A review of the determination of persistent organic pollutants for environmental forensics investigations

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David Megson[1,2], Eric J. Reiner[1,3], Karl J. Jobst[3,4], Frank L Dorman[5], Mathew Robson [6], Jean-François Focant[7]

1. University of Toronto, Department of Chemistry, Toronto, ON, Canada,
2. School of Science and the Environment, Manchester Metropolitan University, Manchester, UK
3. Ontario Ministry of the Environment and Climate Change, Laboratory Services Branch, Toronto, ON Canada M9P3V6
4. Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON, Canada, L8S 4M1
5. Penn State University, Biochemistry and Molecular Biology. Forensic Science Program, University Park, PA 16802
6. Department of Chemistry, Brock University, St Catharine's, ON, Canada
7. University of Liège Organic and Biological Analytical Chemistry , B6c B-4000 Liège Belgium

Abstract

The field of environmental forensics emerged in the 1980s as a consequence of legislative frameworks enacted to enable parties, either states or individuals, to seek compensation with regard to contamination or injury due to damage to the environment. This legal environment requires stringent record keeping and defendable data therefore analysis can sometimes be confined to data to be obtained from certified laboratories using a standard accredited analytical method. Many of these methods were developed to target specific compounds for risk assessment purposes and not for environmental forensics applications such as source identification or age dating which often require larger data sets. The determination of persistent organic pollutants (POPs) for environmental forensic applications requires methods that are selective but also cover a wide range of target analytes which can be identified and quantified without bias. POPs are used in a wide variety of applications such as flame retardants, fire suppressants, heat transfer agents, surfactants and pesticides mainly because of their chemical inertness and stability. They also include compounds such as dioxins that can be unintentionally produced from industrial activities. POPs are persistent in the environment, bioaccumulative and/or toxic and therefore require analytical methods that are sensitive enough to meet the low detection limits needed for the protection of the environment and human health. A variety of techniques, procedures and instruments can be used which are well suited for different scenarios. Optimised methods are important to ensure that analytes are quantitatively extracted, matrix coextractables and interferences are removed and instruments are used most effectively and efficiently. This can require deviation from standard methods which can open the data up to further scrutiny in the courtroom. However, when argued effectively and strict QA/QC procedures are followed the development and optimisation of methods based on investigation specific scenarios has the potential to generate better quality and more useful data.

Keywords

Persistent organic pollutants; Environmental forensics; Analysis; Environment

1 Introduction

The Stockholm Convention on persistent organic pollutants (POPs) targets 26 compounds or compound groups including the original dirty dozen which comprises of nine organochlorine pesticides, polychlorinated biphenyls (PCBs) polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) [1]. An additional nine pesticides, flame retardants and surfactants were added in 2009, endosulfan was added in 2011, hexabromocyclododecane added in 2013 and hexachlorobutadiene, pentachlorophenol (and its salts and esters) and polychlorinated naphthalenes in 2015 [1]. There are currently four compounds/groups: decabromodiphenyl ether (BDE 209), dicofol, short-chain chlorinated paraffins (SCCPs), and pentadecafluorooctanoic acid (PFOA) its salts and related compounds, that are currently under review [1] (Table 1).

Table 1 Stockholm Convention POPs List

Annex	A - Elimination	B- Restriction	C- Unintentional Production
Original List 2001	Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene, Polychlorinated biphenyls (PCBs)	DDT	Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, Polychlorinated biphenyls (PCBs), Hexachlorobenzene
Added May 2009	α-Hexachlorocyclohexane, β-Hexachlorocyclohexane, Chlordecone, Hexabromobiphenyl, Hexabromodiphenyl ether and heptabromodiphenylether, Lindane (gamma-hexachlorocyclohexane) Pentachlorobenzene Tetrabromodiphenyl ether and pentabromodiphenyl ether	Perfluorooctanesulfonic acid (PFOS), and its salts perfluorooctanesulfonyl fluoride (PFOSF)	Pentachlorobenzene
Added May 2011	Endosulfan		

Added May 2013	Hexabromocyclododecane (HBCD)		
Added May 2015	Hexachlorobutadiene Pentachlorophenol and its salts and esters Polychlorinated naphthalenes		Polychlorinated naphthalenes
Under review	Decabromodiphenyl ether (BDE 209), Dicofol, Short-chain chlorinated paraffins (SCCPs), Pentadecafluorooctanoic acid (PFOA), its salts and related compounds		

This is only a list of priority pollutants and there are over 100,000 chemicals are currently in use or present in consumer products with over 30,000 considered to be in wide commercial use (in consumer products at >907kg/year) [2]. Many of these compounds are persistent, toxic and bioaccumulative and are detected in all types of environmental matrices. In environmental forensics investigations it can be prudent to adopt non targeted methods which can screen for the presence of a large number of contaminants rather than focusing solely on traditional accredited methods that target only a limited number of analytes. Forensic investigations usually involve establishing the source of a contamination event, this can occur from a direct chemical spill, fugitive emissions of chemicals from manufacturing plants, transportation and storage of consumer products and leaking or leaching from final products. A variety of post release processes may alter source signatures of POPs including; volatilization and dispersion, biodegradation, uptake in biota, biotransformation and elimination. This results in environmental samples containing very complex patterns of POPs which can be difficult to interpret. It is therefore important to consider the sample collection, preparation and analysis carefully so that the accuracy and uncertainty of the technique is acceptable to meet the required data quality objectives and the analytical method used is fit for the purpose for which it was intended [3]. This manuscript provides an overview of the available sample preparation methods and analytical techniques. It discusses pertinent issues surrounding method development and identifies points to consider when undertaking an environmental forensics investigation involving POPs.

2 Sample preparation

2.1 Collection

A well designed sampling program is integral to any environmental forensics investigation. There are many factors that can potentially bias data and lead to erroneous results and these need to be understood if they are to be defended in a courtroom. Detailed information on sample collection for environmental forensics investigations has been produced by Mudge [4], Morrison and Murphy [5] and Murphy and Morrison [6]. With any investigation it is essential to understand the environmental chemistry of compound in question so that the correct matrix can be targeted. Consideration should also be given to designing an appropriate sample strategy based on the question posed. Commonly asked questions include; what are the potential sources of contamination, what is the extent of the contamination, was the wildlife affected by the contamination or was a regulatory threshold limit exceeded? Each of these questions may involve the collection of different samples for a specific purpose.

Numerous samples are gathered during the course of an environmental forensics investigation. These might be collected from a variety of different matrices such as; air particles, gas phases, vegetation, soils, water and animals. In all cases, samples should be clearly labelled and stored in containers appropriate for the analysis being undertaken. All samples should be transported to the laboratory as soon as possible (preferably within 24 hrs) with appropriate chain of custody documentation. Failure to follow appropriate best practice guidance can lead to errors in the data and may ultimately result in the findings being dismissed from the courtroom. It is clearly preferable to follow the best practice guidance, however failure to follow best practice guidance does not necessarily mean that the data should be completely disregarded [7]. There have been cases in the U.S. such as *People v. Hale* (56Cal.App3d [1994]) where deviations from the best practice guidance did not preclude the introduction of the information as evidence [8].

