7 Environmental Forensics Related to Soil Background

7.1 Introduction

Environmental forensics is a well-established discipline that considers scientific, operational, and historic information to interpret the potential sources and/or ages of contamination detected at a site, typically at anomalous concentrations. Although a common objective of an environmental forensic evaluation is to identify causation and timing of contamination (Morrison and Murphy, 2006), in the context of this guidance its value is focused on determining whether the observed chemical concentrations in soils may be representative of natural or anthropogenic ambient background or are due to site-related contamination. Using environmental forensics to determine whether a contaminant is representative of background requires an expert who is knowledgeable about these methods and the chemistry of the contaminant being evaluated.

Contamination requiring risk assessment can take many forms. Some forms are compositionally simple and their presence in the environment can be measured by only one or a few individual chemicals or elements (for example, arsenic or metals). Assessments of these simpler forms of contamination relative to background can often be achieved using numerous statistical tests (Section 11) and geochemical evaluations (Section 5). Other forms of contamination are compositionally much more complex, being comprised of scores of different chemicals, some with related chemical structures and similar but not identical chemical properties. Risk assessment of these more complex forms of contamination relative to background can often benefit from environmental forensics. Specifically, the complexity of these contaminants not only provides a basis to distinguish among different sources of the same contaminant but also, and of relevance herein, to distinguish contamination from background, particularly at low contaminant concentrations.

In this section, five different groups of chemicals that occur in the environment as both contamination and background are considered, namely:

- polycyclic aromatic hydrocarbons (PAHs; Section 7.2)
- total petroleum hydrocarbons (TPH; Section 7.3)
- polychlorinated biphenyls (PCBs; Section 7.4)
- polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F; Section 7.5)
- per- and polyfluoroalkyl substances (PFAS; Section 7.6)

The varying compositions of these five groups of chemicals in different contaminant sources can be exploited to distinguish contamination from background. As such, the application of environmental forensics is clearly relevant, albeit perhaps underused, in the human health and ecological risk assessment of soils, and therefore, warrants consideration by risk assessors.

In addition, this section also includes information on remote sensing (Section 7.7), whose application relies not on the chemical complexity of different source contaminants, but rather on the spatial and temporal differences that can be recognized in a study area using various remote (noninvasive) techniques.

7.2 Polycyclic Aromatic Hydrocarbons

PAHs are ubiquitous in soils worldwide (Nam, Sweetman, and Jones 2009). Some PAHs are acutely toxic and have carcinogenic properties (Menzie, Potocki, and Santodonato 1992), and as a result their occurrence in soils is regulated in most jurisdictions. Their ubiquity arises because (1) PAHs are formed by many natural and anthropogenic processes, and (2) once formed, PAHs can be spread throughout the environment, often by atmospheric transport. Some PAHs form naturally from the degradation of plant debris in soil (biogenic PAHs) or during the formation of crude oil (petrogenic PAHs) over geologic time. The latter can enter the environment both naturally (crude oil seeps) or due to anthropogenic spillage/leakage of crude oils and refined petroleum. Most PAHs, however, are formed by the incomplete combustion of organic matter (pyrogenic PAHs), such as wood, petroleum, coal, or even garbage. Again, combustion can be either natural (for example, wildfires) or anthropogenic (for example, fossil fuel burning or residential wood burning), and the resulting emissions and residues can be spread through the environment via runoff, atmosphere transport, or as redistributed contaminated fill.

The variety and widespread occurrence of PAHs' sources and their persistence during transport result in a certain level of PAHs in all soil that is attributable to background. In some soils, these PAHs can be derived predominantly to exclusively from natural processes, which impart a natural background. In other soils, PAHs can be derived from the diffuse occurrence of PAHs from anthropogenic ambient sources, such as atmospheric deposition, or from other sources that are not a result of a site release, such as runoff or fill.

Distinguishing PAHs in soils attributable to natural and/or anthropogenic ambient soil background from those PAHs due to

contamination (for example, spilled oil or coal tar) is important with respect to soil risk-based values used in risk assessment. When PAH concentrations are high, background threshold values used in lieu of the soil risk-based value can sometimes be established through statistical assessments of PAH concentrations in large datasets (Section 11). This distinction, however, is much more difficult in soils containing relatively low concentrations of contaminants, in which case-specific, sometimes subtle, chemical differences among different PAH sources can be useful. Environmental forensic assessments can aid in assessing the character of statistical outliers to determine whether they represent background or contamination.

In the following section, the basic methods used in the forensic analysis of PAHs in soils are presented. For additional information the reader is directed to the multitude of studies conducted over the past 50 years that assessed PAH sources (Appendix C).

7.2.1 Forensic analysis of PAHs in soils

Assessments of PAH in soils are conducted with the intention of determining impacts of local anthropogenic sources (contamination), both historic and current. This can sometimes be achieved through the use of the descriptive and inferential statistical techniques described in Section 11, but forensic analysis, which can include multivariate statistical analyses, may be warranted to support or refute any statistical determinations regarding background. Forensic analysis requires not only an understanding of the PAHs present in specific forms of contamination, but also the ability to distinguish PAHs attributable to contamination from those attributable to representative background based upon chemical patterns.

