this technique. They did not discuss the recoveries for lower concentrations. The work carried out on contaminated soils in the current project demonstrates that soils containing BTEX concentrations approaching 1 mg/kg are not frequently detected by the headspace/GCMSD and DCM extraction/GCFID methods compared to the P&T/GCMSD method.

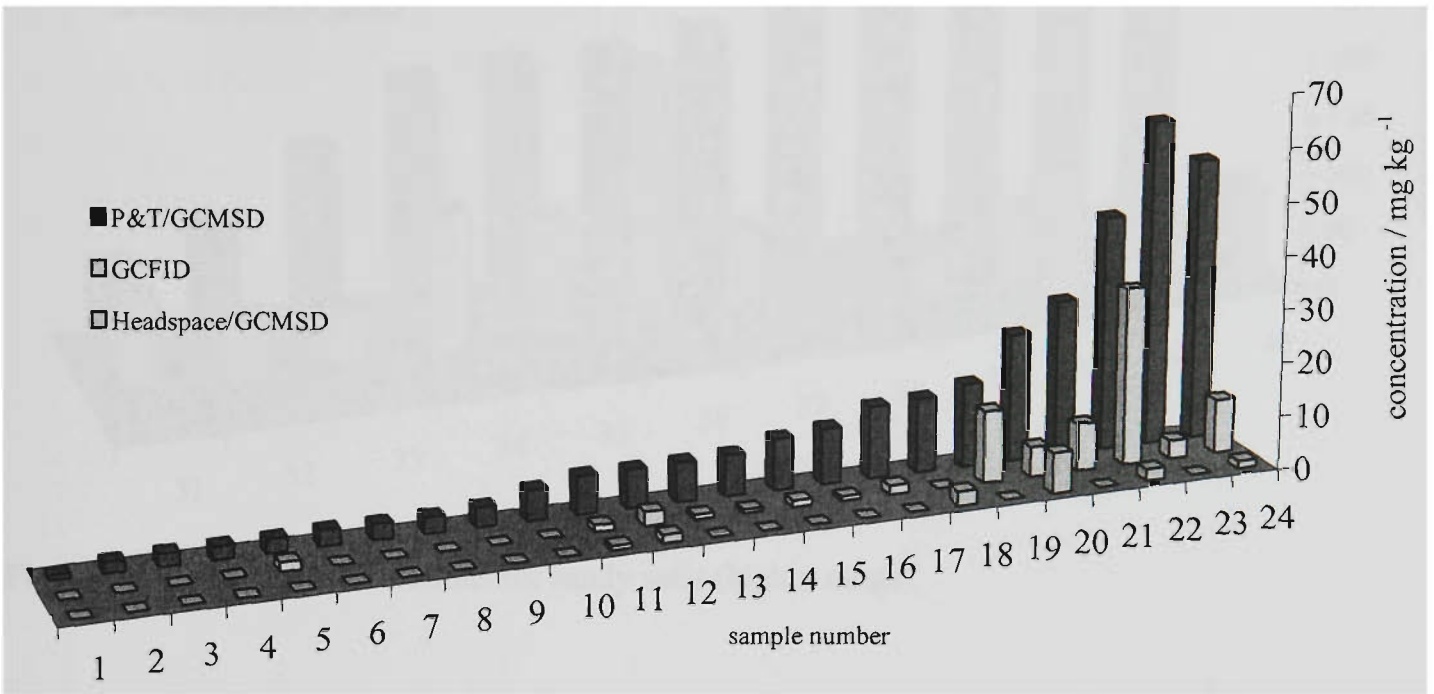

Figure 7.7: BTEX concentrations for sandy soils (lower range).

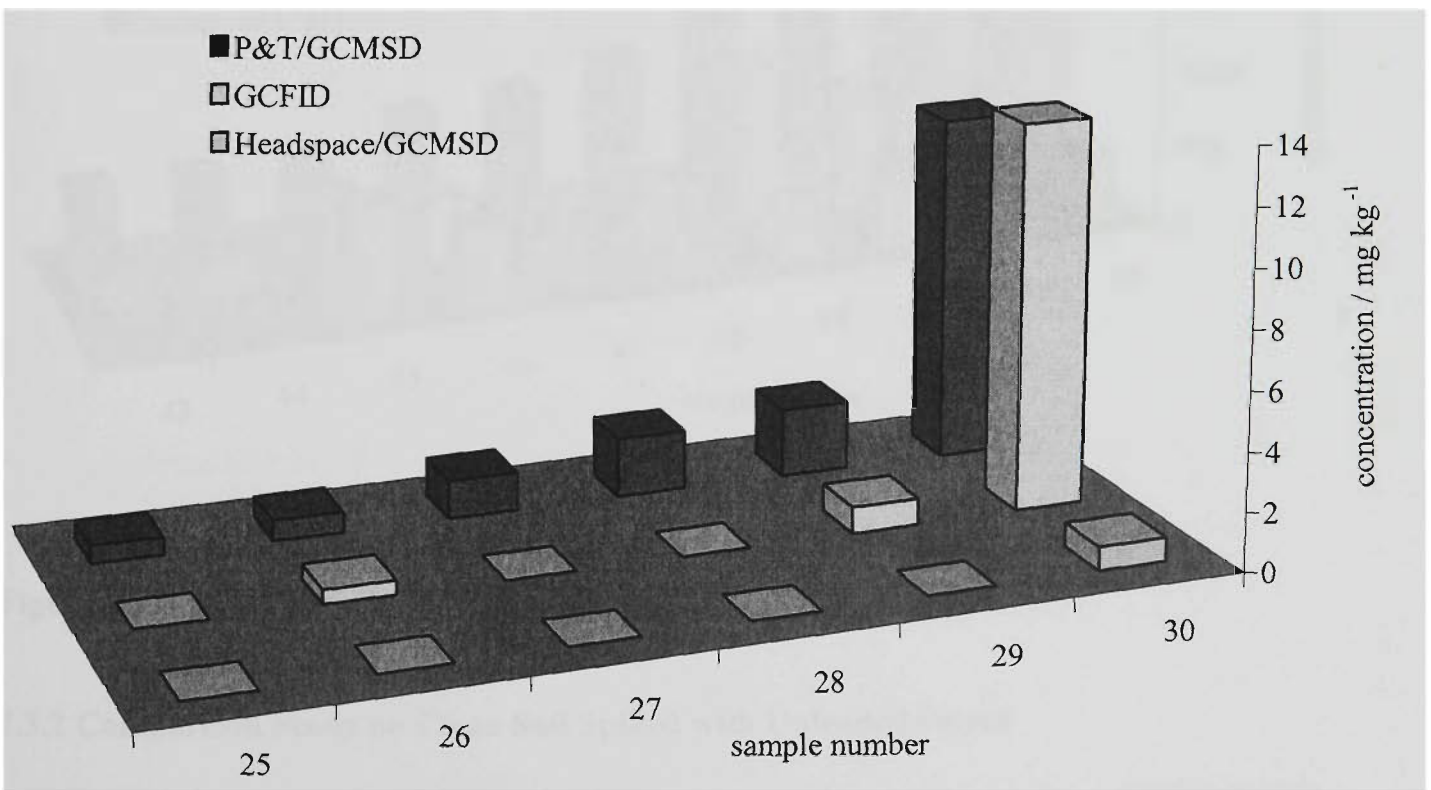

Figure 7.8: BTEX concentrations for sandy soils (medium range).

