Chapter 10

FINAL CONCLUSIONS AND RECOMMENDATIONS

INTRODUCTION

In the preceding chapters of this thesis, analytical methods have been developed and evaluated for the determination of specific target analytes in water and soil samples, and their suitability for hazard identification, health risk assessments and implementation for high quality chemical fingerprinting. Special attention was given to the analytical performance, method detection limits and the ability of these methods to distinguish target analytes from co-extracted compounds that often have concentrations of up to orders of magnitude higher than the target analytes. The ability of the methods to differentiate among the various isomers of the alkyl substituted polycyclic aromatic hydrocarbons (alkyl-PAHs) was also important.

Based on the low guideline concentrations specified by the USEPA (see **Table 3.1**), the sensitivity and reliability of the method for carcinogenic PAHs is critical for risk assessments. On the other hand low detection limits for all the PAHs (including alkyl-PAHs) are required for chemical fingerprinting and to link pollutants positively to their sources. In the following sections, the limitations and strengths of the developed chemical analyses and interpretative methods are discussed. Recommendations are given for future development work in the field of analytical methods to determine poly aromatic hydrocarbons (PAHs) in soil and water samples.

STATE OF THE ART ANALYTICAL METHODOLOGY

The determination of PAHs in groundwater and surface water samples

Considering the present level of sophisticated analytical equipment used in conjunction with modern sample preparation technologies such as Solid Phase Microextraction (SPME), it can be concluded that PAHs in water samples can be analysed with a high level of reliability. SPME was compared to liquid-liquid extraction (LLE) and found to be superior to traditional extraction methods with regard to many aspects. The main advantages of the SPME-GC/MS method include:

- The elimination of toxic solvents and increased automation reduced analytical costs and improved turnover times.

- The simple pre-treatment procedure reduced the uncertainty of the overall results.

- The small amount of sample required was better suited for sampling, sample handling and transportation.

- The method showed superior analytical performance when compared to the liquid-liquid extraction method with much lower Method Detection Limits (MDLs) and procedural blank values.

- The technique was characterised by excellent selectivity and the ability to distinguish target analytes from interfering compounds

- ☐ It was possible to differentiate among various alkyl-PAH isomers that could be used for the calculation of source and weathering ratios.

- ☐ Detection limits found with SPME-GC/MS were all lower than the health risk based guideline concentrations of PAHs specified by the USEPA (see **Table 3**), which make the method suitable for health risk assessments.

The following disadvantages were identified when using SPME:

- ☐ The quantification of alkyl-PAHs is complicated by the fact that SPME is based on partition equilibrium with significant differences among the extraction efficiencies of the target analytes. Two consecutive analyses are required (multiple extraction SPME) for the application of advanced chemical fingerprinting.

- ☐ The technique (as used under the conditions specified in this study) is not reliable for the accurate quantification of 5-ring PAH compounds (indeno[123-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,I]perylene, which show poor analytical performance.

- ☐ The concentrations of dibenzothiophene and phenanthrene isomers in coal tar contaminated samples (used for diagnostic ratios) were often found to occur in concentrations lower than the MDL.

Based on the advantages and disadvantages listed above, SPME coupled with Gas Chromatography and Mass Spectrometry (SPME-GC/MS) is the preferred method for the analysis of trace quantities (< 10 ng/cm^3) PAHs in water samples. For samples containing larger amounts of PAHs the liquid-liquid extraction method would be better suited, especially if the results are required for advanced chemical fingerprinting, or if accurate results for the 5-ring PAHs are required.

The analyses of soil and sediment samples

The development of more efficient analytical equipment for the extraction of organic compounds from soil and sediment samples (Accelerated Solvent Extraction - ASE) used in conjunction with GC/MS, resulted in a reliable method for the determination of PAHs. The ASE method was found to be superior to traditional extraction methods, for example Soxhlet extractions in many respects. The main advantages include:

- ☐ The system is automated and exhibits similar or improved recoveries of target compounds.

- ☐ Compared to Soxhlet, the procedure is significantly less time- and solvent-consuming.

- ☐ Savings in labour and time are possible due to the large sample capacity and high efficiency of the ASE system.

The only drawback that was observed, which is not related to the ASE technique but to the nature of the pollution source is that the isomers of C_2-P, C_3-P, C_2-D and C_3-N often occur in soils and sediments in concentrations below the method detection limit (MDL). Advanced chemical fingerprinting (ACF) is, therefore, not always possible.

