THE IMPORTANCE OF ACCURATE, RELIABLE GAS CROMATOGRAPY MASS SPECTROMETRY DATA IN ECOLOGICAL AND HUMAN HEALTH RISK ASSESSMENTS: HOW YOUR DATA CAN INFLUENCE MANAGEMENT DECISIONS.

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Introduction

One of the largest challenges in environmental management is presenting analytical data, used to investigate possible risk due to environmental toxicant exposure, into a language that can inform management decisions in a universally accepted approach. Critical decisions regarding the monitoring and remediation of organic compounds in the environment are made on the basis of environmental and human risk assessments. A human risk assessment measures the probability of adverse health effects caused by exposure to a chemical in a contaminated environment[1]. An ecological risk assessment converts scientific data into information that can be used to identify the environmental risks. Both these risk assessments have five basic steps: (1) problem formulation, (2) hazard identification, (3) hazard characterisation, (4) exposure assessment and (5) risk characterization linking the information gathered to risk management[1].

Scientific data generated in analytical laboratories contributes to the hazard identification; characterisation and exposure assessment which are an integral part of evaluating risk. Therefore, accurate and reliable analytical data has become crucial in modern environmental management programs. Many guidance documents are dedicated to describing performance criteria required before analytical data is considered adequate to be used in risk assessments. Erroneous data could lead to either an over or underestimation of risk resulting in inappropriate management decisions. On the larger scale, this can result in a misrepresentation of current levels and associated risk, which informs new local and international policies.

Now the question arises: How does chromatographic quality affect the process of risk assessment? As described above, the risk assessment is only as good as the data that is used. Most, if not all, exposure data is based on the concentration of contaminants in environmental matrices, and these concentrations are generally determined by means of analytical techniques such as gas chromatography coupled to mass spectrometry (GC-MS).

Interest in the concentration of polycyclic aromatic hydrocarbons (PAHs) within environmental media has increased in recent years as these compounds have a myriad of negative health impacts including carcinogenicity, mutagenicity, immunotoxicity, as well as an aryl-hydrocarbon receptor activity similar to that of dioxins. Due to toxicity concerns, PAHs are routinely monitored and form part of the Aarhus Protocol on Persistent Organic Pollutants (POPs)[2] in addition to the Convention on Long-Range Transboundary Air Pollution. Currently the US.EPA has listed 16 PAHs as priority pollutants (**Table 1**; **Figure 1**). Toxic equivalency factors (TEFs), have been assigned to these PAHs, where benzo(a)pyrene and dibenzo[a,h]anthracene are considered to be the most toxic (**Table 1**) and frequently used for ecological and human health risk assessments. The analysis reports on these compounds generally include positive identification, recovery values along with the limit of detection and quantification. Additional analytical criteria include: possible interferences, signal saturations due to high environmental levels and concentrations lower than the method blank.

The analysis of (PAHs) from soil was used as a case study to investigate the effect of chromatographic data on a risk assessment. Although there are many areas where errors can occur during analysis, the case study only focused on two areas of concern: accurate identification and the effect of efficient analyte recovery, when the compound of interest is incurred within an environmental matrix such as soil.

Materials and methods

In the proposed scenario, PAHs were extracted and quantified from soil sampled in a petrochemical industrial area with residential areas located in close proximity to the industries. PAH concentrations were determined using GC-MS data. This data was used to investigate possible sources of contamination, to differentiate between recent and historic contamination and to perform a preliminary risk assessment for individuals in the area using exposure scenario's from literature[4,5].

Table 1: PAH compounds and their corresponding TEFs[3].

Name	Abbreviation	Nr of rings	TEF value
Naphthalene	Nap	2	0.001
Acenaphthylene	Acy	3	0.001
Acenaphthene	Ace	3	0.001
Fluorene	Flu	3	0.001
Phenanthrene	Phe	3	0.001
Anthracene	Anth	3	0.01
Fluoranthene	Flt	4	0.001
Pyrene	Pyr	4	0.001
Benz(a)anthracene	BaH	4	0.1
Chrysene	Chr	4	0.01
Benzo(b)fluoranthene	BbF	5	0.1
Benzo(k)fluoranthene	BkF	5	0.1
Benzo(a)pyrene	BaP	5	1
Benzo(e)pyrene	BeP	5	0.01
Dibenzo[a,h]anthracene	DB(ah)A	5	1
Indeno(123-cd)pyrene	Ind	6	0.1
Benzo(ghi)perylene	B(ghi)P	6	0.01

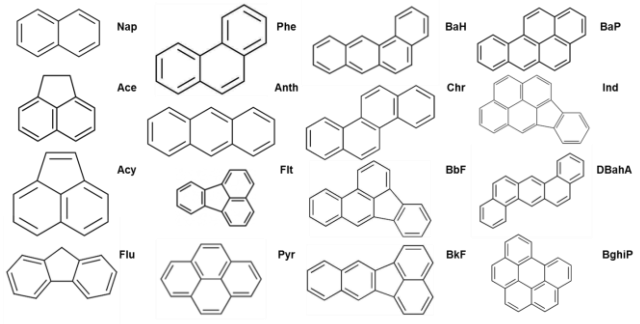

Figure 1: Structure of 16 priority PAHs, structural similarities can complicate positive identification in complex environmental samples.