2.2 Extraction

Extraction of the sample is a critical step that is required to separate the compounds of interest from the bulk matrix. Prior to extraction, internal standards are typically added to the sample to allow for quantification, quality control (QC) and to measure the extraction efficiency and recovery rate. Isotopically labelled analogues of the target compounds are preferred as they behave the same way as the native compounds in the sample which results in the most accurate and precise data for calibration and quantification [9]. However, isotope labelled solutions can be very expensive and in some cases there may not be labelled standards available. In these cases a representative compound with similar properties to the target compound can be used to calculate recovery rates. The accuracy and precision of the method can be strongly dependent on the number of internal standards and type of calibration used. In environmental forensics investigations samples can be obtained from a variety of different matrices, each of these may require a different extraction procedure to efficiently separate the compounds of interest.

2.2.1 Air, aqueous and liquid matrices

Aqueous and other liquid samples like biological fluids have classically been extracted using liquid/liquid extraction. If samples contain particles, they can be filtered to isolate the precipitates/particles and the two fractions either determined separately or recombined at a later stage depending on the aims of the project. This is particularly important for hydrophobic compounds such as BDE 209 that may be present almost exclusively in the particulate phase. An alternative to liquid/liquid extraction that has become more common is solid phase extraction (SPE). This technique uses a stationary phase / resin in an extraction cartridge or disc to extract non-polar analytes like dioxins from polar liquids. Extraction of samples by SPE [10-12] also allows for the particles to be trapped on top of the extraction disc or bed. Quantitative elution of the particles and disk can be done in several steps to separate several compound classes, or in one step for many analytes which can significantly reduce solvent usage and analytical time [9]. There are several other methods that have been successfully used for the extraction of POPs such as; stir-bar sorptive extraction (SBSE) with thermal desorption directly into the gas chromatograph [13], hollow fiber liquid-

phase microextraction (HF-LPME) [14], Solid phase micro extraction (SPME) [15], and passive samplers, including semipermeable membrane devices (SPMD) or polyethylene strips [16]. Air sampling for POPs is traditionally conducted using polyurethane foam (PUF) or XAD resin [17], or a mixture of both to capture the more volatile gas phase analytes, combined with a Teflon or glass fibre filter (GFF) to capture those analytes found predominantly in the particulate phase. More recently researchers have also used passive samplers such as low-density polyethylene passive samplers (LDPE-PAS) to sample both the aquatic and atmospheric environment [16]. PAS have the benefit of little to no infrastructure requirements, easy extraction, potentially long deployment times and high capacities for POPs. PAS have been used in a number of studies for the source tracking of PCBs [18-20] and OCPs [21, 22].

2.2.2 Solid matrices

Solid matrices (e.g., soil/sediment, biota or vegetation) have classically been extracted using Soxhlet extraction or an automated version of Soxhlet called Soxtec. Pressurized liquid extraction (PLE – also known as accelerated solvent extraction (ASE)) [23-25], microwave assisted extraction (MAE) [26, 27] and sonication have also be used. PLE and MAE are automated techniques that subject the samples to elevated temperatures and pressures that can result in faster more efficient extractions than Soxhlet and sonication. The use of PLE for the extraction of POPs in environmental samples has recently been reviewed by Vazquez-Roig and Picó [28]. Supercritical fluid extraction (SFE) [29, 30] is a procedure that uses supercritical carbon dioxide and requires no solvent for extraction and only a very small amount of solvent to trap the analytes or elute them from the carbon or C18 trapping material. Solid matrices can also be digested by using an acid or base and then extracted using SPE or liquid/liquid extraction [31, 32], however care must be taken when using an acid or base as they may breakdown potential compounds of interest such as BEHTBP and other susceptible HFRs. Many of the techniques discussed in section 2.2 are relatively expensive as they require a lot of time and need to be conducted by an experienced scientist to produce acceptable results. QuEChERS (quick, easy, cheap, effective, rugged, safe) provides a cheaper alternative where the cost per sample can be less than $10. Many specific QuEChERS methods have been developed

for different applications based on the original method of Anastassiades et al. [33]. The sample is extracted in the presence of a dispersant in a disposable tube providing a relatively clean injection ready extract, although additional cleanup steps are often used. Although initially developed for the determination of vetenary drugs the method has modified to determine non-polar analytes like PAH and PCBs and is an excellent choice for initial sample screening [34-36]. The use of QuEChERS for the determination of persistent organic pollutants in environmental matrices has been reviewed [37, 38].

A summary of available extraction techniques for the different matrices is presented in Table 2. It provides a brief overview of each technique and lists a couple of pertinent references which can be referred to for further information.

Table 2. Summary of extraction techniques

Method	Main Matrix(es)	Brief overview	Example references
Solid Phase Extraction (SPE)	Aqueous / Liquid	A sample is passed through a stationary phase / resin in an extraction cartridge or disc which extracts analytes from liquids. These can then be collected with a solvent.	[9,10,11,12]
Stir-bar sorptive extraction (SBSE)	Aqueous / Liquid	A small bar coated with sorbent is added to the liquid mixture and stirred to extract analytes. These can then be collected with a solvent.	[13]
Hollow fibre liquid phase microextraction (HF-LPME)	Aqueous / Liquid	Sample is passed into a small hollow fibre coated with adsorbent where it is retained. These can then be collected with a solvent.	[14]
Solid phase micro extraction (SPME)	Aqueous / Liquid	An adsorbent coated fibre is inserted into the sample to extract analytes. These can then be collected with a solvent or the fiber inserted directly to the injector.	[15]
Semipermeable membrane devices (SPMD)	Aqueous / Liquid	The sampler is normally placed in a watercourse and left for a period to adsorb analytes. These can then be extracted from the membrane with a solvent.	[16]
Low density polyethylene strips	Aqueous / Liquid & Air	A strip of polyethylene is placed in a watercourse or outdoor sample case and left for a period to adsorb analytes. These	[16, 19, 21, 22]

(LDPE-PAS or LOPE)		can then be extracted from the membrane with a solvent.	
Polyurethane foam (PUF) and XAD resin	Air	Sample is pumped through a foam / resin disk/filter which absorbs gaseous phase analytes. It can be used in combination with a Teflon or glass fibre filter to trap particulates. These can then be collected with a solvent.	[17,18, 20]
Pressurised liquid extraction (PLE) & Accelerated solvent extraction (ASE)	Solid	Sample is placed in a cartridge and solvent passed through under a designated temperature and pressure to extract analytes.	[23-25, 28]
Microwave assisted extraction (MAE)	Solid	Samples are placed in a temperature controlled vessel and microwaves used to digest sample and extract analytes into a solvent.	[26, 27]
Supercritical fluid extraction (SFE)	Solids	Samples are placed in a temperature controlled vessel and pressurised with supercritical CO_2 to dissolve the sample, the gas is then depressurised causing the analytes to precipitate in a collector with a small amount of solvent.	[29, 30]
Saponification / acid digestion and extraction	Solid	Sample is digested with an acid or base, the resultant solution can be separated by liquid/liquid extraction or SPE. These can then be collected with a solvent.	[31,32]
QuEChERS (quick, easy, cheap, effective, rugged, safe)	Solids	A solvent (typically acetonitrile) is added to the sample along with water and salts (typically magnesium sulphate and sodium acetate). This is shaken and the salts precipitate out leaving the analytes in the solvent.	[33, 34-38]