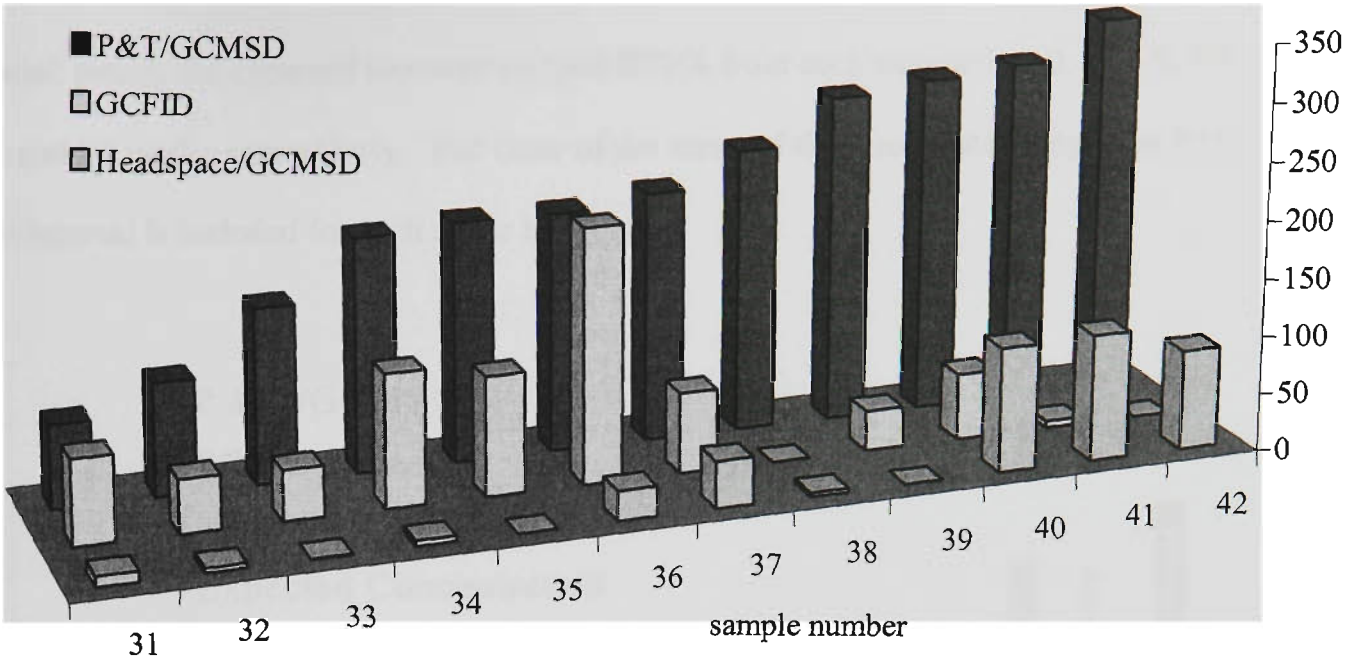

Figure 7. 9: BTEX concentrations for sandy soils (higher range).

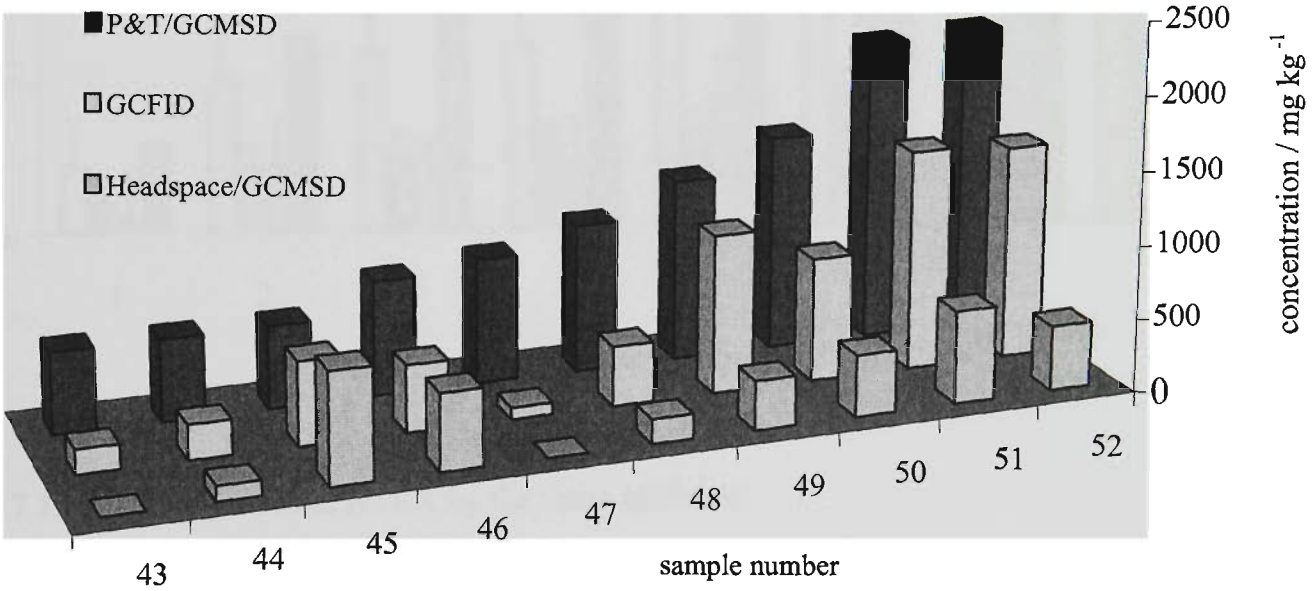

Figure 7.10: BTEX concentrations for sandy soils (very high range).

7.3.2 Comparison Study on Clean Soil Spiked with Unleaded Petrol

The recovered percentage of the total BTEX concentrations achieved from P&T/GCMSD, DCM extraction/GCFID and headspace/GCMSD methods for the 8 soils spiked with unleaded petrol are presented in Figure 7.11. The recoveries are compared for clean soil spiked with unleaded petrol at 30, 65, 80, 85, 100, 150, 180 and 200 mg/kg respectively. Assuming that

the BTEX in the unleaded petrol (as informed by the refinery) to be approximately 10% of the total unleaded petrol, the expected recovery of total BTEX from each sample is 3.0, 6.5, 8, 8.5, 10, 15, 18 and 20 mg/kg respectively. The error of the mean of three replicate analyses at 95% confidence interval is included for each of the histograms.

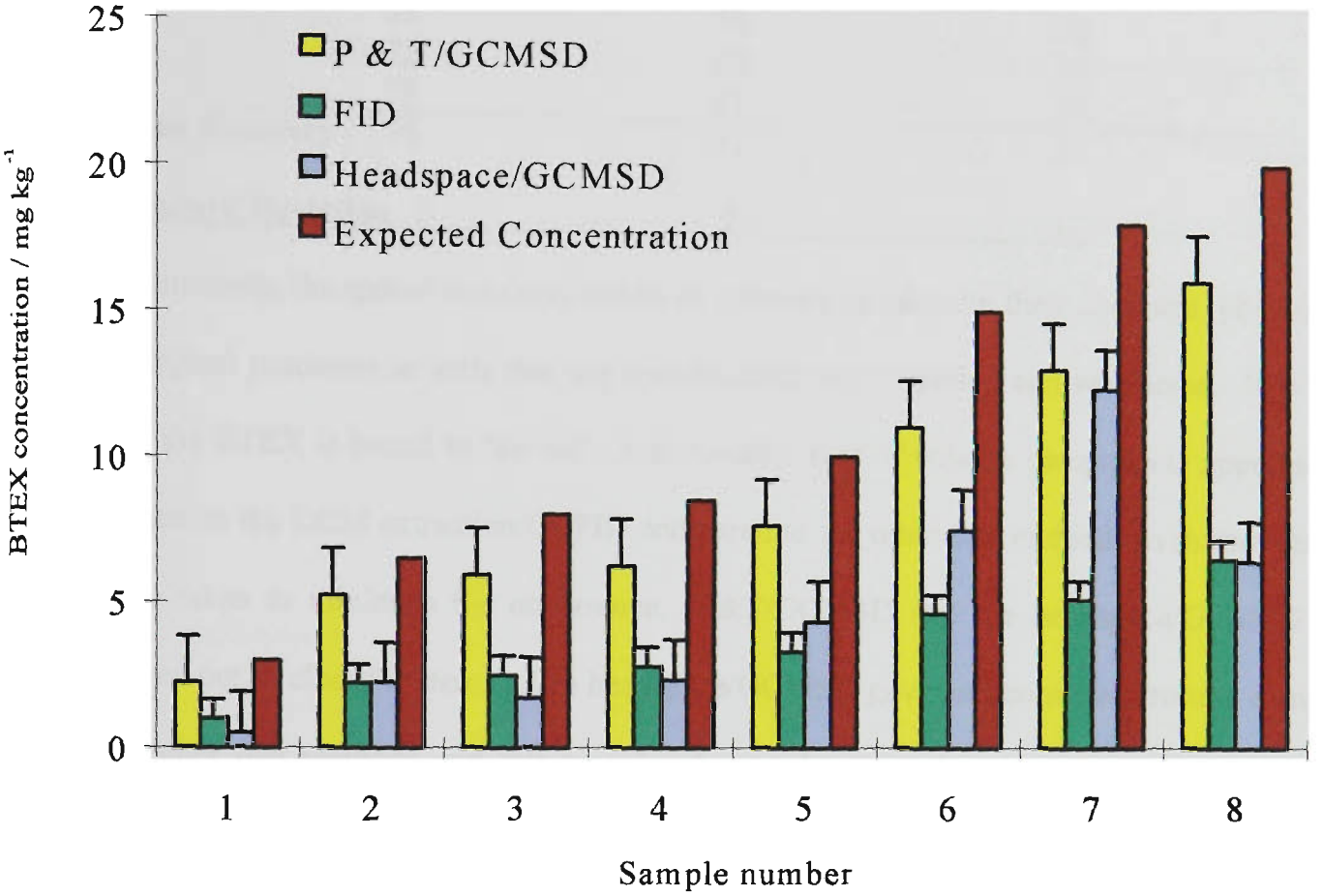

Figure 7.11: Recovery of total BTEX by the three methods.