Results and discussion

As with many pollutant classes, PAHs with the same number of rings, have similar chemical structures (**Figure 1)** and properties. Therefore, during quantification these structurally related PAHs can be misidentified. Additionally, structurally related compounds are not necessarily chromatographically separated which can cause a positive bias in results, as co-eluting compounds will be quantified as a single compound. Common co-elutions in PAH analysis include (**Figure 2)**: Phe and Anth; BaH, Chr and triphenylene; BbF, BkF, benzo[j]fluoranthene and benzo[a]fluranthene; BaP and BeP as well as DB(ah)A with a host of closely related isomers. Co-elutions are further complicated by matrix interferences in complex samples such as sediment, soils and tissues.

The elimination of possible positive bias or misidentification is critical for toxicity assessment, as the two compounds seen as most toxic, BaP and DB(ah)A, have known chromatographic interferences. Ind and DB(ah)A often co-elute, and if these two compounds are not correctly identified or are not separated, a tenfold bias can be introduced as Ind has a TEF value of 0.1and DB(ah)A has a TEF value of 1.

Additionally, diagnostic ratios of PAHs are often employed to identify the source of the PAH contamination, where source identification and source strength contributions are evaluated[6]. Common ratio's used in these investigations include: Flu/Pyr as an indicator of petrol or diesel emissions; Anth/Phe and Flt/Pyr as an indicator of petrogenic or pyrogenic activity; BaH/Chr; Ind/B(ghi)P and BeP/Bap used to differentiate between different fuel sources as well as petrogenic or pyrogenic activity, and BeP/BaP that can be used to distinguish between aged and non-aged deposits. Therefore, if one of these isomers are incorrectly identified the wrong conclusions can be drawn on sources in addition to whether the deposited PAHs are from historical or recent activity.