2.3 Sample extract cleanup

Most extraction procedures for POPs are quantitative and able to extract a variety of organic compounds as well as other organic matrix co-extractables. Therefore, extract cleanup procedures are required to remove the potentially large quantities (up to a gram or more) of organic material and interfering compounds, but still retain as much of the desired analytes as possible. Most clean up procedures involve combinations of silica, alumina, Florisil® and carbon adsorbents or size exclusion materials (e.g. gel permeation

chromatography) to remove matrix and interfering compounds [39-44]. If required more aggressive clean up techniques can be used such as the use of sulphuric acid to clean up extracts for PCB determination (EPA Method 3665A). However, care must be taken as the method may breakdown many pH sensitive analytes including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate as well as halogenated flame retardants such as BEHTBP and EHTBB. There are several on-line cleanup systems that have also been used to provide an automated high throughput alternative [45, 46].

In forensics cases it is very important to ensure that the absence of a key compound from a sample is not due to the sample preparation step. Selecting the appropriate concentration technique is critical as using an inappropriate procedure could result in significant losses and bias. For further reading Reiner et al. [9], Lambbropoulou [47], Fidalgo-Used et al. [48], Rawa-Adkonis et al. [49], Tang, [50] and Xu et al. [51] have all reviewed a variety of extraction and clean up techniques for environmental samples.

3 Sample analysis

3.1 Chromatographic separation

In order to achieve accurate quantification, compounds must be fully resolved from each other. In a number of cases this may be possible by using selective detection. While several chromatographic techniques are potentially useful, gas chromatography (GC) and high performance liquid chromatography (HPLC) are clearly the most widely used techniques for environmentally-relevant separations. Since the early 2000's, ultra-high performance liquid chromatography (UHPLC) has also been successfully used for many environmental separations, mostly in an effort to increase laboratory throughput [9]. An overview of the different separation techniques is presented in Table 3.

Table 3. Summary of separation techniques

Technique	Advantages	Disadvantages	Analytes investigated using the method and selected references

Liquid chromatography	•wide range of potential analytes including non-volatile, thermally labile, polar and ionic analytes •short run times •variety and complementary nature of potential ionisation techniques	•Lower number of theoretical plates gives poorer separation potential compared to GC	OC Pesticides [57,58, 113, 117, 124] PBDEs [135, 136, 137] HBCD [55, 56, 60-62, 135, 136, 137] Perfluorinated chemicals [64-68, 141, 142]
Gas chromatography	•Good separation potential	•Restricted to use on more volatile compounds	OC Pesticides [45, 57, 112-116, 118, 121-123] PCBs &/or PCNs [45, 121, 123-128] PCDD/F [99, 123, 129-131] PBDEs [120, 127, 128, 132, 134, 135, 136, 138, 139] HBCD [138, 139] Perfluorinated chemicals [51]
Multidimensional gas chromatography	•Excellent separation potential	•Restricted to use on more volatile compounds •Large file size and more data processing often required	OC Pesticides [86] PCBs &/or PCNs [32, 82] PCDD/F [89] PBDEs [133]

3.1.1 Liquid chromatography

In HPLC separations the difference in retention is a complex process involving equilibria of the analytes between the stationary phase ligand, the mobile phase composition, and possible adsorption forces to the particle. Since this competitive equilibria is complex, it is not easy to determine how to adjust the chemical variables in order to improve separation. Modelling programs are available that aid in the optimization of the chemical variables, however these can be expensive. A cheaper option can be to use predictive models based on tabulated data. Tabulations based on the hydrophobic subtraction model (http://www.usp.org/app/USPNF/columnsDB.html) are particularly useful in selection and also in cross-over of column chemistry for method development [9]. Reverse phase liquid chromatography is the most widely used separation technique for environmental samples. This is usually performed using octadecyl (C18)-bonded silica and octyl (C8)-bonded silica. Other bonded phase materials on polymeric, monolithic,

non-porous and superficially porous supports and special aqueous phase materials have also become available [52]. The use of LC-MS in the determination of contaminants in the environment and foodstuffs has recently been reviewed by Aceña et al. [53] and Hird et al. [54].

The key benefits of LC separation in environmental forensic investigations are its wide range of potential analytes (e.g. non-volatile, thermally labile, polar or ionic analytes), short run times (often less than 15 mins), and variety and complimentary nature of potential ionisation techniques (e.g. ESI, APCI, APPI). A good example of the benefits of LC analysis in environmental forensic investigations is shown by Zhang et al. [55] who determined the diastereoisomer profiles of HBCD in soils from coastal regions in Northern China and identified different industrial sources of HBCD to the environment. Similarly, Managaki et al. [56] used a HBCD diastereoisomer specific LC-MS/MS method to determine the likely sources of HBCD to the Tsurumi river catchment flowing through the Tokyo metropolitan area.

The combination of fast speed of analysis achieved by liquid chromatography in combination with high sensitivity/selectivity with tandem MS detection often makes LC the preferred choice for the determination of pesticides [57, 58] although similarly short (<10 min) run times have recently been achieved by gas chromatography [59]. Most POPs have physiochemical properties that make them well suited to analysis by gas chromatography. The improved degree of separation that is achievable by gas chromatography allows for a more detailed congener specific detection which often makes analysis by gas chromatography preferable in environmental forensics investigations. However, LC is the preferred choice for polar non-volatile and/or thermally labile POPs, such as hexabromocyclododecane (HBCD) [60, 61]. Sales et al. [62] recently proposed the use of gas chromatography with atmospheric pressure chemical ionisation for initial HBCD screening and quantification and compared the results against previously used GC and LC methods. However, there are three main HBCD isomers (α, β, and γ) which interconvert at elevated temperatures during analysis by GC–MS and therefore only total HBCD should be determined this way [63].

The perfluorinated chemicals identified by the Stockholm Convention are predominantly determined by liquid chromatography [64]. PFOSF (a major precursor of PFOS) determination by GC has been attempted,

although it was not well retained by a variety of GC columns (DB-5, DB-1 and MEGA WAX) [51]. The majority of analytical methods are targeted and involve MS/MS, however more recently methods have been developed to screen for the presence of other per and polyfluorinated alkylated substances (PFASs) [65-68].