Further assessments of total BTEX concentrations obtained for the spiked soils were conducted by calculating the percent recovery relative to the expected concentration. Table 7.5 summarises the percent recovery of total BTEX by the three methods. The highest recoveries on Table 7.5 are achieved by the P&T/GCMSD technique. Therefore, it is most likely that the BTEX in spiked soils behaves differently during the application of the three methods compared to BTEX in natural soils. This factor is especially prominent in clay soils which appears to be tightly compressed and difficult to extract.

Table 7.5: Percent recovery of total BTEX by the three methods.

	Percent BTEX by P&T/ GCMS	Percent BTEX by GCFID	Percent BTEX by Headspace GCMS
	76	33	16
	80	34	35
	74	31	22
	75	33	27
	76	33	44
	75	30	50
	72	28	68
	78	32	32
Mean Recovery	75	32	37
Standard Deviation	2	2	17

Additionally, the spiked soils may not be as complex in nature in their chemical, physical and biological processes as soils that are contaminated over a period and weathered. It is likely that the BTEX is bound to the soil. Additionally, loss of volatile components appears to be greater in the DCM extraction/GCFID compared to the other two methods even though steps were taken to minimise the occurrence. P&T/GCMSD and the headspace/GCMSD were carried out in closed systems. The headspace/GCMSD gave less consistent results compared the other two methods and this may be due to the limited control over the sample after formation of the headspace. In samples containing a number of volatile components each component can compete to occupy the headspace by other vapour components. The P&T/GCMSD method is the best method for total BTEX analysis due to P&T being efficient, easily controlled and with a capacity to concentrate material in the trap. The only drawback is the possible cross contamination of the trap by samples containing higher concentrations of material.

The results in Table 7.6 demonstrate that the highest percent recovery of BTEX is achieved by the P&T/GCMSD technique. The concentrations measured for the eight spiked samples of clean soil were also statistically analysed. The results indicate that P&T/GCMSD has the highest mean recovery of 75 ± 2% compared to values of 32 ± 2% and 37 ± 17% for

DCM/GCFID and headspace/GCMSD respectively. This indicates that both DCM/GCFID and headspace/GCMSD produce relatively low recoveries.

The error bars which overlap or are closest to the range of the spiked concentrations as shown in Figure 7.11 are those from the P&T/GCMSD. This further confirms that the P&T/GCMSD produces concentrations which are relatively closer to the expected concentration compared to the other two methods. At a confidence interval of 95% the mean percentage recovery values for P&T/GCMSD, DCM/GCFID and headspace/GCMSD are 75 ± 13, 32 ± 13 and 37 ± 113 respectively (t = 2.36 for 7 degrees of freedom). Therefore among the three methods the P&T/GCMSD method appears to be the most suitable for total BTEX analysis of soil. Since recovery corrections are not applied in BTEX analyses the preferable method is P&T/GCMSD due to its relatively higher percent recoveries compared to the other two methods.

7.4 Conclusion

Two studies were conducted to compare the BTEX concentrations achieved using three commonly used methods in Australia found through surveys among soil testing laboratories. The first study included 109 BTEX contaminated soils analysed by P&T/GCMSD, GCFID and headspace/GCMSD. The results of this study showed that the P&T/GCMSD technique to be the most reliable method to determine BTEX. This was especially prominent in soils containing BTEX concentrations approaching 1 mg/kg. The second study included the analysis of BTEX on spiked soil using the same three methods. The highest percent recovery of BTEX was achieved by the P&T/GCMSD. The samples tested by the GCFID and the headspace/GCMSD produced relatively low recoveries of BTEX. Therefore the current preference in Australian laboratories to use any one of the three methods can produce unreliable BTEX measurement which may not comparable against each other.

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Chapter Eight: The Validation of a Method for the Simultaneous Analysis of TPH (C_6-C_9) and BTEX By P&T/GCMSD

8.1 Introduction

The purpose of this chapter is to demonstrate by validating a method to be able to determine all volatile TPH fractions including BTEX using P&T/GCMSD. GC is extensively used for the analysis of trace concentrations of volatile TPH (C_6-C_9). Three such GC methods that are applied to the analysis of BTEX, a sub-class of TPH (C_6-C_9), are discussed in Chapter 7 of this thesis[1-9]. One of the most effective methods for BTEX determination and quantification has been demonstrated to be P&T/GCMSD. BTEX is a significant soil contaminant due to its toxic properties[10-15]. The P&T/GCMSD is capable of detecting BTEX to low parts per billion concentrations in soil, as required by regulators around the world[2-4,16-18]. Table 8.1 shows some of the constituents of petrol which fall within the TPH (C_6-C_9) fraction.

Table 8.1: Typical TPH (C_6-C_9) compounds found in petrol (BTEX represents 21% and monoaromatic hydrocarbons are represented by MAH.

Class of Compounds		Compound	Percent by Weight
MAH	BTEX	Benzene	1.9
		Toluene	8.1
		Ethylbenzene	1.7
		m-Xylene	4.6
		o-Xylene	2.5
		p-Xylene	1.9
		1,2,4-Trimethylbenzene	3.0
		1,3,5-Trimethylbenzene	0.98
Aliphatics		*2*-Methyl-*1*-butene	1.1
		2-Methylpentane	3.9
		3-Methylpentane	2.5
		2-Methylhexane	3.0
		3-Methylhexane	1.7
		2,2,4-Trimethylpentane	2.4
		Methylcyclopentane	1.8
		n-Hexane	2.4
		n-Heptane	1.1
Other		Other (PAHs, Phenols)	55.42

From the Table 8.1 it's clear that BTEX forms a significant component of the TPH (C_6-C_9) fraction. For any given sample of contaminated soil, the BTEX concentration should be less than the total concentration of TPH (C_6-C_9) measured. The following example demonstrates

the measured concentration of BTEX and TPH (C_6-C_9) obtained from seven homogenised, contaminated sandy soils. The BTEX in this case study was analysed by extracting one sub-sample of soil with methanol and determining the concentration by P&T/GCMSD. The TPH (C_6-C_9) was analysed by extracting a second sub-sample with DCM and determining the concentration with GCFID[19]. The concentration of BTEX and TPH (C_6-C_9) obtained by the two methods are tabulated in Appendix 8.1 and are depicted in Figure 8.1.

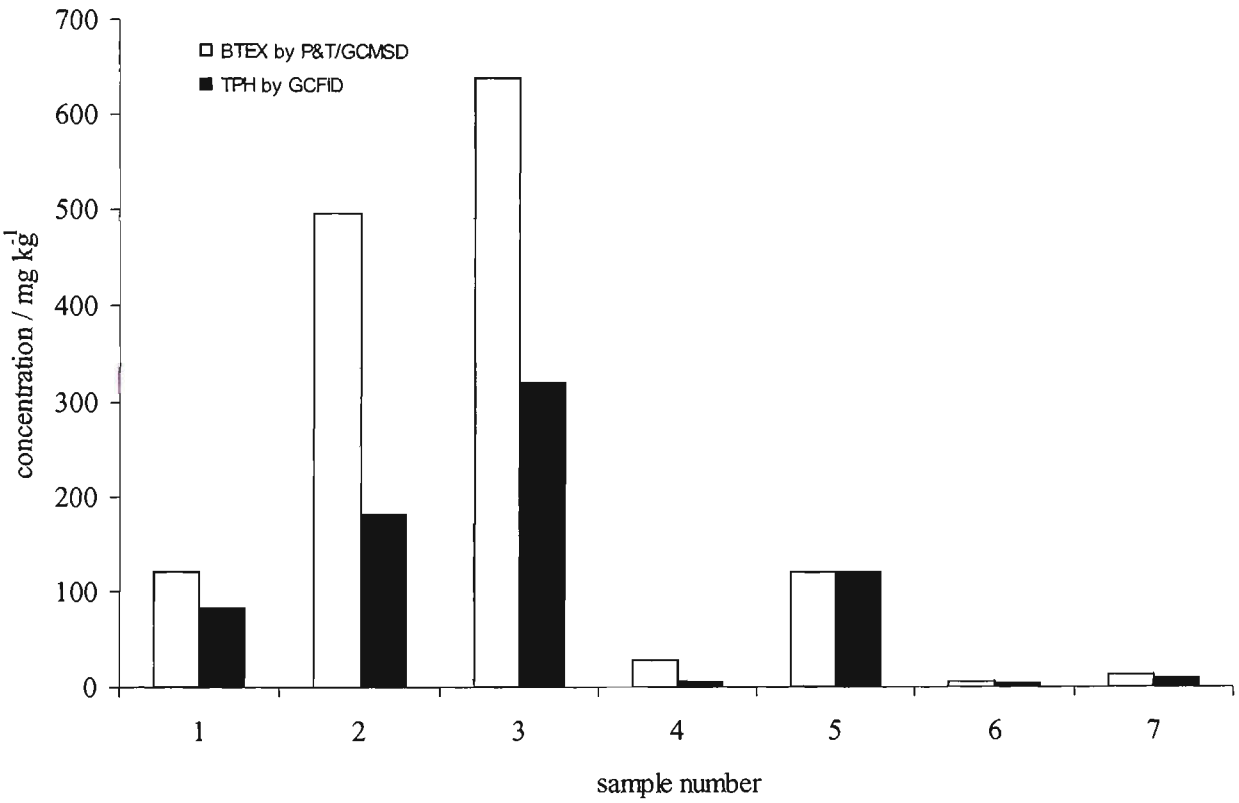

Figure 8.1: Comparison of BTEX and TPH (C_6-C_9) concentrations determined by P&T/GCMSD and GCFID.