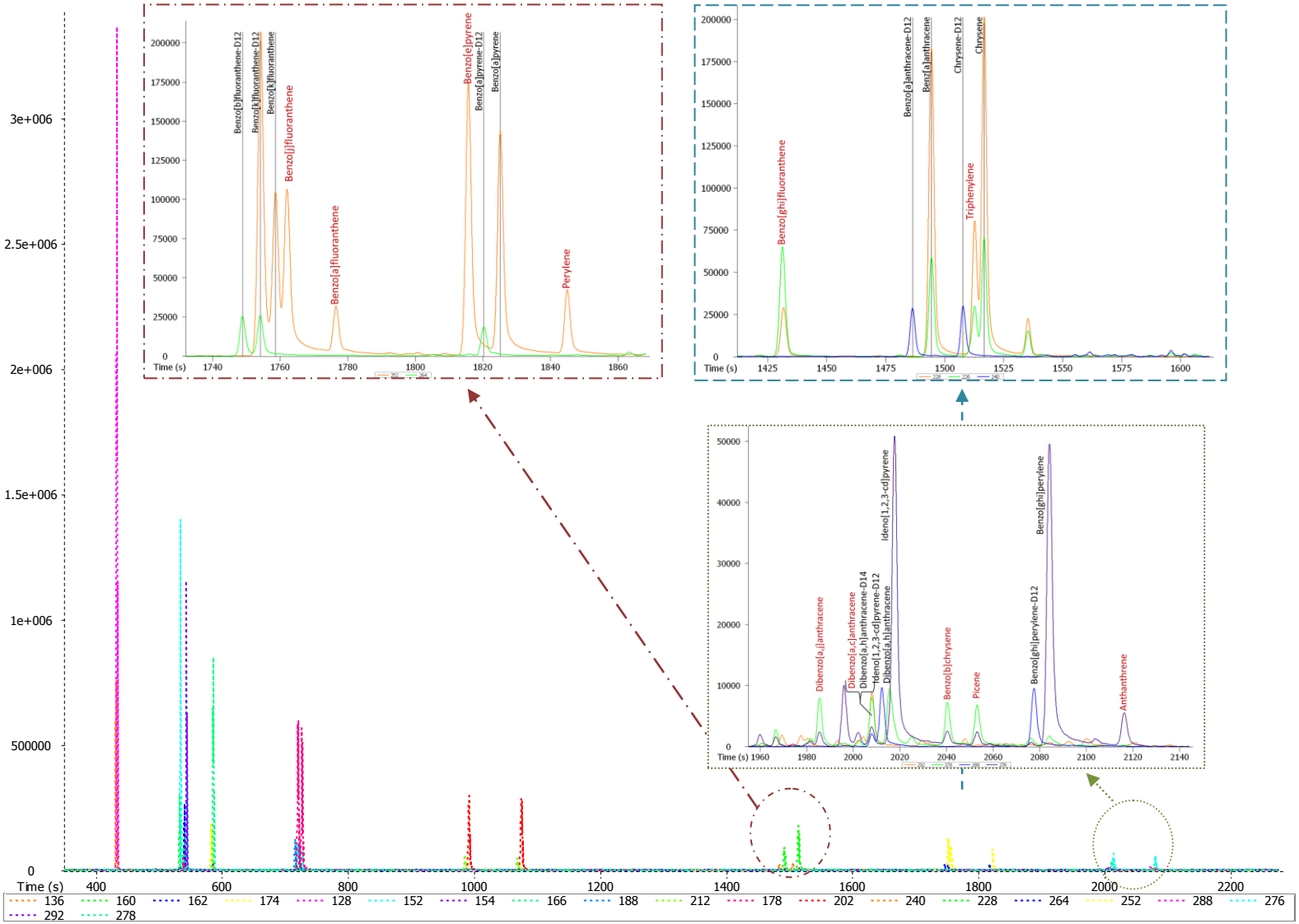

Figure 2: Separation of the US.EPA priority PAHs illustrating possible co-elutions that could impact quantification.

The recovery of incurred contaminants is one of the single most important factors in accurate quantification. Due to a lack of matrix matched certified reference materials (CRMs), spiked matrix tests are used to assess recovery. These tests are good indicators of losses during the experimental procedure, but do not provide information on the efficiency of the extraction in removing naturally incurred pollutants from the matrix. The difference between the recovery estimated from spiked samples (80–120%) and the recovery estimated from a CRM (70 and 10%) greatly impacts the results of an incremental lifetime cancer risk (ILCR) calculation. Where initial results (Table 2) indicate that the ILCR from exposure to PAHs in soil is negligible; a 70% recovery indicates that only industrial exposure would be of concern; while a 10% recovery calls for concern in residential areas. This will have a significant impact on management decisions, where no action may be required at an industrial site as soil contact is limited, whilst in residential areas, where children are playing in soil and often consuming home-grown produce may require remediation or stringent industrial controls. However, without the use of a matrix matched CRM no information on extraction efficiency would have been known and no action taken for dangerously high levels of PAHs.

Table 2: ILCR risk as an example of human health risk assessment indicating the effect of recovery of incurred PAHs from soil. ILCRs that are no longer negligible are indicated in bold.

ILCR for soil from various classifications	Data as reported		Average recovery of 70%		Average recovery of 10%	
	Child	Adult	Child	Adult	Child	Adult
INGESTION						
Industrial	3.63E-06	2.70E-06	4.72E-06	3.50E-06	6.97E-06	5.17E-06
Agricultural	2.34E-08	1.74E-08	3.04E-08	2.26E-08	4.49E-08	3.34E-08
Residential	3.90E-07	2.90E-07	5.07E-07	3.76E-07	7.49E-07	5.56E-07
DERMAL						
Industrial	***7.82E-05***	***8.76E-05***	***1.02E-4***	***1.14E-4***	***1.50E-04***	***1.68E-04***
Agricultural	3.20E-07	3.58E-07	4.16E-07	4.66E-07	6.14E-07	6.88E-07
Residential	5.33E-06	5.97E-06	6.93E-06	7.76E-06	***1.02E-05***	***1.14E-05***
INHALATION						
Industrial	2.33E-11	1.73E-11	3.03E-11	2.25E-11	4.47E-11	3.32E-11
Agricultural	1.50E-13	1.11E-13	1.95E-13	1.45E-13	2.88E-13	2.14E-13
Residential	2.50E-12	1.86E-12	3.25E-12	2.41E-12	4.80E-12	3.57E-12
SUM EXPOSURE TO SOIL						
Industrial	3.36E-06	2.70E-06	***1.06E-04***	***1.17E-04***	***1.57E-04***	***1.73E-04***
Agricultural	3.43E-07	3.76E-07	4.46E-07	4.89E-07	6.59E-07	7.22E-07
Residential	5.72E-06	6.26E-06	7.44E-06	8.14E-06	***1.10E-05***	***1.20E-05***

In conclusion, ecological and health risk assessments are only as reliable and useful as the data used to generate them. In the end poor analytical science, including chromatography, will lead to bad decision making. Therefore the use of traceable calibration standards and matrix reference materials to ensure effective quality control is critical.

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