3.1.2 Gas chromatography

When using gas chromatography the separation of compounds in a mixture occurs chiefly due to the different boiling points of each compound and interactions with the stationary phase of the column. Understanding how the stationary phase chemistry effects GC separation is fairly easy to predict and calculations can be performed using commercially available software packages such as "Pro ez-GC" (Restek Corporation, Bellefonte, PA). These programs can be exceptionally useful for both column selection and the optimization of a separation, even for compounds that are not found in the included libraries [9]. By optimising the resolution of compounds as well as possible within the chromatographic space it places less demand on detection systems, and thus improves the overall quality of the total analysis. This can be particularly useful in environmental forensics investigations as the ability to resolve more compounds will produce a more detailed chemical fingerprint which increases the power of statistical tests that are often used for source identification. There are many different chromatographic phases available from a variety of manufacturers. A list of selected available phases and related applications for the determination of POPs are summarised in the supplementary information (SI 1). Selection of a general purpose column (such as a 5% diphenyl dimethylpolysiloxane) can be a good initial step for screening samples to identify potential contaminants of concern or compounds of diagnostic value. This can then inform further phases of analysis which may involve the use of a more species specific column to focus on compound specific analysis (such as a propietry PCB column) or chiral analysis (such as cyclodextrin) which can be used to answer specific environmental forensics questions [32].

3.1.3 Multidimensional chromatography

Comprehensive two dimensional gas chromatography (GCxGC) was developed at the end of the 20th century by the late John Philips [69]. The technique has several advantages over single dimensional chromatography as it can significantly increase peak capacity (selectivity), increase sensitivity and reduce analysis times by eliminating ejections on multiple chromatographic phases. Detailed reviews on the development and applications of multidimensional chromatography have been produced by Adahchour et al. [70], Bordanjandi et al. [71], Mondello et al. [72], Murray [73], Meinert and Meierhenrich [74], Mostafa et al. [75], Marriott et al. [76], Ramos [77] and Seeley and Seeley [78]. In GCxGC, two GC columns of different phases are connected by the modulator, a thermal or valve controlled device, which traps compounds from the first column and then re-injects them in a tight band onto the second column usually of a complimentary phase where further separation occurs. The best chromatography is achieved when compounds are passed through two columns containing different stationary phases, which results in two degrees of separation based on different physiochemical properties, e.g. boiling point and polarity. Ideally this results in an orthogonal separation where isomers elute in bands at about a 45 degree angle (Figure 1). This also allows several groups of POPs to be identified in the same analytical run and in most cases can provide an extra degree of separation as the target analytes are separated from any remaining sample matrix. One of the greatest challenges of this technique is to be able record a minimal number of measurements across the very narrow peaks produced in the modulation process which are approximately 400 ms wide. In order to accurately define a second dimension GC peak, about 20 spectra per second are required to obtain seven to ten data points. Less than 7 measurements will not be representative of a Gaussian-shaped peak and can therefore result in significant quantitative bias [9].

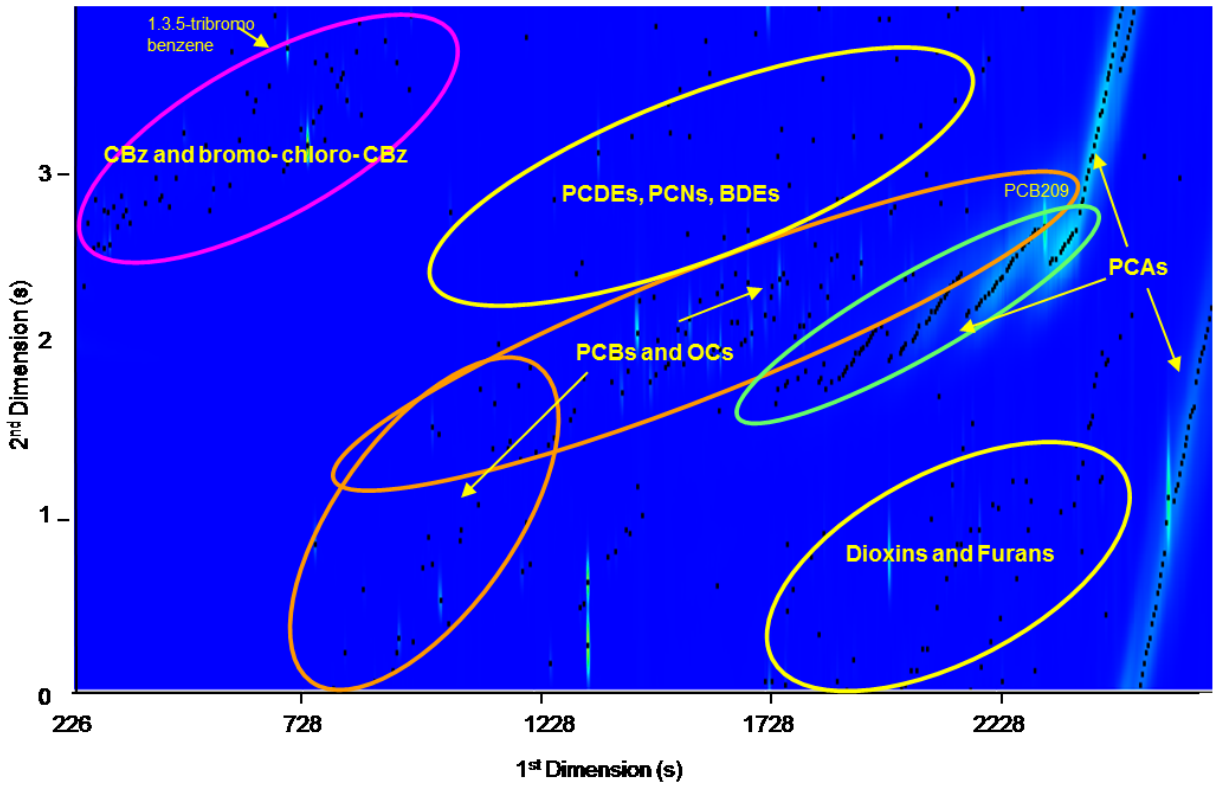

Figure 1. GCxGC-ECD chromatogram for POPs determination of a sediment sample (reproduced with permission from Reiner et al. [9]).

There are several major advantages to analysis by GCxGC over one dimensional techniques. It can eliminate the need for fractionation or multicolumn analysis and the modulation process produces much narrower and taller chromatographic peaks which can increase signal-to-noise ratios (sensitivity) by up to an order of magnitude. As well as being utilised for targeted analysis GCxGC has been used for the screening of non-target compounds [79-86] The complex patterns detected in the GCxGC chromatograms can also be used as fingerprints to characterize sources of contamination. The detailed congener specific data generated by GCxGC makes it very well suited for environmental forensics investigations involving complex biological matrices [32, 87]. GCxGC techniques are now at the stage where they can be used for routine analysis, an example of this is the determination of PCBs, organochlorines and chlorobenzenes by GCxGC-μECD using the Ontario Ministry of the Environment and Climate Change method MOE E3487 [86]. Despite the unparalleled peak capacity; the successful determination of complex environmental,

petrochemical, and biological samples; and substantial advancements in instrumentation, the use of GCxGC in the forensic domain has remained relatively scarce since its introduction in 1991 [88]. A review of GCxGC applications in forensics investigations was undertaken by Sampat et al. [88], who recorded only 36 peer reviewed articles by 12 research groups/collaborations between 2001 and 2015.