There is no single method for achieving this objective as no two datasets or study areas are the same. Instead, distinguishing PAHs in soils due to contamination from those due to representative background is best achieved through careful analysis, which often relies upon some combination of the following four forms of forensic analyses:

- Pattern recognition includes visual, qualitative comparisons of the available PAH concentration histograms (and corresponding TPH chromatograms), including comparison to known standards in a sample library and/or site-specific samples of known origin(s)
- Diagnostic ratios based upon parent and/or alkylated PAH concentration data, again sometimes including comparisons to known standards and/or site-specific samples of known origin(s)
- Spatial and/or temporal analysis of PAH patterns, diagnostic ratios, and/or concentrations, including a comparison to historical information compiled for the area (as part of the CSM)
- Quantitative source apportionment analysis that serves to allocate contributions between multiple PAH sources present, such as principal component analysis (PCA), chemical mass balance (CMB), and positive matrix factorization (PMF)

There is extensive literature on all of these methods, so each is only briefly discussed in the following paragraphs.

7.2.1.1 Pattern recognition

The human eye remains a powerful tool and, although experience in viewing PAH histograms can reveal subtle differences, even an inexperienced interpreter can visually compare the PAH histograms of different samples and assess any likely relationships (Stout et al. 2002). Because PAHs are usually derived from sources that also contain other (non-PAH) chemicals, the value of TPH chromatograms also cannot be underestimated. Good gas chromatography with flame ionization detection (GC/FID) (for example, USEPA Method 8015) of all the extractable compounds or hydrocarbons in a soil can often aid in understanding the source(s) of the PAHs alone (Section 7.3).

Qualitative fingerprinting is perhaps most useful in instances wherein marked differences exist between contamination and background PAH fingerprints. For example, combustion-derived particles in soils that are attributable to anthropogenic ambient soil background are dominated by 4- to 6-ring PAHs, which can be readily distinguished graphically from an impact of petroleum, such as used diesel fuel.

The long-recognized differences in the skewed versus bell-shaped PAH homolog profiles (Blumer 1976) can be easily recognized through qualitative inspection (if alkylated PAH data are available (see (Douglas et al. 2015) for details on alkylated PAH analysis). For example, Figure 7-1 shows the PAH distributions and concentrations for PAH sources often found in soils proximal to roadways, namely, abraded asphalt and soot (urban dust). The former exhibits bell-shaped PAH homologue patterns dominated by alkylated PAHs, whereas the latter exhibits skewed patterns dominated by the parent (non-alkylated) PAH. These serve to demonstrate the differences between petrogenic and pyrogenic PAH patterns, which are made more obvious with the availability of the alkylated PAH data. Of course, the influences of weathering on the PAH distributions must always be considered, which requires greater understanding of the effects of evaporation, water-washing, and biodegradation on PAH fingerprints (for example, (Elmendorf et al. 1994)).

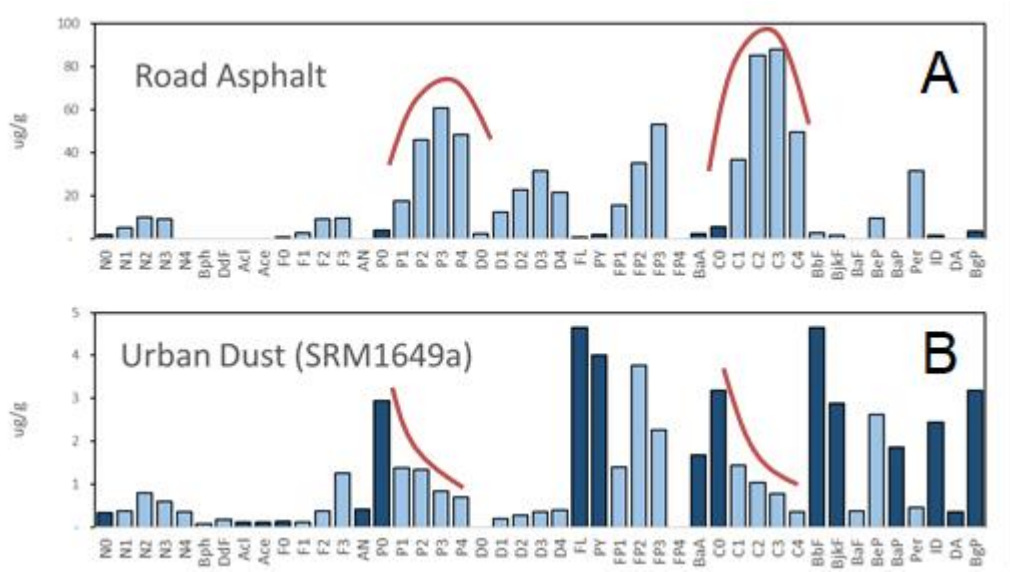


Figure 7-1. PAH histograms for materials that can contribute to anthropogenic ambient soil background. (A) road asphalt and (B) urban dust (NIST SRM1649a). Dark blue bars represent USEPA priority pollutant PAHs; light blue bars represent alkylated PAHs often used in forensic assessments; red lines depict (A) bell-shaped and (B) skewed homologue profiles (see (Stout et al. 2015) for additional details).
Source: (Compiled and plotted from Stout, Uhler, and Emsbo-Mattingly 2004).