Among the seven contaminated soils only one (sample number 5) is found to give sensible comparison between TPH (C_6-C_9) and BTEX concentrations. The remaining six soils show BTEX concentrations which are significantly greater than TPH (C_6-C_9). Such an outcome is clearly unacceptable. However, both methods were validated by the laboratory and accredited by the National Analytical Testing Authority (NATA) . This highlights the importance of choosing methods which not only are "validated and accredited" but which are actually

capable of producing concentrations which reflect the realistic relationship between BTEX and TPH (C_6-C_9). Even though the two methods are individually validated and accredited, they are not appropriate for simultaneous use to determine the required relationship between BTEX and TPH (C_6-C_9). One way to overcome this is to use a single method for both analyses. By selecting a single method the analyst will have more control over the analysis and therefore the uncertainty factors generated by two methods will be reduced.

The P&T/GCMSD method was demonstrated to be an appropriate method for BTEX analysis in Chapter 7 where recoveries were shown to be superior to those from the other two methods[9,19-21], namely GCFID and headspace/GCMSD.

This chapter includes a robust P&T/GCMSD method for the *simultaneous* analysis of TPH (C_6-C_9) and BTEX in petrol-contaminated soil. The method can be applied to contaminated soils to obtain the TPH (C_6-C_9) and BTEX concentrations with the proportions which are at reliable ratios. This ratio is frequently effected using most of the current methods. The method is based on the USEPA Method 8260[9], modified to incorporate TPH (C_6-C_9)[21]. The method has been validated to identify and quantify BTEX at a concentration range of 0.1-100 mg/kg and TPH (C_6-C_9) at a concentration range of 10-10,000 mg/kg in soil. When concentrations exceed the upper values, the extracts are diluted to fall within the validated range. This can be achieved since the components of TPH (C_6-C_9) are totally soluble in methanol.

8.2 Method Outline

The method involves extracting contaminated soil with methanol, transferring 100-1000 μL of the extract into water and bubbling helium through the water to purge the volatile components that are trapped in a tube containing a sorbent material. When purging is complete, the sorbent tube is heated and back-flushed with helium to desorb the trapped components. The components are evaporated and transferred onto a narrow bore capillary GC column for

separation and analyses by MSD. The GC column is temperature programmed to separate the components which are detected by the interfaced MSD. Qualitative identifications was confirmed by analysing standards and comparing mass spectra and GC retention times. BTEX components quantified by relating the MSD response for selected ions of the relevant standard to the TPH (C_6-C_9) computed by: (i) confirming all major peaks using the mass spectrometry library, (ii) removing compounds which are non-hydrocarbons and (iii) comparing the total ion chromatograms (TIC) of standards with those of the samples.

8.3 Reagents and Standards

All references to water in this method refer to organic-free reagent water. The P&T analysis was found to be extremely sensitive and prone to cross contamination by ultra trace vapour concentrations in the environment. For this reason, care was taken to segregate stock solvents from samples and instrumentation. Pesticide analysis quality methanol was used to prepare stock solutions and secondary dilution standards from pure material or standards purchased from Ultra Scientific, Australia. The standard solutions were prepared in methanol, as described under the standard preparation. Surrogate standards (SS) used were toluene-d_8, 4-bromofluorobenzene and dibromofluoromethane. Internal standards (IS) were chlorobenzene-d_5, *1,4*-difluorobenzene, *1,4*-dichlorobenzene-d_4 and pentafluorobenzene. The MSD was tuned using 25 ng/μL 4-bromofluorobenzene (BFB) in methanol. Calibration standards were prepared at five concentrations and matrix spiking standards for validations were prepared from BTEX and normal alkanes representing TPH (C_6-C_9).

8.4 Apparatus

The P&T consists of three separate parts; the sample purge, the trap and the de-sorb. The P&T sampling device was assembled as a separate unit coupled to the GCMSD. The purging chamber was designed to accept 5 mL samples, with a water column at least 3 cm deep. The gaseous headspace between the water and the trap contained a volume of less than 15 mL. The purge gas passed through the water column as fine bubbles having a diameter of less than

3 mm. The purge gas was introduced below 5 mm from the base of the water column. The trap was at least 25 cm long and had an internal diameter of at least 2.68 mm. Starting from the inlet, the trap contained layers of 2,6-diphenylene oxide; silica gel; and coconut charcoal all in equal proportions. The desorber was capable of rapidly heating the trap to 180 °C. The trap was baked-out by maintaining the temperature just below 220 °C. The purging chamber was maintained over the temperature range of ambient to 100 °C.

The P&T System included an OI-Analytical 4551 sampler, sparge tube of 5 mL capacity, a chamber with a 10 µL sparge tube for the addition of the IS. The trap was a Tenax/Silica Gel/Charcoal (OI-Analytical 219972), the purge pressure was set at 145 kPa with ultra high purity helium and the purge flow was set at 30-40 mL/min. The P&T was operated under the following settings: sampler purge time of 8 min, dry-purge for 1.00 min at 20 °C, de-sorb for 4.00 min at 180 °C, trap bake for 10.00 min at 180 °C, transfer line temperature 100 °C, valve 100 °C, sample volume 5 mL, 3 washes per sample, loop fill time 0.13 min, loop transfer time 0.20 min, needle depth 90% and cycle time 23.33 min.

The GCMSD data were assessed by the Enviro Quant data system. The GCMSD included a temperature-programmable GC suitable for splitless injection and accessories such as syringes analytical columns and gases. The GC was equipped with flow controllers to maintain constant column flow rate throughout de-sorption and temperature program operation. The capillary column was coupled to the MSD. The GC column was a 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco, Pty. Ltd.), 1.5 µm film thickness. The MSD was capable of scanning 35-300 atomic mass units (amu) every 2 s or less, using 70 V (nominal) electron energy in the electron impact ionisation mode. The mass spectrometer was capable of producing a mass spectrum for BFB, which met the mass-intensity specifications when 50 ng was injected [9,21]. Appendix 8.2 contains the BFB ion mass and required relative abundance required to validate the GCMSD.

The MSD was required to acquire at least five spectra while the sample component eluted from the GC. This ensures sufficient precision of the mass spectral data. The GC was interfaced to the MSD with a glass enrichment device and a glass transfer line.

A computer system, which allowed continuous data acquisition, was interfaced to the MSD. The software enabled searching for GCMSD data files for ions of a specified mass and for plotting ion abundance versus time or scan number (Extracted Ion Current Profiles (EICP)). The software also allowed the integration of the abundance in EICP between specified time/scan-number limits. The mass spectral library (i.e. Wiley Library of the HP Chemstation) was used for compound searching.

Micro syringes used for the measurements included volumes of 10-1000 μL. Two-way syringe valves with lure ends (three each) were used in the purging device. Syringes having 5, 10, or 25 mL volumes which were gas-tight with shut-off valves, as well as an analytical balance capable of weighing 0.0001 g and a top-loading balance capable of weighing 0.1 g were required. Glass scintillation vials with a capacity of 40 mL, with Teflon ™ -lined screw caps, were used for holding samples. Pasteur pipettes, class A volumetric flasks (10-100 mL) and spatulas were also required.

8.5 Procedure

8.5.1 Preparation of Reagents and Standards

Stock solutions were prepared by adding approximately 9.8 mL of methanol to a 10 mL calibrated ground-glass-stoppered volumetric flask and allowing the flask to stand, un-stoppered, for approximately 10 min or until alcohol-wetted surfaces were dry. The flask was weighed to the nearest 0.0001 g and the reference material was added as described. Solutions were transferred drop wise using a 100 μL syringe and the mass was recorded. This process was continued until the required mass was achieved. The standard was transferred into methanol. When the weighing was complete the volume was adjusted to the mark on the

flask with methanol, stoppered and mixed by inverting several times. The concentration was calculated in mg/L from the net gain in mass. When compound purity was assayed to be 96% or greater, the mass was used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards were used if they were certified. The stock standard solution was transferred into a Teflon ™ lined screw-cap bottle and stored at –10 °C in the dark with minimal headspace to limit vapour generation.