3.2 Analyte detection

Once the compounds of interest have been separated there are a variety of options available for detection and quantification. Sensitivity, selectivity and speed of analysis are the main considerations when selecting the detector. Nowadays, simple detectors such as flame ionization and electron capture detectors (FID and ECD) are mainly used for quick screening, although these techniques can still prove powerful tools, especially when coupled to GCxGC [86, 89]. ECD detectors are especially sensitive to halogenated compounds and so can provide comparable detection limits to many mass spectrometers for halogenated compounds such as PCBs (Table 4). Recent advances in mass spectrometry have resulted in commercially available instruments that are highly sensitive, selective, automated, and simple to operate with reduced cost and maintenance. As a consequence, bench-top quadrupole and time-of-flight mass spectrometers have in some case supplanted FID and ECD for both screening and quantitative applications. More sophisticated tandem mass spectrometers (MS) and high resolution MS instruments have become more accessible and these can be found in some form in most analytical laboratories. Mass Spectrometers are a versatile detector which offers excellent sensitivity, dynamic range and also offers the key advantage of being able to use mass labelled internal standards, which can significantly increase accuracy and precision [9]. For qualitative work, no other technique can provide the same wealth of structure information of little more than a few picograms of a chemical compound. Detailed reviews on the instrumental determination of POPs have been produced by Guo and Kannan [90], Van Leeuwen and de Boer [40], Petrovic et al. [91], Hernández et al. [92], Farré et al, [93] and Xu et al. [51].

3.2.1 Ionization techniques in mass spectrometry

There are several techniques by which ions can be generated and mass analysis can be performed. The most commonly used technique for the identification of POPs is electron ionization (EI), which is typically coupled with GC. EI mass spectral libraries have been developed for matching spectra for non-target compound identification. Significant fragmentation occurs under EI conditions, which is crucial to the success of library matching. However, it can also result in elimination of the molecular ion and thus, the possibility of obtaining an elemental composition. Increasing the pressure in the ion source leads to chemical ionization (CI), which is a much softer form of ionization that can result in an improved yield of molecular ions as well as, in some cases, diagnostic ion-molecule reactions [94]. Electron capture negative chemical ionization (ENCI) is a particularly helpful technique for the determination of halogenated POPs [94, 95] because it is selective towards compounds with a high electron affinity. Despite the selectivity benefit, ENCI is not usually employed for routine methods and dissociative electron capture into Cl- and Br- can hamper analysis. Other forms of "softer" ionisation include field ionisation (FI) and photo ionisation (PI). Field ionisation uses high electrical fields in the close proximity of emitter needles. During photoionisation molecules are ionised by absorption of two or more ultraviolet (UV) or one single vacuum ultraviolet (VUV) photon. These forms of ionisation make detectors highly sensitive and selective for aromatic species, however the laser based photo-ionisation technologies are still too expensive and sophisticated for a broader application [96].

Liquid chromatography (LC) and the associated atmospheric ionization methods such as electrospray (ESI) are now widely used for the determination of polar non-volatile and/or thermally labile POPs. Additional ionisation techniques include atmospheric pressure chemical ionisation (APCI), and atmospheric pressure photo ionisation (APPI). APPI is typically used for non-polar compounds like halogenated flame retardants and PAH. APCI and APPI have mainly been coupled to LC, but recently these ionization techniques are also being used for GC analysis [97]. Methods have been developed for specific POPs, including dioxins [98, 99] and polybrominated diphenyl ethers [100, 101].

3.2.2 Nominal mass resolution mass spectrometers

Mass analysers are broadly classified as being capable of performing either nominal or high mass resolution measurements. The resolution of a mass spectrometer ($R=M/\Delta M$) is defined by the degree of peak overlap at a 10% valley (10%V) or full width of a peak at half peak height (full width half maximum - FWHM). Quadrupole and quadrupole ion trap mass spectrometers usually provide nominal mass resolution (R = 100 – 1000). High resolution mass spectrometers include magnetic sector (HRMS) and some time-of-flight (HRTOF) instruments, which are capable of operating at R=10,000 – 50,000. Fourier transform ion cyclotron resonance (FTICR) and Orbitrap mass spectrometers may be considered *ultra*high resolution instruments (R = 100,000 – 1,000,000), which can resolve mass spectral peaks that differ by as little as 1 mDa [102].

Mass resolution is important but it is not the only parameter that needs to be considered. The sensitivity of the instrument is also important as there is no benefit to being able to distinguish two compounds of a similar mass, if you are unable to detect them in a sample at environmentally relevant concentrations. The linier range of a detector is also important, in environmental investigations there are often several orders of magnitude difference in concentrations between samples and also between individual congeners of the same compounds class. Whilst some of these issues can be overcome by dilution or concentration and reanalysis, there are obvious time and cost benefits of not having to incur this extra level of sample preparation and analysis.

Quadrupole instruments were the first bench-top instruments, becoming commercially available in the 1980s, which significantly reduced the cost of mass spectrometry detection. They are now very wide spread and can be found in most commercial and research laboratories. A quadrupole instrument is typically limited to unit mass resolution measurements, but its excellent linear dynamic range (4-6 orders of magnitude), sub picogram sensitivity, ease of use and low operating costs make it a popular choice for initial screening using targeted compound analysis and full scan applications. They can also be a cost

effective option when analysing samples where low detection limits are not essential, such as the determination of PBDEs [103] and PAHs [104] in dust.

Tandem instruments usually consist of two quadrupole mass analysers, sandwiching an ion guide collision cell. Other hybrid types incorporate a quadrupole ion trap, time-of-flight, FT-ICR or Orbitrap as the final mass analyser. The first quadrupole is used for initial selection and focusing. The collision cell is filled with a collision gas (helium, nitrogen, oxygen or argon) to produce specific fragments that are subsequently mass separated by the final mass analyser. Tandem mass spectrometry has the advantage of being able to filter out non target ions and can therefore reach low femtogram detection levels because the chemical noise is substantially reduced. Most MS/MS instruments exhibit a good linear dynamic range (4-6 orders of magnitude) which makes this technique an excellent choice for targeted determination of trace level contaminants; such as PBDEs and other POPs in biota and food webs [105-107]. Drawbacks of MS/MS instruments are that MS/MS experiments are more complex to develop and optimize than single stage MS experiments, and non-target compounds are not detected.

3.2.3 High resolution mass spectrometers

The magnetic deflection instruments are capable of both HRMS and tandem MS, but usually only the former mode is used for targeted compound analysis in environmental and environmental forensics applications. Modern magnetic sector instruments are routinely tuned to achieve a resolution of >10,000 (10% valley), and they can achieve low-femtogram instrument detection limits (IDLs) or even attogram IDLs when coupled to cryogenic zone compression gas chromatography [108]. Such instruments also exhibit an excellent dynamic range of 6 to 7 orders of magnitude. However, most analysis is undertaken using selective ion monitoring (SIM) where the detector only focuses on several target ions. This has helped to establish HRMS as the technique specified by the U.S. EPA for low level congener specific analysis of compounds such as PCBs (Method 1668C), PCDD/F (Method 1613) and PBDEs (Method 1614). Whilst SIM increases the sensitivity by a factor of 10 to 100 it does mean that non-target compounds are not

detected. Nowadays, the main drawbacks of magnetic deflection instruments are commercial availability and the significant costs associated with maintenance and user training.

