

# CHARACTERISATION OF ENVIRONMENTAL POLLUTION BY GC-MS ANALYSIS OF POLYCYCLIC AROMATIC COMPOUNDS IN WATER AND SOIL

By

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## SUMMARY

Polycyclic aromatic hydrocarbons (PAHs) have long been known to pose health risks in humans and have become one of the major environmental issues. Coal tar products, refined petroleum products and lubricating oils are among the anthropogenic sources, which contain highly toxic substances of which benzo[a]pyrene and dibenz[a,h]anthracene are the most potent carcinogens. Sensitive and reliable chemical analyses of contaminated soil and water are imperative for health risk assessments and chemical fingerprinting. The development of techniques that can determine the pollution source is motivated in part by the cleanup costs, legal fees, and fines incurred by the polluter.

In this thesis, direct solid-phase microextraction (DISPME), followed by capillary gas chromatography (GC) and mass spectrometry (MS) in the selected ion storage (SIS) mode was investigated for the determination and characterisation of PAHs in aqueous samples. The SPME method of extraction is also compared to a traditional liquid-liquid extraction method that was based on USEPA method 8270. It was found that several factors affected

the extraction efficiency with a single stage SPME extraction, such as the degree of alkylation, fiber condition, absorption time, sample pH, sample matrix, sample temperature, agitation method, etc. The technique of multiple extractions (MESPME) was investigated and found to compensate for variations in analytical conditions or sample matrix. The suitability of the method for health risk assessments was investigated. The results were acceptable for this purpose because the limits of detection were estimated at the  $\text{pg}/\text{cm}^3$  levels that were considerably lower than the health risk based guideline concentrations ( $10^{-6}$  cancer risk) for drinking water specified by the United States Environmental Protection Agency (USEPA). The guideline concentration for dibenz[a,h]anthracene (the most potent carcinogen) is for example  $0.0092 \text{ ng}/\text{cm}^3$  compared to a detection limit of  $0.0045 \text{ ng}/\text{cm}^3$  achieved with the SPME-GC/MS method. Detection limits for the other carcinogenic PAHs were also found to be lower than the USEPA guideline concentrations. The method was also developed to include the quantification of alkyl-PAHs, which is important for interpretative methods such as chemical

fingerprinting (source identification). For this purpose detection limits of at least  $0.01 \text{ ng/cm}^3$  are required for individual PAHs. The SPME extraction method used in conjunction with GC/MS was found to be sensitive enough for this purpose with detection limits lower than  $0.01 \text{ ng/cm}^3$  for all the PAHs. The method was in many respects superior to traditional extraction methods.

A headspace SPME (HSSPME) method, followed by GC/MS, was developed for the screening of soil samples. Vapor pressures of target analytes were determined using a capillary GC method to identify environmentally important components with a sufficiently high vapor pressure to be analyzed in the headspace mode. The method was optimized under non-equilibrium conditions with simplicity and automation in mind and does not require any extraction procedure or sample preparation, other than grinding, drying and homogenizing. The analytical performance

and the significance of the results for the purpose of chemical characterisation, source discrimination, determination of individual isomer distributions and the calculation of source and weathering ratios, are discussed. The SPME method of extraction was also compared to the relatively new extraction technique known as Pressurised Liquid Extraction (PLE). HSSPME was found to be a very efficient and sensitive technique for the confirmation of PAHs of up to four-ring structures and suitable for a tiered and adaptive approach.

The selective extraction and analysis techniques that have been developed in this thesis were finally used to develop diagnostic ratios, which can be used to trace contamination in the environment to its source. The successful use of the analytical data to match the chemical patterns of target analytes with potential sources was shown.

# KARAKTERISERING VAN OMGEWINGSBESOEDELING IN GROND EN WATERMONSTERS DEUR GC/MS EN DIE ANALISE VAN POLISIKLIESE AROMATIESE VERBINDINGS

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## SAMEVATTING

Die gesondheidsrisiko wat polisikliese aromatiese koolwaterstowwe (PAHs) vir mense inhou is lankal reeds bekend en het in een van die mees belangrikste omgewingskwessies ontwikkel. Besoedelingstowwe soos koolteer, petroleum produkte en smeermiddels bevat heelwat giftige en karsinogene verbindings waarvan benso[a]pireen en dibenso[a,h]antraseen die giftigste is. 'n Sensitiewe en betroubare chemiese analise van grond- en watermonsters word vir die ondersoek na PAH en ge-alkileerde PAH besoedeling, gesondheids gebaseerde risikobepalings en chemiese karakterisering benodig. Koste verbonde aan opruiming, regs-koste en boetes is deels die motivering vir die ontwikkeling van metodes wat besoedelingsbronne kan identifiseer.