The secondary dilution standards were prepared using stock standards. These standards contained the required compounds, either singly or in combination. They were stored with minimal headspace. A stock solution of the SS was prepared at a concentration of 50-250 µg/10 mL in methanol. Each sample for GCMSD analysis was spiked with 10 µL of the SS prior to analysis. The material used as SS were compounds not found in real samples, that can be separated and identified from sample peaks by the GCMSD. The use of SS allowed the comparison of recoveries with respect to a system blank. The following ions were monitored in SS: dibromofluoromethane (113), toluene-d_8 (98) and *4*-bromofluorobenzene (95, 174 , 176).

The IS and secondary dilution standards were prepared in methanol using the procedures described below. The secondary dilution IS was prepared at 25 mg/L each. The addition of 10 µL of IS into a 5.0 mL of sample or calibration standard was the equivalent of 50 µg/L in solution. The IS were added to all samples. The IS were not regarded to be found in natural samples and could be separated, identified and quantified. The IS were used for the quantification of target compounds using calibration curves. Consequently they adjusted for fluctuations in purge efficiency and various injection errors. The following ions were monitored in IS: pentafluorobenzene (168), *1,4*-difluorobenzene (114), chlorobenzene-d_5 (117) and *1,4*-dichlorobenzene-d_4 (152).

Calibration standards were prepared at 5 concentrations from the secondary dilution of stock standards using organic-free reagent water. The matrix spiking standards for the validation were prepared in methanol, with each compound at 250 μg/10.0 mL. Standards in methanol were stored at –10 °C in amber bottles with Teflon ™ lined screw caps. The calibrations were carried out with the tuning set to maximum sensitivity using perfluorotributylamine (PFTBA) ions 69, 219 and 502. The automated tuning program to optimise the MSD with respect to bromofluorobenzene (BFB) also used the BFB. The BFB tune evaluation was carried out by purging 50 ng of BFB. The P&T/GCMSD was calibrated using BTEX at 2, 10, 25, 60 and 100 mg/L and *n*-C_6, *n*-C_8 and *n*-C_{10} at 4, 20, 50, 120 and 200 mg/L. The IS and SS at 10 mg/L of each component was spiked into all samples. Figure 8.2 contains a profile of the TPH (C_6-C_9) standard. Note that the smaller peaks in the background are due to responses by the SS/IS.

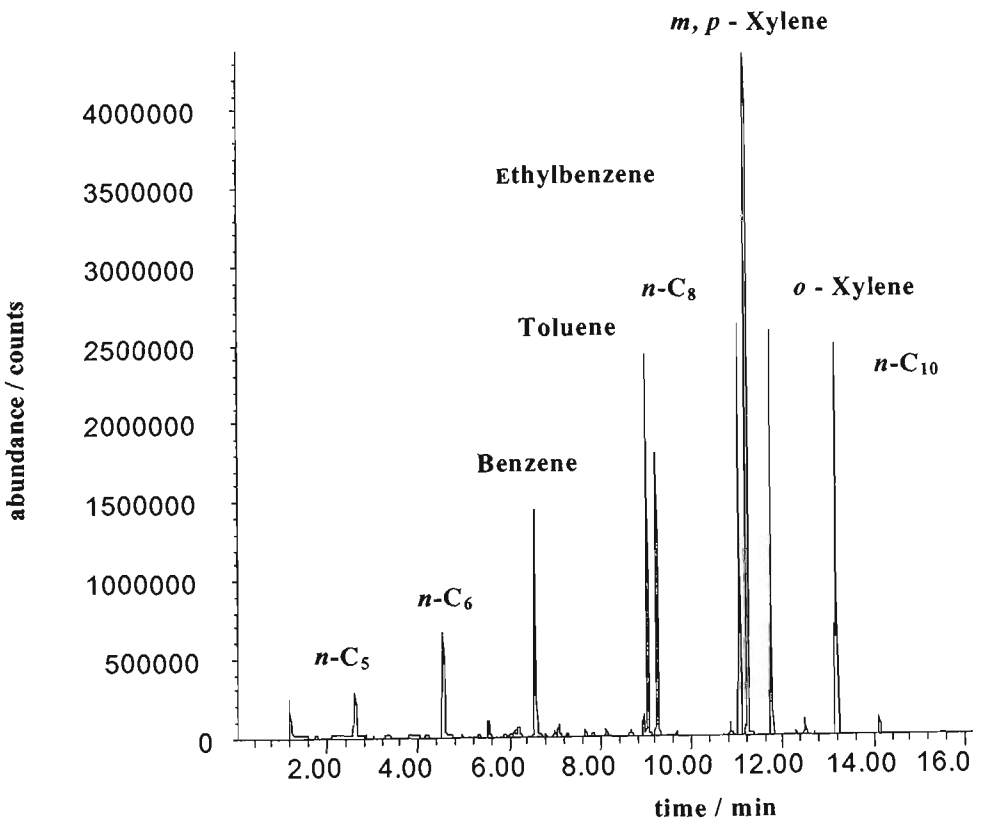

Figure 8.2: Profile of the TPH (C_6-C_9) standard containing aliphatic and aromatic hydrocarbons.

8.5.2 Trap Conditioning

The trap was conditioned at 180 °C by back flushing with an inert gas flow of 20 mL/min. The trap effluent was vented after disconnecting the column. Prior to daily use, the trap was conditioned for 10 min at 180 °C. The trap was vented to the analytical column during daily conditioning; however, the column was run through the temperature program prior to the analysis of samples. Signs of a deteriorating trap were uncharacteristic recoveries of SS, especially toluene-d_8, a loss of the response of the IS during a 12 h run and a rise in the baseline in the early portion of the scan.

8.5.3 Chromatographic Conditions

The instruments included the OI-Analytical 4551 P&T sampler, HP 5890 Series II plus a GC interfaced to a HP 5972 MSD and HP G1032C Enviro Quant software, HP 624, 25 m x 0.2 mm x 1.12 µm column and ultra high purity helium carrier gas. The GC conditions including an injector temperature of 220 °C, interface temperature of 250 °C, inlet split of 20:1, a temperature program with initial temperature 35 °C held for for 4 min, temperature ramp rate of 10 °C/min, final temperature 240 °C held for 0.5 min.

8.5.4 P&T/GCMSD Calibration

The GCMSD hardware was tuned to meet the BFB mass-intensity specifications. A set of 5 calibration standards was used. The area response of the characteristic ions (Appendix 8.3) was tabulated against the concentration of each compound and each IS. The response factors (RF) for each compound relative to one of the IS were calculated. The IS selected for the calculation of the RF was the one with a retention time closest to the compound being measured.

The RF was calculated as follows:

$$RF = (A_x.C_{is}) / (A_{is}.C_x)$$

where: A_x = area of the characteristic ion for the compound being measured; A_{is} = area of the characteristic ion for the specific IS; C_x = concentration of the compound being measured; C_{is} = concentration of the specific IS. The average RF was calculated and recorded for each compound.

Using the RFs from the initial calibration, the percent relative standard deviation (% RSD) for

calibration check compounds (CCC) were calculated as follows:

$$\% \text{ RSD} = (\text{SD} / x_{\text{mean}}) (100)$$

where: % RSD = percent relative deviation; x_{mean} = mean of 5 initial RFs for a compound; SD = standard deviation of average RFs for a compound

The % RSD for each CCC was required to be less than 30%. The CCCs used were toluene and ethylbenzene. The GCMSD was calibrated by injecting 50 ng of the BFB. The resultant mass spectra was required to satisfy all of the mass-intensity specification criteria. After every 12 h of analysis time, a calibration standard at a concentration near the mid-point for the working range of the GCMSD was used to check if there were changes. After the system performance was verified, the validity of the initial calibration using the CCC was checked. The percentage difference was calculated using the following equation:

$$\% \text{ Difference} = ((RF_{I\,ave} - RF_C) / RF_{I\,ave}) (100)$$

where: $RF_{I\,ave}$ = average response factor from initial calibration; RF_C = response factor from current verification check standard.

If the difference for any compound was greater than 20%, it was considered a warning. If the difference for each CCC was less than 25%, the initial calibration was assumed to be invalid. If the retention time for any IS changed by more than 0.5 min from the last daily calibration, the chromatographic system was inspected for malfunctions.