TOF instruments are relatively simple in design and easy to maintain, tune, calibrate and operate. They are available as low resolution, mid resolution (7,000 to 10,000) and high resolution (> 20,000) instruments. Recent improvements over the last decade have allowed low femtogram detection levels to be achieved. The major disadvantage of most TOF instruments is the low dynamic range which is usually limited to 4 orders of magnitude. The chief advantage of the TOF is its high data acquisition rate (20-200 scans/second) while recording full-scan mass spectra. This makes them the detector of choice for fast GC and environmental forensics GCxGC applications for POPs [31]. The ability of the TOF to collect data for an entire mass range gives them the excellent potential as a tool for non-targeted screening and for the simultaneous determination of multiple POPs [82, 107, 109, 110].

There are two instrument types available that can operate at ultra-high resolution. These include Fourier transform ion cyclotron resonance (FT-ICR) and orbitrap mass analyzers. Both are capable of achieving a mass resolution of >100,000. Newer instruments are quite sensitive, with LC and GC amenable compounds detectable in the mid femtogram range. Since these detectors work by trapping a finite number of ions in a cell, they suffer from space charge effects which limit the instrument to approximately 4 orders of magnitude. The acquisition rate and resolving power of these instruments are limited by the length of the transient, i.e., the time the ions are confined during detection. Longer transients result in higher resolution. The timescale is most compatible with LC and direct infusion (> 1 scan/second); but GC experiments are still possible. For example Peterson et al. [111] used a GC-Enabled QLT-Orbitrap for the determination of dioxins in environmental samples. Due to their exceptional high mass resolution FT-ICR and orbitrap mass analyzers instruments are well suited to the determination of complex samples or when an unknown sample needs to be characterised [107, 109, 110].

3.2.4 Comparison of different detectors for the determination of POPs

There is not one technique that can be considered the best for the forensic determination of POPs, the various advantages of the different techniques are presented above and have been summarised in Table 4. Whilst the extraction method used will have a large influence on the method detection limits a summary of recent detection limits in various environmental matrices for different POPs is included. Reviews on the determination of POPs have been undertaken by many authors, recent examples include; Reiner et al. [9], Xu et al. [51], Farre et al. [93], Tang [50]. The vast majority of methods reported in the analytical literature have been developed to meet a set of criteria constant with a specific regulatory limit. The method development is therefore focused on proving that the technique has detection levels below this limit so there can be confidence if a sample has exceeded it or not. Whilst this makes sense for a screening exercise it does mean that some diagnostic information which would be useful for a forensic investigation may not be recorded as much lower detection limits could be achieved using the same instrument. A good example of this is for the determination of pesticide residues in foods. The majority of methods on different instruments all present a limit of detection in the range of <10 ng/g [57, 112-117] to coincide with regulatory maximum residue limits. However, there are examples where much lower detection limits of <500 pg/g can be achieved for these compounds [86, 118].

As well as focusing on a specific regulatory limit, many methods focus on one compound class. This type of measurement favours techniques such as MS/MS which can filter the data to get excellent signal to noise ratios and low detection limits for a specific set of compounds. A recent example of this was Organtini et al. [99] who used APGC-MS/MS to detect 2 fg of dioxins (on column) resulting in detection limits of <1 ng/kg in soil. Again whilst this makes sense for a screening exercise it does mean that some diagnostic information which would be useful for a forensic investigation may not be recorded. There are several advantages of collecting full scan data on an instrument such as TOFMS. This can allow for the determination of multiple POPs in the same run [80]. Data can also be re-evaluated later to check for the presence of other potential contaminants of concern without the need for re-analysis. This allowed Megson

et al. [119] to identify an additional group of toxic organophosphates in jet oil following an initial screening exercise in a forensic investigation. Finally if a new potential POP is discovered its presence can be checked for in historic samples to identify when it arrived in the environment. Nowadays some instruments are able to combine multiple functions and collect both MS/MS data and full scan TOF data, this may prove to be a very powerful tool in future investigations.

Table 4. Comparison of different detectors used for the determination of POPs

		Detector type					
		ECD	qMS	TOFMS	HRMS (magnetic deflection)	MS/MS	Orbitrap
	Mass resolution	na	nominal	nominal → >20,000	>10,000	nominal → >20,000	> 100,000
	Linier range (orders of magnitude)	4 to 5	4 to 6	3 to 4	6 to 7	4 to 6	3 to 4
	Cost of analysis	low	low	low → high	high	high	high
	Selectivity	v.low	low	high	high	high	high
	Sensitivity	high (halogenated) → low (non-halogenated)	moderate	moderate → high	high	high	moderate → high (depending on acquisition settings)
Limit of detection	OC Pesticides, including; Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene, DDT, α-Hexachlorocyclohexane, β-Hexachlorocyclohexane, γ- Hexachlorocyclohexane (Lindane), Chlordecone, Pentachlorobenzene, Endosulfan	<10 ng/g (various foods) [57,112,113] <5 pg/g [118], <500 pg/g*[86] (soil) 8-33 pg/g (fish) [120]	<10 ng/g (various foods) [114, 115] <500 pg/g (soil) [118] <1 ng/g (soil) [121]	<50 pg / L (water) [122]	<10 ng/L (serum) [45, 123]	<10 ng/g (various foods) [113, 115, 116]	<2 µg/L (analytical standard) [124] 10 ng/g (various foods) [117]
	**Polychlorinated biphenyls (PCBs) and **Polychlorinated naphthalenes (PCNs)	<140 pg/g, [125] (sediment) <1.6 ng/g* [86] (soil) <2.4 µg/L (water) [126] 10 pg/g (fish) [127] 8-33 pg/g (fish) [120]	<1 ng/g (soil) [121] < 0.14 µg/L (water) [126]	1 to50 pg/µL ***(analytical standard) [32] 0.5 to 10 pg/µL ***(analytical standard) [82] 1-15 pg/µL ***(serum) [82]	<80 ng/g (soil) [128] <30 pg/L (water) [128] <50 ng/L (serum) [45, 123]	< 3 pg/g (sediment) [125]	only reported LOD of 10 fg for octafluoronaphthalene [111]