Die toepassing van direkte vastestof mikroekstraksie (solid-phase micro-extraction - DISPME), gevolg deur kapillêre gaschromatografie (GC) en massaspektrometrie (MS) in die geselekteerde ioon (selected ion storage - SIS) mode is vir die bepaling en karakterisering van PAHs in watermonsters ondersoek. Die SPME

ekstraksiemetode is ook met die tradisionele vloeistof-vloeistof ekstraksiemetode, gebaseer op die USEPA metode 8270, vergelyk. Daar is gevind dat die effektiwiteit van 'n enkelstap SPME-ekstraksie deur verskeie faktore beïnvloed word, soos byvoorbeeld die graad van alkilerings, die SPME vesel se toestand, absorpsietyd, monster pH, monsternatry, monster temperatuur, ens. Die tegniek van veelvuldige ekstrasies (MESPME) is suksesvol ondersoek om vir die variasies in analitiese kondisies en monsternatry te kompenseer. Deteksielimiet vir individuele PAHs was in die  $\text{pg/cm}^3$  gebied wat aansienlik laer is as die riglynkonsentrasie ( $10^{-6}$  kanker risiko), soos deur die USEPA (United States Environmental Protection Agency) voorgekryf. Die riglynkonsentrasie vir benso[a]pireen is voorbeeld  $0.0092 \text{ ng/cm}^3$  in vergelyking met 'n deteksielimiet van  $0.0045 \text{ ng/cm}^3$  wat met die SPME-GC/MS metode verkry is. Deteksie limiet vir die ander karsinogene PAHs was ook almal laer as die USEPA riglynkonsentrasies. Die metode is ook vir die kwantitatiewe bepaling alkiel-PAHs aangepas. Hierdie analietkomponente is belangrik vir



interpreteringsmetodes, soos gevorderde chemiese karakterisering (bronallokering). Vir hierdie doel word 'n deteksielimiët van  $0.01 \text{ ng/cm}^3$  vir al die PAHs vereis. Die SPME ekstraksiemethode, gevolg deur GC/MS, het aan hierdie vereistes voldoen en deteksiemiete van laer as  $0.01 \text{ ng/cm}^3$  is vir al die PAHs verkry. Die metode was in baie opsigte beter as die tradisionele metodes is.

'n Dampruim SPME (HSSPME) metode, gevolg deur GC/MS, is vir die siftingsprosedure van PAHs in grondmonsters ontwikkel. Die dampdrukke van analietkomponente is met 'n kapillêre GC metode bepaal om vas te stel watter komponente in die dampruim geanaliseer kan word. Die metode is onder nie-ewewigskondisies geoptimeer met eenvoud en outomatisasie in gedagte, terwyl geen spesiale monstervoorbereiding anders as droog, maal en homogenisering vereis word nie. Die betroubaarheid van

die metode en die geskiktheid van die resultate vir chemiese karakterisering, bronallokering, bepaling van isomeer verspreidingspatrone en die bepaling van bron- en verouderingsverhoudings is ondersoek. Die metode is ook met die relatief nuwe ekstraksie metode, naamlik "Pressurised Liquid Extraction (PLE)" vergelyk. Daar is gevind dat HSSPME 'n baie effektiewe en sensitiewe metode vir die bepaling van PAHs tot en met vier-ringstrukture is.

Die selektiewe ekstraksie- en analiese metodes wat in hierdie studie ontwikkel is, is uiteindelik vir die ontwikkeling van diagnostiese verhoudings tussen twee analiete gebruik. Hierdie verhoudings kan gebruik word om plaaslike besoedeling aan 'n besoedelingsbron te koppel. Daar is ook aangetoon dat die analitiese data suksesvol gebruik kan word om die chemiese patrone van analietkomponente in omgewingsmonsters aan potensiële bronne te koppel.