7.2.1.2 Diagnostic ratios

Qualitative differences between PAH patterns can become less clear when a greater number of potential PAH sources are involved. In such situations, or in studies involving large numbers of samples, comparisons among the PAH fingerprints can be achieved through the use of diagnostic ratios. (See Appendix C for additional sources of information). Most diagnostic ratios involve PAH isomers (same molecular mass, but different molecular structure) and thereby similar physico-chemical properties, which better ensure that the ratios remain stable during weathering (as the isomers undergo similar environmental fates). As such, differences in diagnostic ratios among samples are commonly attributed to different PAH sources. Table 7-1 provides a partial inventory of some common PAH diagnostic ratios reported in two widely referenced studies.

Table 7-1. Diagnostic ratios used to assess PAH sources
Source: Scott A. Stout, NewFields Environmental Forensics Practice, LLC.

Ratio	Value/Range	Reported Source
AN/(P0+AN)	<0.1	Petrogenic
	>0.1	Pyrogenic
FL/(PY+FL)	<0.4	Petrogenic
	0.4–0.5	Petroleum combustion
	>0.5	Coal & biomass combustion

BaA/(C0+BaA)	<0.2	Petrogenic
	0.2–0.35	Coal combustion
	>0.35	Petroleum combustion
IND/(GHI+IND)	<0.2	Petrogenic
	0.2–0.5	Petroleum combustion
	>0.5	Coal & biomass combustion
See text for cautions regarding use of diagnostic ratios. PAH abbreviations: AN-anthracene; P0-phenanthrene; FL-fluoranthrene; PY-pyrene; BaA-benz[*a*]anthracene; C0-chrysene; IND-indeno[*1,2,3-cd*]pyrene; GHI-benzo[*g,h,i*]perylene.		

The simplicity of calculating and plotting diagnostic ratios among PAHs unfortunately can lead to the unquestioning application of this method in PAH source identification—or the ratios from one set of samples or site being inappropriately applied elsewhere (Boehm et al. 2018). There is a generally large degree of scatter in the ratios among samples from large PAH datasets with no clear cutoff in values, although cutoffs are often identified to exist (Table 7-1). The diversity of fuels (gasoline, diesel, biomass) or different combustion conditions can result in large variations in the ratios in combustion emissions reported among pyrogenic and petrogenic sources (Lima, Farrington, and Reddy 2005). As such, diagnostic ratios from one study may not reflect results obtained when different source materials are involved. An example of this was demonstrated by Lima, Farrington, and Reddy (2005), who showed that a cross-plot of the ratios of fluoranthene/pyrene and phenanthrene/anthracene ratios for a large number of known sources did not accurately reflect those predicted by published ratios (Table 7-1). Furthermore, some diagnostic ratios (for example, AN/(P0+AN)) appear to be unstable during some forms of weathering (Uhler and Emsbo-Mattingly 2006).

As such, diagnostic ratios' validity in source differentiation is often questioned ((Lima, Farrington, and Reddy 2005), (Galarneau 2008), (Katsoyiannis and Breivik 2014), (Tobiszewski and Namieśnik 2012), (Zou, Wang, and Christensen 2015)) and they should not be blindly applied—and used only with caution and only within the context of the area under study ((Lima, Farrington, and Reddy 2005), (Boehm et al. 2018)).

7.2.1.3 Spatial and temporal analysis

Spatial analysis of PAH concentrations or diagnostic ratios can further reveal lateral or vertical trends that can help in distinguishing contamination from background. More importantly, these techniques can help identify PAH concentration gradients or hot spots, either of which could suggest the location of a possible point source of PAHs relative to overall diffuse background conditions. The identification of possible point source locations can be bolstered if the locations happen to correspond to existing or former facilities at which PAH-containing materials were handled or produced. Conversely, if spatial displays of PAH data do not reveal hot spots or concentration gradients associated with a specific point source under investigation, then the contribution of the suspected source should be re-evaluated relative to representative background conditions in the study area.

7.2.1.4 Quantitative source apportionment

Finally, forensic evaluations of PAH datasets using PCA, CMB, or PMF provide bases to evaluate large datasets in an unbiased manner, in ways that are not confounded by the number of candidate sources. PCA is likely the most widely used multivariate analysis to identify the different profiles of the principal components determined, that can then be attributed to specific sources. As an example, the factor score plot produced from a PCA analysis of the 16 priority pollutant PAHs (EPAPAH16) concentrations in 350 sediment samples from an urban river is shown in Figure 7-2 (Stout and Graan 2010). The results revealed variably weathered creosote in some samples, whereas most contained mixtures of weathered creosote and PAHs derived from background.

PCA's factor scores for each sample (Figure 7-2) subsequently can be used to calculate the percent contributions of the major sources that are identified using multiple linear regression ((Larsen and Baker 2003), (Zuo et al. 2007), (Wang et al.