	**Polychlorinated dibenzo-p-dioxins and **polychlorinated dibenzofurans,	< 5.2 pg/g* (sediment) [89]	< 1 pg/g fat (beef) [129]	<0.5 pg/µL ***(2,3,7,8-TCDD analytical standard) [130]	0.54-5.04 ng/g (sediment)[131] <2 ng/L (serum) [123]	2 fg/ul (analytical standard) & <1 pg/g (soil) [99]	
	**Polybrominated diphenyl ethers (PBDEs) and Hexabromobiphenyl	8-33 pg/g (fish) [120]	0.005-0.1 µg/L (water) [132] 0.25-5 ng/g (soil) [132] 10 pg/g (fish) [127]	0.025-5 ng/g ***(fish) [133]	<200 ng/g (soil) [128] <50 pg/L (water) [128] <10 ng/L (serum) [123]	<0.1 ng/g (sediment) [134] 1-80 ng/g (dust) [135] 1–25 ng/g (dust) [136]	1-250 pg/g (fish) [137]
	Hexabromocyclododecane (HBCD)	6 pg/g (milk) [138]	0.03 µg/L (water) [139]	<30 pg/g**** (fish) [61] 0.9-4.5 pg/g (fish) [61]	5 ng/g (dust) [139]	<9 pg/g (fish) [61] 0.9-2.1 pg/g (fish) [61] 1 ng/g (dust) [135] 1–25 ng/g (dust) [136]	10 pg/g (fish) [137] <13 pg/g (fish) [61] 1.1-3.0 pg/g (fish) [61]
	**Perfluorooctanesulfonic acid (PFOS), and its salts **perfluorooctanesulfonyl fluoride (PFOSF)	Response detected – no LOD reported [51]	0.05 µg/L (water) [141]	0.027-2.820 ng/g (dust) [142]		0.01–2.00 ng/L (water) [143] 0.04–8.00 ng/g (sediment) [143] 0.02–2.26 ng/g (biota) [143] 5-50 pg/g (fish) [67] 0.25-1 ng/g (dust) [136]	0.3-3 ng/L (water) [144] 5 to 200 ng/L [68]

*analysis by GCxGC-µECD
** reported values for one congener, not total of all congeners
***analysis by GCxGC-TOFMS
****analysis by HRTOFMS

4 Discussion

4.1 Method development, validation and QA/QC

In environmental forensics investigations it is especially important to follow strict QA/QC procedures and keep records of the work undertaken. In forensics investigations, a laboratory is required to have a comprehensive quality assurance / quality control (QA/QC) program that often includes accreditation to ISO 17025. Accreditation ensures that laboratories are following proper procedures and participating in performance evaluation studies to assess data quality. Whilst this makes perfect sense from a legal standpoint and in routine screening and compliance, it may not always be achievable in a forensics investigation. There may be instances where new and unknown chemicals have been detected, in these cases there may not be analytical standards or an accredited method available for analysis.

Methods are characterized by their data quality objects which include sensitivity (detection limits), and selectivity (precision or uncertainty and accuracy). Analytical cost and speed of analysis are also important considerations when selecting or developing a method. Just because a method is accredited it does not specifically mean it is the method that should be selected. For example if a lab is accredited to undertake EPA Method 608 (GC-ECD) or 625 (GC-MS) for PCBs this may be suitable for a routine screening. However, in a forensics investigation the methods are unlikely to be able to provide the detection limits required, may underestimate actual PCB concentrations, would not necessarily capture degraded PCBs that contain non-Aroclor congeners, and may therefore lead to erroneous quantification of Aroclors that are not necessarily attributed to the source of contamination [145].

In some cases analytical methods can be overlooked because they haven't been accredited. This can be detrimental if the method is capable of providing better quality, more useful data than the accredited method. However, if a non-accredited method is used can the court still have the same confidence in the quality of the data or applicability of the method? In 1993, the United States Supreme Court issued a landmark decision in Daubert v. Merrell Dow Pharmaceuticals, Inc., 509 United States (US) 579, which

made significant changes in the standards for admissibility of expert opinions in federal courts. These changes included a gatekeeping requirement in Rule 104(a) under which courts must screen expert opinions for reliability and exclude 'junk science.' In Daubert, the Supreme Court also established a new, more flexible set of criteria for reliability and admissibility of expert opinion [146-149].

According to Kanner [148], for a method to be accepted in court it needs to satisfy the following Daubert criteria:

- the scientific technique (or "theory" applied) must be testable and verifiable;
- the technique has been published in a peer-viewed journal or other similar publication;
- the technique has a defined rate or margin of error;
- the technique is used with appropriate standards and controls;
- and, the scientific community has accepted the technique or theory to a significant degree.

In all cases the production of accurate and precise results is critical and a laboratory must have a comprehensive quality assurance / quality control (QC/QC) program. Accreditation of a method is preferable, however non-accredited methods should not be discounted as they have and will continue to be accepted in a court of law. The most important requirement for any method is that it is fit for the purpose it was intended i.e. it satisfies all the data quality objectives needed for the client to make correct decisions using the data produced by the method [3]. Different jurisdictions allow different types of methods, procedures and instrumentation for regulatory work. Some jurisdictions (e.g. United States) typically require prescriptive methods and others (e.g. Ontario, Canada) allow more flexible methods and procedures that are performance based, as long as they are fully validated. Method validation requires a number of steps that involve the testing of spiked matrix samples and certified reference materials to determine method characteristics (detection limits, accuracy, and uncertainty) and to ensure the method is rugged, generally free of interferences and data are reproducible. Details on the various steps for method development and validation can be obtained in Reiner et al [9] and HimaBindu et al [150].

4.2 PCBs as an example for environmental forensics investigations

PCBs are one of the most widely studied group of POPs; however there is no commonly used method for PCB determination. PCBs were first detected as interferences in organochlorine pesticide GC-ECD chromatograms and it took almost 7 years to identify and confirm PCBs as environmental contaminants [9]. There are such a large number of PCB methods currently in use that when comparing data it is rare to find laboratories that used the same method. Early methods such as EPA Method 608 or 8082A used GC-ECD with PCB technical mixtures like Aroclors to calibrate and quantify results [44], however there are many limitations to these methods, which are discussed in Johnson et al. [145]. There are relatively few methods, such as EPA Method 1668C, that use GC-MS and GC-HRMS and are designed to determine all 209 PCBs, instead the vast majority of congener methods determine a reduced set of congeners. One of the main justifications for this has been because all 209 PCBs are not found in detectable concentrations in environmental samples. Out of the 5 Aroclors (A1016, A1242, A1248, A1254 and A1260) that contribute to >97% of Monsanto's sales [151] only 157 of the 209 possible PCBs are present, and only about 130-150 PCBs have ever been detected in environmental samples [9, 31].

Many commercial laboratories provide limits of detection for PCBs in the range of 10 – 1000 μg kg^{-1}. This can be a significant limitation as background total PCB concentrations (in UK urban soils) are between 0.01 – 40 μg kg^{-1} [152]. Therefore, sample clean-up and analysis by HRMS is often required to improve limits of detection to less than 1 μg kg^{-1} by removing or filtering out many interfering compounds. In many environmental forensics investigations there can be multiple sources of contamination which makes source identification a challenge, especially if the original signature has been altered by post depositional processes such as; volatilization and dispersion, biodegradation, uptake in biota, and biotransformation and elimination. In such cases it is important to select a method that has the required sensitivity but is also able to quantify as many individual congeners as possible to improve the potential power of the statistical methods used. In this instance GCxGC is a very useful tool as it provides an extra dimension of separation which significantly increases the resolving capacity. Using GCxGC has allowed for the identification of

over 190 of the 209 PCB congeners along with simultaneous identification of other organohalogenated contaminants [81, 31]. This method has been successfully applied to several environmental forensics applications such as determining the provenance of sea birds [87] and establishing the source of PCB exposure in humans [32].