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*Thank You*  
Willie

## GLOSSARY AND ABBREVIATIONS

<b>ACF</b>	- Advanced chemical fingerprinting
<b>Alkyl-PAHs</b>	- Alkyl substituted polycyclic aromatic hydrocarbons
<b>Anthropogenic</b>	- Pollution caused by humans
<b>ASE</b>	- Accelerated solvent extraction
<b>ATSDR</b>	- Agency for Toxic Substances and Disease Registry
<b>Carcinogenicity</b>	- Ability of a substance to cause cancer.
<b>Coal tar</b>	- Heterogeneous mixture of various classes of compounds
<b>CRM</b>	- Certified reference material
<b>DCM</b>	- Dichloromethane
<b>DISPME</b>	- Direct solid phase microextraction
<b>DL</b>	- Detection limit
<b>DNAPL</b>	- Dense non-aqueous phase liquid
<b>DQO</b>	- Data quality objectives
<b>Fugacity</b>	- Relative escaping tendency
<b>GC</b>	- gas chromatography
<b>HSSPME</b>	- Headspace Solid Phase Microextraction
<b>HPLC</b>	- High performance liquid chromatography
<b>K<sub>oc</sub></b>	- Sorption coefficient on soil/sediment
<b>K<sub>ow</sub></b>	- Octanol-water partition coefficient
<b>LNAPLs</b>	- Light Non Aqueous Phase Liquids
<b>m/z</b>	- Mass over charge
<b>MCL</b>	- Maximum contaminant level
<b>MDL</b>	- Method detection limit
<b>MESPME</b>	- Multiple extraction solid phase microextraction
<b>SQL</b>	- Method quantification limit
<b>MS</b>	- mass spectrometry
<b>NAPL</b>	- Non-aqueous phase liquid
<b>ng</b>	- Nanogram.
<b>PAH</b>	- Polycyclic aromatic hydrocarbons
<b>PDMS</b>	- Poly dimethylsiloxane
<b>pg</b>	- Picogram.
<b>PLE</b>	- Pressurised liquid extraction
<b>P<sub>L</sub><sup>0</sup></b>	- Vapor pressure
<b>psi</b>	- Pounds per square inch
<b>QA</b>	- Quality assurance
<b>QC</b>	- Quality control
<b>QL</b>	- Quantification limit
<b>R<sup>2</sup></b>	- Regression coefficient
<b>RI</b>	- Temperature programmed retention index
<b>RRF</b>	- Relative response factor
<b>RSD</b>	- Relative standard deviation
<b>S/N</b>	- Signal to noise ratio

<b>Sediment</b>	- Mud and debris
<b>SIM</b>	- Single ion monitoring
<b>SIS</b>	- Selected ion storage
<b>SPME</b>	- Solid Phase Microextraction
<b>SRS</b>	- Standard reference soil
<b>STD</b>	- Standard
<b>S<sub>w</sub></b>	- Water solubility
<b>t<sub>R</sub></b>	- Retention time
<b>USEPA</b>	- Unites States Environmental Protection Agency
<b>Weathering</b>	- Dissolvation, evaporation, bio-degradation, photo oxidation

## CHEMICAL COMPOUNDS

<b>A</b>	- Anthracene
<b>AC</b>	- Acenaphthene
<b>AE</b>	- Acenaphthylene
<b>BA</b>	- Benzo[a]anthracene
<b>BB</b>	- Benzo[b]fluoranthene
<b>BI</b>	- Biphenyl
<b>BP</b>	- Benzo[ghi]perylene
<b>BAP</b>	- Benzo[a]pyrene
<b>BTEX</b>	- Benzene, toluene, ethyl benzene and xylenes
<b>C1-</b>	Methyl group
<b>C2-</b>	Methyl-methyl or ethyl group
<b>C3-</b>	Trimethyl, methylethyl or propyl group
<b>C4-</b>	Tetramethyl, ethylethyl, methylpropyl or butyl group
<b>C</b>	- Chrysene
<b>C1-C</b>	- C <sub>1</sub> -Chrysene
<b>C1-D</b>	- C <sub>1</sub> -Dibenzothiophene
<b>C1-F</b>	- C <sub>1</sub> -Fluorenes
<b>C1-N</b>	- C <sub>1</sub> - Naphthalenes
<b>C1-P</b>	- C <sub>1</sub> -Phenanthrene/anthracenes
<b>C2-C</b>	- C <sub>2</sub> -Chrysene
<b>C2-D</b>	- C <sub>2</sub> -Dibenzothiophene
<b>C2-F</b>	- C <sub>2</sub> -Fluorenes
<b>C2-N</b>	- C <sub>2</sub> - Naphthalenes
<b>C2-P</b>	- C <sub>2</sub> -Phenanthrene/anthracenes
<b>C3-C</b>	- C <sub>3</sub> -Chrysene
<b>C3-D</b>	- C <sub>3</sub> -Dibenzothiophene
<b>C3-F</b>	- C <sub>3</sub> -Fluorenes
<b>C3-N</b>	- C <sub>3</sub> - Naphthalenes
<b>C3-P</b>	- C <sub>3</sub> -Phenanthrene/anthracenes
<b>C4-N</b>	- C <sub>4</sub> - naphthalenes
<b>C4-P</b>	- C <sub>4</sub> -Phenanthrene/anthracenes
<b>D</b>	- Dibenzothiophene
<b>DA</b>	- Dibenz[ah]anthracene
<b>DI</b>	- Dibenzofuran



<b>F</b>	-	Fluorene
<b>FL</b>	-	Fluoranthene
<b>IP</b>	-	Indeno[123-cd]pyrene
<b>N</b>	-	Naphthalene
<b>P</b>	-	Phenanthrene
<b>PY</b>	-	Pyrene

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