2010)). CMB fits the soil data with pre-defined (known or presumed) PAH source fingerprints (Li, Jang, and Scheff 2003). In contrast, PMF generates candidate PAH source fingerprints, which can then be identified through comparison to known source fingerprints and used to allocate the contributions from each ((Wang et al. 2009), (Stout and Graan 2010)).

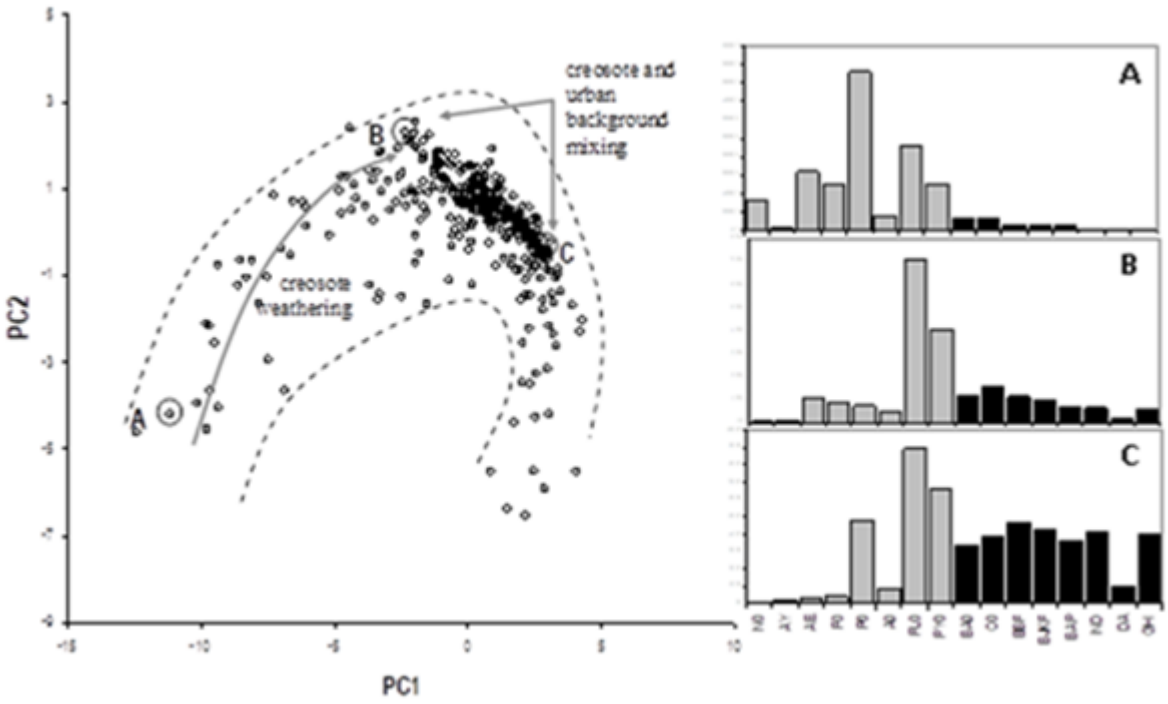


Figure 7-2. Principal component factor score plot. PC1 vs. PC2 (left) showing overall trends among PAHs in 350 sediment samples. Most samples appear as mixtures of weathered creosote and urban (anthropogenic ambient) soil background. PAH profiles for representative samples (A-C) are shown (right).
Source: Reprinted with permission from Stout and Graan (2010). Copyright 2010, American Chemical Society.

7.3 Total Petroleum Hydrocarbons (TPH)

ITRC has developed guidance on TPH and its risk at petroleum-contaminated sites (ITRC 2018). This earlier document provides a thorough assessment of TPH as it relates to petroleum. However, not all hydrocarbons in soils are attributable to petroleum (crude oil, fuels, lubricants, or oil-related wastes). Hydrocarbons in soil can also be derived from natural and anthropogenic ambient soil background sources, as well as from forms of contamination *other* than petroleum, for example, coal tar, creosote, or pitch. Thus, "TPH" is a misnomer since its detection in soils does not necessarily indicate the presence of petroleum. This section specifically focuses on natural and/or anthropogenic ambient background hydrocarbon in soils due to biogenic materials and particulate coal.

7.3.1.1 Applications and limitations of different types of TPH data

The TPH concentration in soil is a method-defined analytical measurement. The applications and limitations of different TPH analyses are described in ITRC (2018) (for example, Table 5-4 and Section 5.9 of ITRC (2018)). TPH concentrations in soils are most frequently determined by solvent extraction followed by gas chromatography with flame ionization detection (GC/FID) per USEPA Method 8015, or comparable chromatographic method (for example, in Canada, (CCME 2007)). This method allows for both the quantification of how much TPH is present in soil and, because of the GC/FID chromatogram produced, an assessment of the boiling range and character of that TPH. Because USEPA Method 8015 measurements are based on the response from the FID, all chromatographable chemicals within a soil sample's extract will be measured. These will include resolved compounds, which appear as peaks on the chromatogram, and unresolved compounds, which appear as "humps" on the chromatogram's baseline. The latter is often referred to as the unresolved complex mixture.