4.3 Determination of Polychlorinated Dioxins and Furans

Although dioxins, furans and PCBs are chemically similar, most dioxin and furan methods are generally much more accurate and precise than most PCB methods. The majority of dioxin and furan methods are based on US EPA 1613 and use isotope dilution with GC-HRMS to determine the seventeen 2,3,7,8-substituted toxic congeners. Because of the highly toxic nature of these compounds, they are regulated globally and are often detected in exposure and contamination assessments and environmental forensics investigations [152-156].

Due to the extensive sample concentration and cleanup steps required for dioxin methods, method turnaround times are long and costs are significantly higher than those for other types of anlaytes [41, 42]. Detailed contaminated site characterization for reclamation can require a significantly large number of samples to delineate the contaminated area, which can be extremely costly. Bioassays have been used, but can require extensive sample extract cleanup to produce accurate results. The QuEChERS procedure uses a modified extraction procedure to significantly reduce sample preparation time. Haimovici et al. [131]; developed a method for site cleanup that significantly enhances productivity and reduces analytical turnaround time by a factor of 3 or more [154, 131].

4.4 Non target-analysis and identification of POPs

There are a few hundred chemicals that make up the Stockholm POPs Convention list (Table 1) [1]. These compounds are typically determined using targeted methods [90]. Using targeted analysis, many thousands of compounds are overlooked; this may be detrimental in an environmental forensics investigation where the source of contamination is unknown. The development of time of flight mass spectrometers [109] and

trapping instruments (Orbitrap) [157] to increase sensitivity, scan speed and resolution enables them to be used for non-target full scan analysis. The use of scanning instruments (TOF, Q-TOF, Orbitrap) enables analysts to obtain full scan spectra which can be reviewed manually to obtain unique mass to charge ratios and assign elemental compositions for the suspect compounds being investigated [109, 157-160]. Comparing the elemental compositions of the fragment ions to the molecular ion and searching databases such as Chemspider (http://www.chemspider.com/) enables the postulation of a possible structure. This can be used for the discovery of new contaminants of concern and may also identify compounds that may be unique to a specific source. There have been many instances where chemical impurities or co-contaminants present in samples have revealed some key information in an environmental forensics investigation. Recent examples include 2,4,6,8-Tetrachlorodibenzothiophene as an impurity in 2,4-D production from a specific manufacturer in Newark Bay [161] impurities in dechlorane plus production from a manufacturer in the Niagara region [162], and xylenyl cresyl phosphates in used jet oil [119]. Had just the main contaminant in question been determined in these investigations then this key diagnostic information would not have been recorded. There are also an increasing number of studies that have used non-targeted methods to identify mixed brominated / chlorinated aromatic compounds such as dioxins, furans and PAHs in environmental samples [107, 110]. Using complimentary non-targeted and targeted methods can help to establish more accurate levels of risk and provide more diagnostic information for forensic investigations.

Mass spectra generated from complex samples can contain many thousand fragment ions. Mass defect plots (MDPs) can be used to process this data and identified many compounds in a single analysis. The mass defect is the difference between the nominal and exact mass of a chemical element or compound. Plotting the mass defect against the mass to charge ratio allows similar compounds (homologues and congeners) to be identified [163]. MDPs can be calibrated to a variety of elements (CH_2, Cl, Br, CF_2) as shown in Figure 2 [107, 164-169]. Once one of the compounds in a row or column is identified, the remaining compounds of each connected row or column can relatively easily be identified as they are likely to be homologues.

These techniques are very useful when samples are chemically complex or when the main compounds of interest have not yet been established.

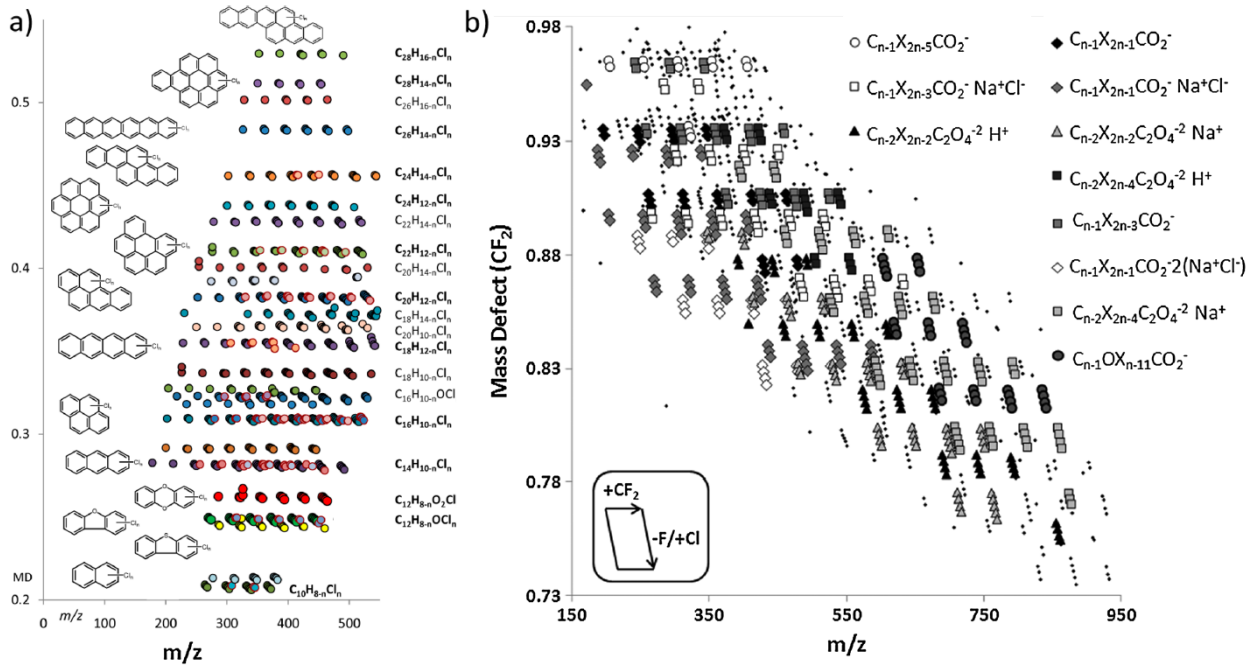

Figure 2. Mass Defect plot using the H/Cl scale of an extract from a plastic manufacturing plant fire (a), and using the CF_2 scale in a perfluorinated compounds thermolysis study (b) Reproduced with permission from Ortiz et al. [109] (original figures a) from Fernando et al. [110] and b) from Myers et al. [169])

5 Conclusions

The determination of persistent organic pollutants for environmental forensics investigations is not straightforward. There are a wide variety of accredited and non-accredited methods available and it can be difficult deciding which one to choose. There is not one analytical technique or method that can solve all the questions asked in an investigation. The decision needs to be made on a case specific basis depending on the required detection limits, linier range, sensitivity and selectivity. Unfortunately there are times when this decision is made by those with little understanding of the different techniques and their decision is based primarily on the cost of the analysis. Taking the time to plan an investigation properly and understand

the merits of the different techniques, will lead to the generation of better quality data which will be more likely to uncover the truth and may also turn out to be the more cost effective option.

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