8.5.5 GCMSD Analysis

P&T is designed to analyse trace levels of volatile components. Therefore, if grossly contaminated samples are introduced they may contaminate the trap, necessitating extensive clean-up. To overcome this problem, the contaminated soils were screened to estimate approximate concentration prior to P&T/GCMSD analysis. Screening was carried out using the DCM extraction/GCFID, method detailed in Chapter 7 [19]. Using DCM extraction/GCFID the TPH (C_6-C_9) and BTEX can be analysed simultaneously while analysing for the semi-volatile TPH (C_{10}-C_{36}) (if required) on the same sample. The approximate concentration of TPH (C_6-C_9) obtained by DCM extraction/GCFID also provided an estimate to carry out dilutions prior to the P&T/GCMSD. The OI-Analytical P&T system incorporated an automatic spiker, which made a 10 µL per 5 mL sparge tube addition of IS. To ensure accuracy, the addition was made into the sample stream while the sparge tube was filled. Soil samples were prepared by weighing 8.0 g into a 40 mL vial fitted with a screw-top cap and Teflon ™ coated septum. The samples were refrigerated to sub-ambient temperature and 20 mL of methanol was quickly added. The samples were then sonicated in a Branson 8210 ultra sonic bath for 30 min. The extract was centrifuged if necessary at 500 rpm for 20 min to separate particles and then refrigerated to sub-ambient temperature to minimise losses. When the sample was chilled below ambient temperature, 1.0 mL of the methanol extract was quickly added into a 40 mL vial containing 39 mL of organic-free reagent water. In some cases an aliquot of the solvent extract was diluted and 100 µL was taken for analysis. The moisture content of each soil was analysed using the method detailed in Section 3.2.6.4 [23]. Concentration of individual analytes was reported on dry weight basis.

8.5.6 Data Interpretation

An analyte was identified by comparing the sample mass spectrum with the mass spectrum of a standard. Mass spectra for references were obtained by analysing the calibration standards.

The following criteria were developed as a part of the study to verify identification:

1. Elution of sample component at the same GC relative retention time (RRT) as those of the standards

2. Comparison of mass spectra of the samples with the relevant mass spectra of the standards.

The retention time (R_t) of a sample was compared within ± 0.06 R_t units of the standard. The standard was analysed within the same 12 h period as the sample.

1. All ions present in the standard mass spectra at a relative intensity greater than 10% of the most abundant ion, had to be present in the sample mass spectrum.

2. The relative intensities of ions must agree within ± 20% between the standard and sample mass spectra. For example an ion with an abundance of 50% in the standard spectra; the corresponding sample abundance must be between 30-70%.

For samples containing components not associated with the calibration standards, a library search was conducted to determine tentative identification. Criteria for making tentative identifications were:

1. Relative intensities of major ions in the reference mass spectrum (ions >10% of the most abundant ion) should be present in the sample mass spectrum.

2. The relative intensities of the major ions should agree within ± 20%. (for an ion with an abundance of 50% in the standard spectrum; the corresponding sample abundance must be between 30-70%).

3. Molecular ions in the reference spectrum should be present in the sample spectrum.

4. Ions in the sample mass spectrum but not in the reference mass spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

5. Ions in the reference mass spectrum but not in the sample mass spectrum should be reviewed for subtraction from the sample spectrum because of background contamination or co-eluting peaks. When a BTEX component was identified, the quantification was based on the integrated abundance from the EICP of the primary characteristic ion. The IS used was the one nearest to the retention time of the analyte.

The external standards *n*-C_6, *n*-C_8 and *n*-C_{10} were used in identifying the range of the TPH (C_6-C_9) and the integration boundaries between the beginning of *n*-C_6 and the beginning of *n*-C_{10} peaks. The TPH (C_6-C_9) determination was conducted in conjunction with BTEX. The BTEX components were determined individually by quantifying ions using the respective calibration curves. The remaining C_6-C_9 were determined against an average response of external standard BTEX and the normal alkanes *n*-C_6, *n*-C_8 and *n*-C_{10}. The following criteria were developed to determine the TPH (C_6-C_9) in this study:

(a) The concentration of each BTEX component was computed using the respective calibration curve.

(b) The total response area was computed using baseline-to-baseline integration technique between the beginning of *n*-C_6 to the beginning of *n*-C_{10}.

(c) The BTEX response area was subtracted from the total area response in (b).

(d) The response area of the water blank including the SS and the IS were subtracted from the total response area in (b)

(e) The areas in (b)-(c)-(d) were converted to concentration using the respective standards.

(f) The concentration of TPH (C_6-C_9) was computed by adding the concentration obtained in (e) to the BTEX concentration obtained from individual BTEX analyses.

The above procedure was applied to ensure that the BTEX and TPH (C_6-C_9) concentrations are obtained by treating BTEX as a subset of the TPH (C_6-C_9).

8.5.7 Quality Control

The quality control (QC) program consisted of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate quality data. The laboratory maintained records to document the quality data through control charts. Ongoing data quality checks were compared with established performance criteria to determine if the results of analyses met the performance characteristics of the method. When results of sample spikes indicated a typical method performance, a quality control check sample was analysed to confirm the measurements were performed in an in-control mode of operation. Before processing samples, it was demonstrated, through the analysis of a calibration blank, that interference from that analytical system, glassware, reagents and the surrounding environments were minimal. When a set of samples was extracted or there was a change in reagents, a reagent blank was analysed as a safeguard against laboratory contamination. The blanks were carried through stages of sample preparation and measurement. The calibration standard was evaluated using the following criteria to determine if the chromatographic system operated properly:

(1) Checking if the peaks shapes were characteristic

(2) If the response was comparable to the previous calibrations (careful examination of the standard chromatogram to indicate whether the column was still useable, if the injector was leaking and if the injector septum required replacing)

(3) If changes were made to the system (e.g. column changed), the system was re-calibrated

(4) The GCMSD was tuned to meet the BFB specifications

The concentration of the spike in the sample was determined as follows:

In compliance monitoring, the concentration of a specific analyte in the sample is checked against a regulatory concentration limit [2-3]. The spike should be at that limit or 1-5 times higher than the regulatory limit.

The percent recovery for each analyte was calculated by the following formula:

$$R = 100\ (A - B)\ \%/T$$

Where: R = percent recovery; B = background concentration; A = concentration after spiking; T = known true value of the spike.

8.5.8 Method Performance

The validation study was conducted by using a 2 kg sample of clean soil, which contained a mixed soil matrix with approximately 50% clay, 20% organic matter and a moisture content of 5%. To achieve the best possible validation data the soil was chosen to represent a mixed soil. Prior to homogenisation, stones and twigs were removed and the sample homogenised using a large mortar and pestle and sieved down to 100 microns. The homogenised soil was cooled to 4 °C and 8 g lots were weighed into 40 mL glass P&T vials. Each vial was spiked at the surface of soil with BTEX. The spiked concentrations are depicted in Table 8.6. The vials were capped with Teflon ™ lined screw caps and quickly shaken to homogenise their contents while maintaining the temperature at 4 °C. Seven replicate spikes were tested at each concentration. After spiking the clean soil with the BTEX, the SS was added to obtain a 50 µg/L concentration in methanol. 20 mL of methanol and the IS (50 µg/L in solution) was then added. The mixture was sonicated for 30 min while maintaining the temperature at 4 °C.

Table 8.2: Concentrations of BTEX used for the validations as seven replicates.

Amount of Spike	Concentration of Each BTEX Component (mg/kg)
8 μL of 100 mg/L	0.1
80 μL of 100 mg/L	1.0
8 μL of 1000 mg/L	10
80 μL of 1000 mg/L	100

A 1 mL sample of the methanol extract was added to 39 mL of organic-free reagent water. Similarly 8 g of the clean soil was spiked with a mixture containing *n*-C_6, *n*-C_8 and *n*-C_{10} as depicted in Table 8.7. Samples spiked with BTEX and alkanes were analysed using methods specified in Sections 8.5.2-8.5.8.

Table 8.3: Concentrations of alkanes used for the validation as seven replicates.

Spike Volume	**Concentration of Each Alkane Component (mg/kg)**
8 μL of 10000 mg/L	10
80 μL of 10000 mg/L	100
8 μL of 100000 mg/L	1000
80 μL of 100000 mg/L	10000

8.6 Results and Discussion

The method was validated for the analysis of contaminated soil containing BTEX each component at a concentration range of 0.1-100 mg/kg and the alkanes each cmponent at a range of 10-10,000 mg/kg. The recovered BTEX and alkanes were assessed (i) against the spiked concentration and (ii) the linearity between the spiked concentration and the selected ion area response for the BTEX and the total ion area response for the alkanes representing the TPH (C_6-C_9). Figure 8.3 contains the spiked concentration of each of the BTEX against the recovered concentration from P&T/GCMSD. The histograms are represented in pairs and the first histogram in each pair contains the spiked concentration of BTEX and the second represents the mean of 7 replicates recovered from spiked soil. No pair of values was found

to be significantly different at the 95% confidence level. The recoveries obtained were all approaching the spiked concentrations (i.e. > 90%) and therefore regarded as valid recoveries in environmental analysis of volatile components. Since a mixed soil containing significant clay and organic content was used it could be regarded as representing a range of soil types[24-26]. Figure 8.4 contains the spiked concentration of each of the alkanes against the recovered concentration from P&T/GCMSD. The histograms are represented in pairs similar to the above BTEX study and the first histogram in each pair contains the spiked concentration of alkane with the second representing the mean of 7 replicates recovered from spiked soil.