Before measurement of TPH concentrations are made by USEPA Method 8015, the extractable materials in a soil sample are removed via extraction with methylene chloride. In addition to *hydrocarbons*, chemicals containing only hydrogen and carbon atoms, this solvent (and most others) will also remove *non-hydrocarbons*, including polar compounds (containing chemicals with atoms of sulfur, nitrogen, or oxygen) present within the soil.

Naturally occurring organic matter in soils can contain both hydrocarbons and non-hydrocarbons (polars). Their presence in any soil extract will be measured as TPH, and unwittingly considered as contamination rather than background if left unrecognized ((Stout and Uhler 2003), (Wang et al. 2012)). The application of cleanup steps (for example, silica gel cleanup) that separate polar and nonpolar components prior to analysis of TPH is described in Section 5.1 of ITRC (2018).

7.3.1.2 Characterization of background TPH

Biogenic Organic Compounds

The most common naturally occurring organic background material encountered in soils is due to the presence of microbial and vascular (land) plant debris, collectively referred to as *biogenic organic compounds* (BOC) or *naturally occurring materials* (NOM). BOC is used herein. BOC consists of mixtures of biochemicals synthesized by living organisms that undergo modest diagenetic changes during their preservation and accumulation in soils and sediments ((Stout and Uhler 2003), (Wang et al. 2009)). Examples of BOCs include n-alkanes, terpenoids, steroids, fatty acids, alcohols, and esters.

The BOC component within soils containing microbial and plant debris can be significant, particularly in moist, highly vegetated environments where peat or other organic-rich soil accumulates (or had in the past). The following studies address contributions of BOC to TPH measurements: (Dworian (1996), Wang et al. (2012), Stout and Wang (2008)).

Particulate Coal

Although rarer than BOC, some soils may contain naturally occurring TPH associated with the organic compounds derived from coal (or organic-rich shales) that has been eroded from sedimentary rock outcrops. Thus, natural background TPH in soils in certain geologic settings where these precursor rock outcroppings exist must be considered ((Stout and Emsbo-Mattingly 2008), (Achten and Hofmann 2009)). Separately, in regions where coal is mined, used, stored, or transported, decades of operations can distribute particulate coal and coal dust in nearby soils (Hindersmann and Achten 2018). In such areas, coal would be considered as an anthropogenic ambient background material, but perhaps difficult to distinguish from natural background TPH due to coal.

The examples described above underscore the importance of having an experienced analytical chemist review the chromatograms from TPH analyses prior to use of TPH data in risk assessment (ITRC 2018).

7.4 Polychlorinated Biphenyls (PCBs)

Please refer to the USEPA's Polychlorinated Biphenyls (PCBs) website as a resource for technical information pertaining to PCBs.

PCBs are a mixture of chlorinated analogs of the biphenyl molecule. During chemical synthesis, mixtures of PCB molecules are produced that can contain between one and ten chlorine atoms (Figure 7-3), resulting in 209 possible PCB congeners. Each congener differs in terms of the number and position of the chlorines on the biphenyl molecule. PCBs are synthetic organic compounds; there are no natural sources of PCB in the environment.

In the United States, PCBs were manufactured almost exclusively by Monsanto Corporation and marketed under the trade name Aroclor. The production of Aroclors ran from 1929 until 1977, when Monsanto voluntarily terminated production because of environmental concerns about PCBs. The USEPA banned the manufacture of PCBs and began phasing out most uses of PCBs in 1979 (USEPA 1979).

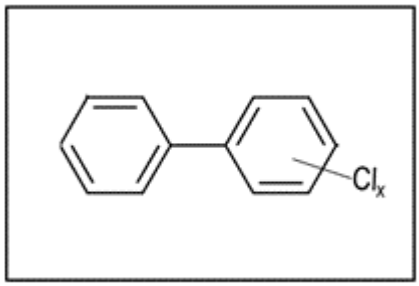


Figure 7-3. General structure for polychlorinated biphenyls. The molecule can contain one to ten chlorine atoms (x), resulting in 209 possible polychlorinated congeners.
Source: A. Uhler, NewFields Companies LLC (unpublished).

The most common Aroclors manufactured by Monsanto were:

- Aroclor 1016

- Aroclor 1242
- Aroclor 1260

- Aroclor 1221
- Aroclor 1248
- Aroclor 1262

- Aroclor 1232
- Aroclor 1254
- Aroclor 1268

The nomenclature used to identify specific Aroclors was the format “Aroclor 12XX,” where the prefix 12 represented the biphenyl molecule (12 carbons), and the second set of digits (XX) represented the approximate percentage of chlorine that composed the Aroclor. For example, Aroclor 1248 is a chlorinated biphenyl mixture containing approximately 48% chlorine. By contrast, Aroclor 1016 was prepared by the fractional distillation of Aroclor 1242, which excluded the higher boiling (more highly chlorinated) congeners (Mayes et al. 1998).

The congener composition of Aroclors has been well studied, and this compositional data can be very useful in forensic evaluation of PCBs in soils. For example, it can be used to determine the compositional feature of PCBs in both background and site-impacted soil samples. Each of the commercial Aroclors contains a distinct distribution of congeners, which varies as a function of total chlorine content (Figure 7-4). The degree of chlorination for the congeners depicted in this figure increases from left to right. These distinctive patterns of congeners (and potential mixtures thereof) form the basis for forensic identification of PCBs in soil samples.