Headspace SPME (HSSPME) was found to be a fast, efficient and selective screening method to extract PAH compounds from polluted soil and sediments, but the sensitivity of the method decreases sharply with an increase in the ring size. The technique does not require any sample pre-treatment, other than grinding, drying and homogenising, and is very useful as a fast screening technique. Savings on chemical analyses and sampling can be realised as the results can be used to identify samples that must be analysed with a more detailed technique such as ASE-GC/MS, or to adapt the sampling and analysis strategy. The technique is associated with the following disadvantages:

- Due to their low vapor pressures, the 4- and 5-ring PAHs cannot be analysed. Information on these compounds is, however, vital for risk analysis and advanced chemical fingerprinting.
- Due to differences in extraction efficiency with the degree of alkylation, the method is not suitable for the quantitative determination of alkyl-PAHs.
- The determination of source ratios and weathering ratios is limited to compounds with similar physico-chemical properties (e.g., C_1-P/C_1-D) for the same reasons as mentioned above.

Advanced chemical fingerprinting analyses

Distinct differences between the PAH analyte distribution patterns of refined oil and coal tar fingerprints have been shown, using results obtained from methods developed during this study. The PAH distribution patterns obtained with these methods are suitable for the differentiation among multiple sources.

The determination of source and weathering ratios in coal tar contaminated samples was associated with several disadvantages. Pyrogenic sources have a decrease in alkyl-PAH concentrations with an increase in the degree of alkylation, which means that certain alkyl-PAHs are normally present in levels lower than the MDL, especially in slightly contaminated samples. Co-extracted compounds are, therefore, often found at levels of a few orders of magnitude higher than the alkyl-PAH isomers. This complicates the determination of reliable diagnostic ratios in coal tar contaminated samples that are only slightly contaminated. The following difficulties were observed with the quantification of trace level alkyl-PAHs:

- Peak overlap of the interfering compounds with the isomer peaks
- Continuous background mass spectral interference
- Poor resolution among certain isomer peaks belonging to the same alkyl homologue
- Low signal to noise ratios
- The time involved in manual integration of each isomer peak

An alternative approach has been investigated to overcome these problems, which is based on the ratio of individual isomers in two different alkyl homologues. One specific isomer was selected in each alkyl homologue, which was used throughout the study to determine isomer-to-isomer ratios. This approach was found to be very efficient, much less time consuming, subjected to less interferences and more reliable. Substantial differences were found in source ratios between petrogenic and pyrogenic sources, which made it possible to successfully distinguish between them. The use of double ratio plots was found to be useful to further enhance these differences.

FUTURE NEEDS AND DEVELOPMENTS

The implications of inaccurate environmental analyses are severe, because mistakes can lead to hazards being undetected or the spurious detection of unreal hazards. It is for this reason that the need to develop more reliable en sensitive analytical methods will continue. Laboratories also face continued pressure to develop environmental methods that are less complicated and can produce analyses at lower costs and faster turnover times, using inexpensive instrumentation. There is also a need for environmental laboratories to have a stronger focus on quality assurance (QA) and quality control (QC) and to become engaged in accreditation programmes. Participation in inter-laboratory studies might offer the possibility to improve the current state of the art methodologies, but is also of strategic importance for laboratories to maintain/increase their level of competitiveness.

Considering the certainties and uncertainties of the current state of the art methodologies, the following developments are recommended:

- ❑ Further refinements to the SPME-GC/MS method discussed in **Chapter 6** with the aim to further improve detection limits, repeatability and the analysis of the 5-ring compounds.
- ❑ Optimisation of the SPME extraction conditions, such as the adjustment of pH and ionic strength of the sample, and optimisation of the ion trap conditions can achieve this.
- ❑ The determination of alkyl-PAHs using GC/MS/MS and chemical ionisation (soft ionisation technique) to create a stable ion for MS/MS isolation. This method will allow lower detection limits and reliable spectral identification of individual isomers for even the most difficult cases.
- ❑ The extraction of PAHs from water samples using multi-channel silicone rubber tubes and thermal desorption as an alternative method to SPME. This technique has the advantage that target analytes are retained quantitatively, opposed to the single equilibrium absorption process of a SPME analysis. The technique will also allow the quantification of alkyl-PAHs with much less complications.
- ❑ The investigation into the correlation between PAHs and inorganic contaminants found in groundwater samples.