The error bars are drawn on the spiked concentration representing the spread of the results of the mean of the replicates. The recoveries obtained were all approaching the spiked concentrations (i.e. > 90%) and therefore regarded as valid recoveries in environmental analysis of volatile components.

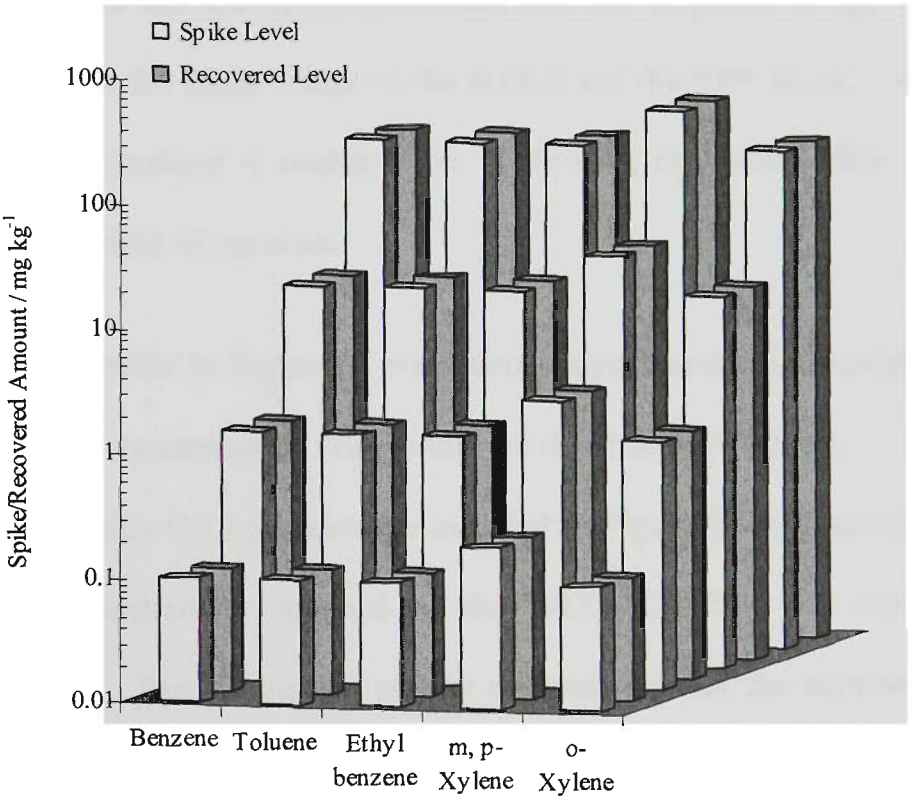

Figure 8.3: Comparison of Spiked BTEX concentrations at 0.1, 1.0, 10 and 100 mg/kg, with reference levels. No pair of values was found to be significantly different at the 95% confidence.

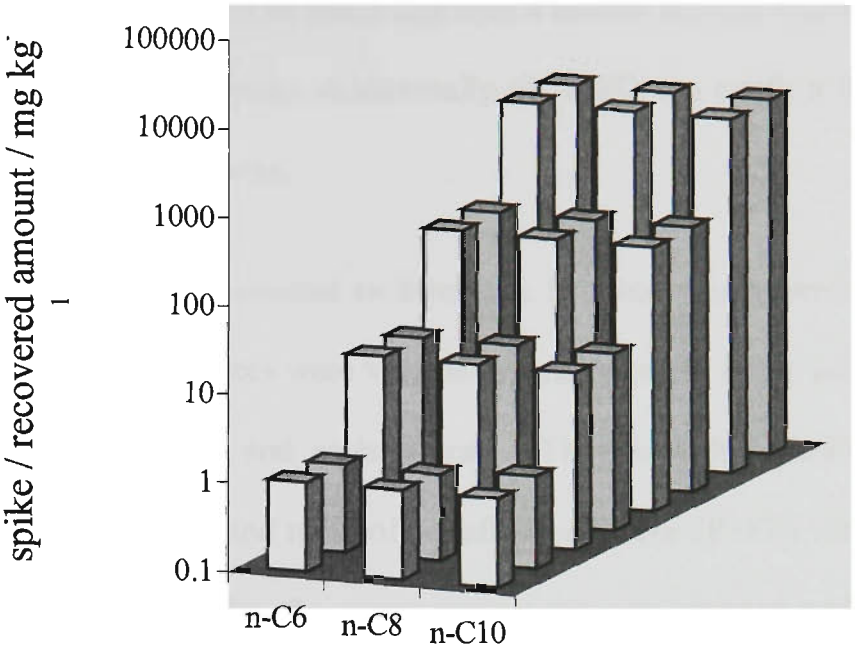

Figure 8.4: Comparison of Spiked *n*-Alkane concentrations at 10, 100, 1000 and 10000 mg/kg, with Recovered Levels. No Pairs of Values was Found to be Significantly Different at the 95% Confidence.

The correlation between the spiked concentration and the response of the GCMSD was assessed to confirm that the linear range of the BTEX and the TPH (C_6-C_9) are within the validated method. Appendices 4 contain plots confirming this relationship including the linearity, and the coefficient of variance.

The seven samples presented in Figure 8.1 were also analysed using this validated method to obtain the TPH (C_6-C_9) concentration. The results are depicted in Appendix 5. A comparison of the BTEX and TPH (C_6-C_9) concentration included in Figure 8.1 was carried out against the TPH (C_6-C_9) concentrations obtained by the P&T/GCMSD. The comparisons are depicted in Figure 8.5. The histograms clearly demonstrate that the expected correlation between the BTEX and the TPH (C_6-C_9) is retained when the analysis of both fractions are carried out by the P&T/GCMSD. The cause to produce higher TPH (C_6-C_9) concentrations by the P&T/GCMSD and the GCFID is most likely due to the ability of the P&T method to trap the material and concentrate prior to introducing to the GC. During this process the

percent loss of volatile components will be much less than a normal solvent extract that has been flash vaporised during a GCFID analysis. Additionally the MSD can confirm the components present in the samples to be hydrocarbons.

The analysis of reagent blanks was essential to determine if contaminants were present in the background. Major contaminant sources were volatile organic vapours in the laboratory air and impurities in the inert purging gas and sorbent trap. They included plastic tubing, flow controllers with rubber components, and non-polytetrafluoroethylene (PTFE) thread sealant. If interfering peaks were noted in blanks, the purge gas source was changed and the molecular sieve used for purge gas filtration was regenerated. Cross contamination was detected during the analysis of samples containing low concentrations immediately after samples containing high concentrations. The preventive technique used was to rinse the purging apparatus and sample syringes with one portion of methanol followed by three portions of organic-free reagent water between samples. Screening of the samples prior to P&T/GCMSD analysis was essential to prevent contamination of the system.

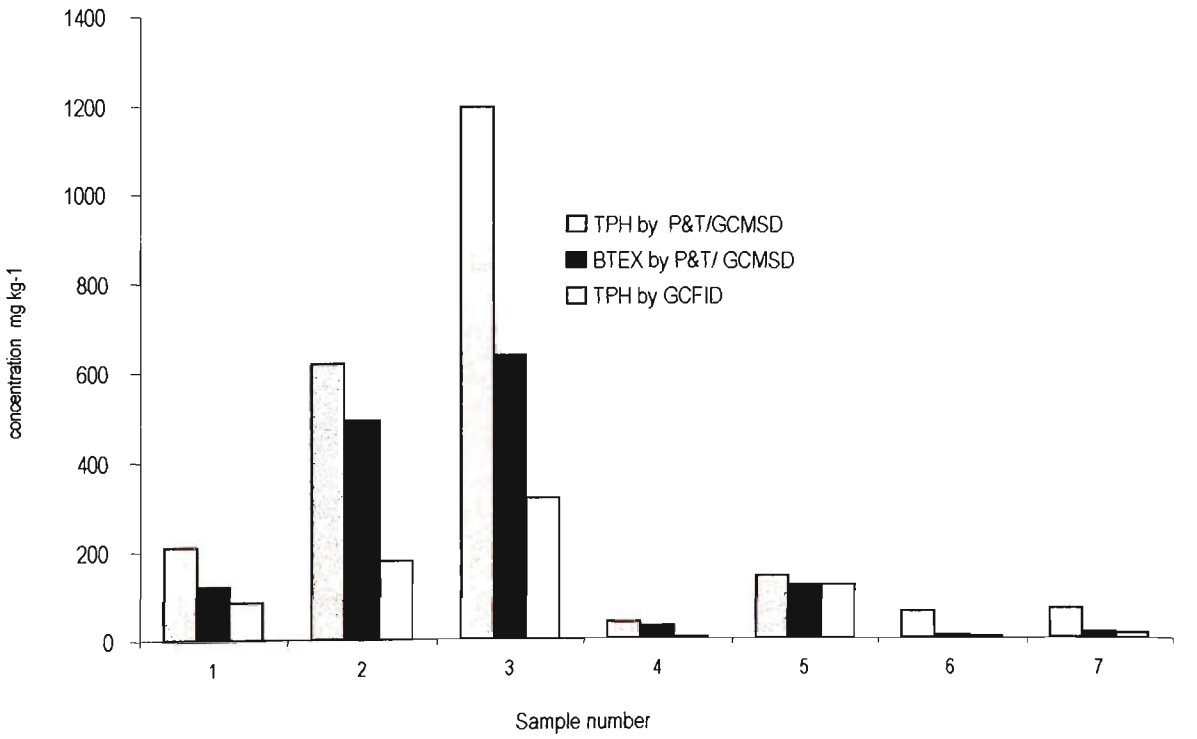

Fig 8.5: Comparison of BTEX and TPH(C_6-C_9) by P&T/GCMSD with TPH (C_6-C_9) by GCFID