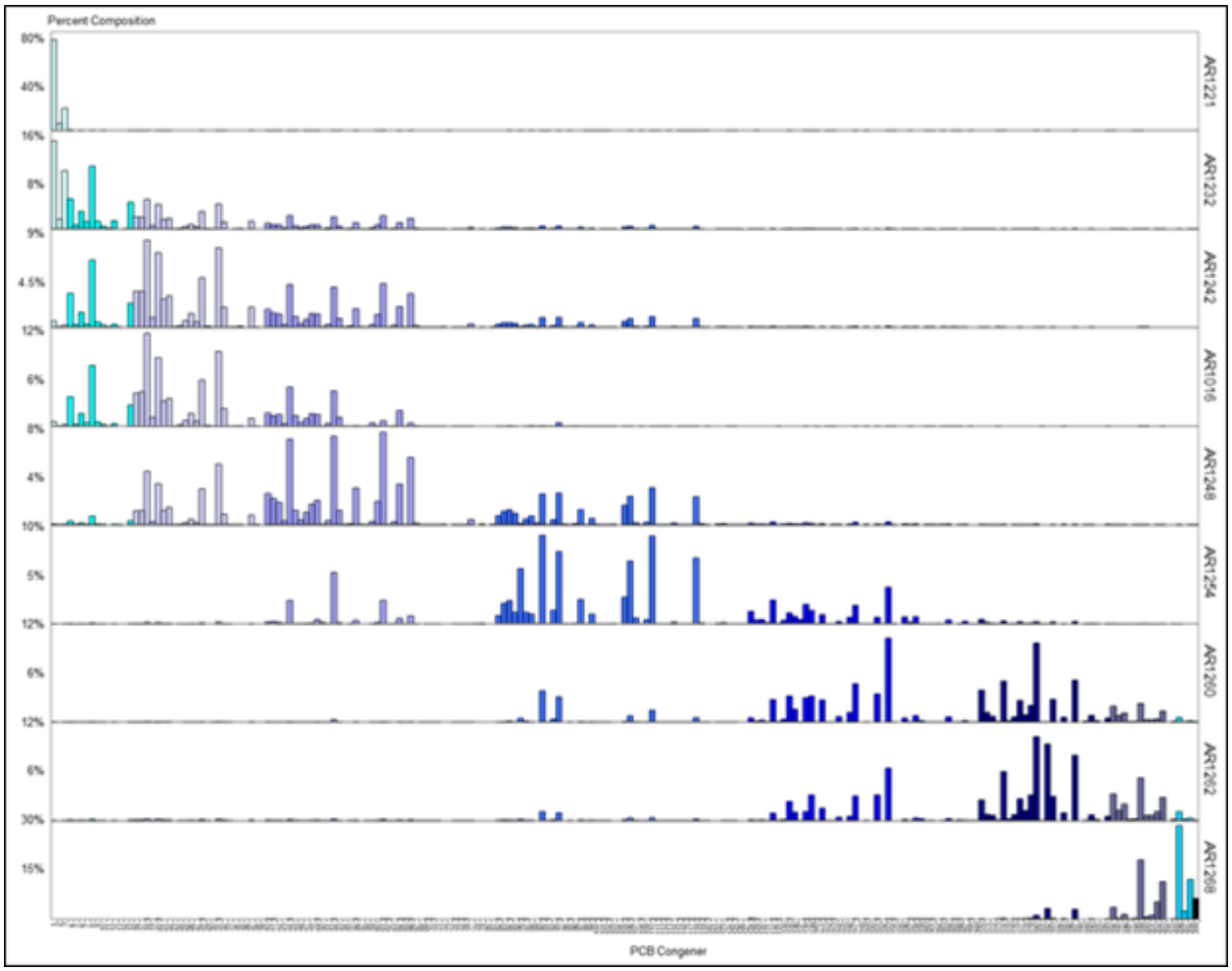


Figure 7-4. The PCB congener distribution for commercial Aroclors. Congener number (and number of chlorines per molecule) and LOC increase from left to right.
Source: A. Uhler, NewFields Companies LLC (unpublished).

Groups of congeners containing the same number of chlorine atoms are referred to as congeners of the same levels of chlorination (LOC). For example, congeners containing one chlorine atom make up LOC1, congeners containing two chlorine atoms make up LOC2, etc., ending with congeners containing 10 chlorine atoms (LOC10). The congeners that make up the various Aroclors are mixtures of differing relative proportions of these LOC (Table 7-2). LOC data are very useful for classifying PCBs measured in soil samples and provide a convenient means to compare the overall PCBs compositional character of background and site-impacted soil samples. This section discussed specific environmental forensics for assessing background in soils. Please refer to USEPA (1979), ATSDR (2000), Douglas et al. (2015), Johnson et al. (2006) for details regarding background information about PCBs that may be helpful for some readers who are not familiar with this information.

Table 7-2. Composition of Aroclors by percent level of chlorination

Source: Scott A. Stout, NewFields Environmental Forensics Practice LLC.

Aroclor	LOC1	LOC2	LOC3	LOC4	LOC5	LOC6	LOC7	LOC8	LOC9	LOC10
1221	97.5	0.69	0.41	0.86	0.21	0.10	0.12	0.05	0.01	0.00
1232	24.0	26.7	26.4	18.5	3.76	0.42	0.16	0.04	0.01	0.00
1242	0.70	13.7	43.4	34.2	7.27	0.66	0.04	0.00	0.00	0.00
1248	0.06	1.40	20.7	55.6	20.2	1.78	0.14	0.03	0.01	0.00
1254	0.02	0.21	0.83	16.1	54.6	25.5	2.71	0.09	0.00	0.00
1260	0.03	0.15	0.40	0.69	9.91	43.6	35.7	8.66	0.82	0.09
1262	0.02	0.34	1.21	1.09	3.44	27.3	45.5	19.3	1.75	0.03
1268	0.00	0.00	0.03	0.09	0.09	0.11	4.89	42.5	45.8	6.46

7.4.1 Forensic analysis of PCBs in soil

Forensic analysis of PCBs in soils, including both those identified as candidate background samples and suspected impacted samples, involves data exploration techniques that combine evaluation of PCB concentrations and PCB pattern analysis. Often, the results of pattern or numerical analyses are paired with geospatial analysis to depict relative geographic locations of samples with similar (or different) PCB compositional patterns.

Evaluation of the distribution of PCB soil concentration data are used to identify subsets of data representative of background and of impacted conditions. The statistical methods to carry out that analysis are described in Section 3 and Section 11 of this guidance. Examples of investigations of background levels of PCBs in soils can be found in ATSDR (2000), Meijer et al. (2003), Creaser et al. (1989), USEPA (2007).

Once candidate background and suspected impacted soil samples are identified, an evaluation of the pattern(s) of PCBs for those classes of samples can be conducted. The steps involved in PCB pattern analysis involve data pretreatment, followed by graphical analysis of diagnostic PCB congener patterns that are descriptive of the composition of the samples, thereby allowing the investigator to describe and contrast the PCB composition of both background and soils suspected of being impacted by PCBs.

Selection of data evaluation methods and/or selection of diagnostic metrics used in forensic analysis is accomplished through critical exploration of the dataset under investigation. The goal of such initial data exploration is to identify compositional characteristics descriptive of the samples and, where the data allow, distinguishing PCB compositional characteristics of background soil samples from those of impacted soils.

7.4.2 Data screening and treatment of nondetects

Effective forensic evaluation of PCB data relies on both the method of chemical analysis used to produce the data and the inherent quality of the dataset. In theory, the PCB congener-specific data produced from USEPA Method 1668 provides more PCB compositional information than the less data-rich USEPA Method 8082 or simple Aroclor-only data produced by USEPA Method 8080. However, the underlying quality of data often dictates how reliable a dataset will be for forensic analysis. The data user is cautioned to carefully screen data quality prior to use in forensic evaluations. The most common systematic problems with PCB datasets are elevated detection limits (for congeners, LOC results, or Aroclor concentrations) and significant co-elution of congener peaks, which can lead to difficulty in interpreting the patterns of PCB congeners, and/or introduces significant biases in numerical analysis of PCB LOC or congener data.

Elevated detection limits that are the result of laboratory artifacts or simply very low PCB concentrations in certain samples can lead to a significant number of nondetects for reported congener or LOC data. Replacing the nondetected values with either the detection limit or one-half the detection limit is a common data preprocessing approach and will standardize the influence of nondetects in multivariate data analysis. However, if certain samples contain a large number of nondetected results, the congener results will be dominated by the substituted detection limit values. Data users should conduct sensitivity analysis to identify and exclude samples where the nondetects bias or skew the results of subsequent forensic analysis of PCB congener patterns. In multivariate analysis or diagnostic ratio analysis, samples biased by detection limit substitutions are usually clearly evident and graphically cluster together, remote from samples based upon reliable congener or LOC data.

Combining PCB data from different sources or from different analytical methods can lead to significant biases in the combined dataset. For example, gas chromatographic traces of PCBs developed by USEPA SW-846 Method 8080 or Method 8082 can vary significantly in resolution, and thus quality, from laboratory to laboratory. Such differences in chromatographic quality can make compositional comparisons problematic. Total PCB concentrations can vary significantly for the same samples analyzed using different analytical methods because of “double counting” of overlapping chromatographic peaks that can occur in traditional Aroclor analysis—a phenomenon that does not affect high-resolution congener analysis data (Wischkaemper et al. 2013). Similarly, congener data produced using the lower resolution USEPA SW-846 Method 8082 can be significantly affected by co-elution interferences compared to congener data produced using the high-resolution USEPA Method 1668. This can lead to apparent congener compositional differences among samples that are actually nothing more than artifacts caused by congener co-elution.

In summary, it is incumbent upon the environmental professional evaluating PCB data to carefully review data for uniformity in reporting limits and resolution quality of PCB congener and/or LOC data prior to conducting forensic evaluation of PCB data. Based on that review, the geochemist can eliminate low quality data or take other remedial pre-evaluation steps (for example, combining potential co-eluting congener data into congener data pairs) prior to conducting forensic evaluation.