After the analysis of a sample containing relatively high concentrations (>10 mg/kg) one or more blanks were analysed to check for cross contamination. After analysing samples containing higher concentrations of water soluble material, suspended solids, high boiling point compounds or high concentrations of TPH (C_6-C_9) it was necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water and dry the purging device in an oven at 105 °C. In extreme situations, the whole P&T device required dismantling and cleaning. Special precautions were taken to avoid dichloromethane (DCM) contamination. The sample storage area was isolated from atmospheric sources of DCM to avoid the formation of the otherwise random background DCM concentrations. The GC carrier gas lines and purge gas plumbing was constructed from stainless steel or copper tubing because of possible DCM permeation through PTFE tubing. Laboratory clothing was kept clean. Clothing previously exposed to DCM and toluene fumes has been proven to contribute to sample contamination. Contamination also occurred by diffusion of DCM, BTEX and fluorocarbons through the sample septum seal during shipment and storage of highly contaminated samples with samples of low contamination. The preparation of a trip blank containing organic-free reagent water, and carried through the sampling and handling steps was found to be useful in monitoring the cross contamination.

The GCMSD was used for the analysis due to its ability to compare mass spectra with a software library or against spectra of known standard compounds, providing confirmatory information other than that generated by retention time comparisons. Even under the best chromatographic conditions volatile non-hydrocarbon solvents eluting and co-eluting within the region in which BTEX and TPH (C_6-C_9) elute can cause errors. These various non-hydrocarbons may include halogeneted aliphatic, halogeneted aromatics, ketones, aldehydes, alcohols, ethers, acrylates and nytriles. The narrow retention window in which a large number of volatile components elute can produce more interference than the larger retention window available for the semi-volatile TPH fraction. Additionally the volatile components

compared to semi-volatile components are greater in their mobility and toxicity. The use of GCFID is arguably desirable for the analysis of semi-volatile TPH (C_{10}-C_{36}) however it is more important to use P&T/GCMSD to uniquely identify BTEX and TPH (C_6-C_9). The GCMSD has the capability to identify and quantify BTEX even when co-eluting with other volatiles. The ability to identify SS/IS among numerous TPH peaks is possible with the use of GCMSD. Relatively higher toxicity of BTEX (especially benzene) requires the implementation of relatively lower concentrations requiring the application of remediation processes. This requirement is been addressed by The National Environmental Protection Measure (NEPM) of Australia[4]. Therefore the determination of benzene requires to be at a higher accuracy (detected at 0.5 mg/kg) compared to TPH (C_{10}-C_{36}) (detected at 1000 mg/kg) which requires a relatively lower accuracy. Therefore the P&T/GCMSD is one of the most suitable methods for simultaneously analyse BTEX and TPH (C_6-C_9).

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Chapter Nine: Conclusions and Recommendations

The experiments described in Chapters 2 – 8 are the representation of literally thousands of experiments that could be considered or carried out in order to further develop the methodologies for the analysis of hydrocarbon in soil. It is hoped that the publication of this work (see publications relevant to the scope of this thesis, conference presentations relevant to the scope of the thesis and Appendix 9.2) will initiate further research so as to put this important area of activity on a more scientific basis. Many of the possible experiments are necessarily stated alone although they obviously impinge on other areas. This is certainly true of the experiments conducted in this thesis.

The work carried out in Chapter 2, under the heading of Comparison of Field and Laboratory Measurements for Measuring BTEX were published in the Journal of The Japan Petroleum Institute, September 2002, 45, 5, 271-278 (see Appendix 9.2.3). The work was published under the heading of "Comparison of Field and Laboratory Methods for Measuring Volatile Organic Contaminants in Soil". However further research in this field needs to be carried out to further improve important aspects in this field. Especially, optimisation of techniques used in the collection of soil which represent the studied site, holding conditions and types of suitable containers to minimise losses due to volatilisation, biodegradation and chemical degradation, if optimum holding times of contaminated soils under controlled conditions does vary with soil types and other material present and to validate and publish an international standard to measure volatile components in the field.

The work carried out in Chapter 3 under the heading of Comparison of Solvents for the Extraction of TPH (C_{10}-C_{36}) will be published in The Journal of The Japan Petroleum Institute, February, 46, 1, 2003 (see Appendix 9.2.4). The work will be published under the heading "A comparison Between the use of Dichloromethane, a Dichloromethane/Acetone Mixture, and Isopropanol, as Extractants Solvents in the Quantitative Analysis of Total Petroleum Hydrocarbon in Soil Samples". However further research is required to investigate if there are environmentally friendly and less toxic solvents which can replace DCM, relation

ship between the concentration of TPH, the soil type and solvent volume required to extract the TPH and effects due to the moisture content on the extractability of TPH from various soil types, identification of non hydrocarbon material co-extracted and counted as TPH, Possible clean-up techniques to remove non-hydrocarbons without loosing hydrocarbons, especially those that are more polar, more toxic and polynuclear aromatic compounds.

The work carried out in Chapters 4 and 5 under the headings of Extraction of TPH from Clay Soils by Sonication and Soxhlet Techniques and Investigations on Extraction Conditions for TPH (C_{10}-C_{36}) respectively were published in The Journal of The Japan Petroleum Institute, February, 44, 6, 378-383, 2001 (see Appendix 9.2.2). The work was published under the heading "Extraction of Hydrocarbons from Clay Soils by Sonication and Soxhlet Techniques". Further research is required to investigate if there are solvents which can replace DCM and provide comparable TPH concentrations, internationally excepted definition for TPH established and implemented so that it is applied by all test facilities, relation ship between the concentration of TPH, the soil type and solvent volume required in extracting and effects due to moisture content on the extractability of TPH from different soil types, identification of non-hydrocarbon material which can be co-extracted and measured as TPH and clean-up techniques to remove non-hydrocarbons without the loss of hydrocarbons.

The work carried out in Chapter 6 under the headings of Comparative Analysis of TPH by GCFID and GCMSD and a part of the research were published in The Journal of Soils and Sediments, November, 2 (3) 137-142 2002 (see Appendix 9.2.1). The work was published under the heading "Method Dependency in the Measurement of BTEX Levels in Contaminated Soil". Further research is required to determine the most appropriate calibration material to be used in volatile and semi-volatile TPH determinations. Additionally when the GCMSD and GCFID are used in TPH measurements, further assessments of suitable standards which can produce comparable concentrations by the two detectors will be also necessary to establish international standards.

The work carried out in Chapter 7 under the headings of Comparative Analysis of BTEX from Contaminated Soils by Three Standard Methods was presented at the 17 th World Congress of Soil Science, August, 2002, Bangkok, Thailand. The work was presented under the heading of "Australian Approaches to improving methods for the analysis of TPH Contamination in Soil". Further research is required to determine if the headspace GCMSD method can be further improved to produce more reliable BTEX concentrations with a higher degree of precision and accuracy. This method currently is been assessed by the International Standards Organisation and if the method modifications can carried out to obtain comparability with the P&T GCMSD measurements it will be more cost effective for the analytical laboratories.

The work carried out in Chapter 8 under the headings of The Validation of a Method for the Simultaneous Analysis of TPH (C_6-C_9) and BTEX by P&T/GCMSD is a very useful technique which will avoid generating data which are not interpretable. Therefore this method will be submitted to the international standards Organisation to be trilled implemented as the measurement standard for TPH (C_6-C_9) and BTEX.

This project has attempted to initiate more vigorous scrutiny of TPH testing in soils. The most important recommendations from this study are

(a) A single internationally agreed definition of TPH

(b) Internationally agreed procedures and materials for extraction, clean-up of the extract, calibration standard, GC baseline construction technique, identification of type of TPH and confirmation technique.

(c) To trial and implement international standards which includes soil sampling methods in the field and sub-sampling in the laboratory for volatile and semi-volatile TPH fractions including optimum procedures for the transport, handling and storage of contaminated soil.

(d) Homogenisation techniques for various soils depending on the type of TPH present (i.e. volatile components).