7.4.3 Forensic PCB compositional pattern analysis techniques

There are numerous techniques for evaluating the PCB composition of background and impacted soils that range from simple (for example, Aroclor identification) to complex (for example, multivariate data analysis). As the degree of complexity of the analysis increases, more subtle distinctions are recognized regarding the PCB composition among background samples or between background and impacted samples. The goals of such forensic evaluations are to (a) describe the background soils; (b) identify potential compositional outliers in background soil datasets; and (c) catalog the compositional features of impacted site soils, and contrast such features with those of the background dataset.

- Aroclor identification. The simplest—and lowest resolution—PCB data evaluation method is based on laboratory-supplied Aroclor identification, which is the most basic output from PCB analytical results such as USEPA Method 8080 or USEPA Method 8082. In this approach, the PCB characteristics of soil samples are simply organized by Aroclor type. Figure 7-5 is an example of how to evaluate such data. In this figure, Aroclor identification data are binned by concentration, and the Aroclor character of the candidate background and potentially impacted soil samples can be evaluated.
- Level of chlorination histograms and cross-plots. Small datasets are amenable to straightforward comparisons of histograms of the relative LOC among samples from data developed from USEPA Method 8082 or USEPA Method 1668. LOC concentration data for samples are normalized and plotted in histogram form from LOC1 through LOC10. Figure 7-6 illustrates that qualitative similarities or differences in LOC composition among samples can be readily observed using this method. In this figure, the average LOC was calculated and used as a descriptive statistic to compare background soil sample data to potentially impacted soil samples.

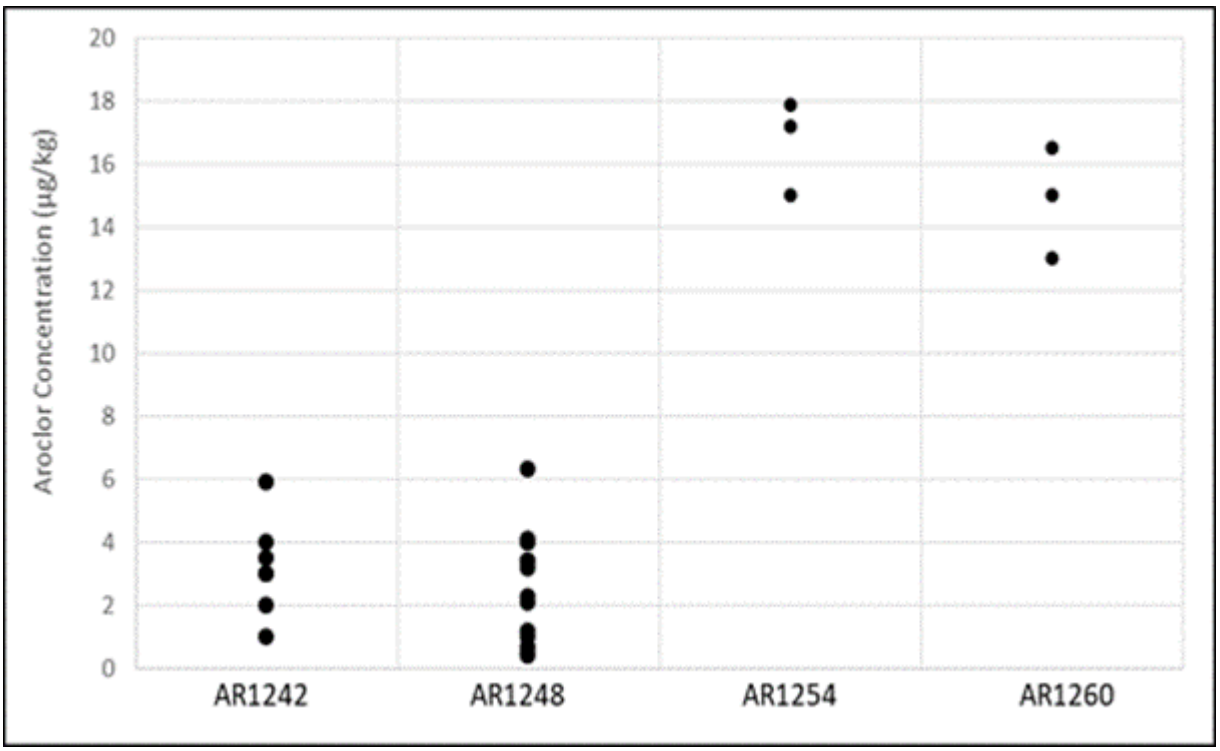


Figure 7-5. Candidate background soil samples organized by Aroclor type and concentration. Sixty-five percent of the samples have Aroclor concentrations less than 7 µg/kg and contained either Aroclor 1242 or Aroclor 1248. Higher concentration (>12 µg/kg) soil samples contained higher molecular weight Aroclor 1254 and Aroclor 1260, suggesting potential point source impacts.
Source: A. Uhler, NewFields Companies LLC (unpublished).

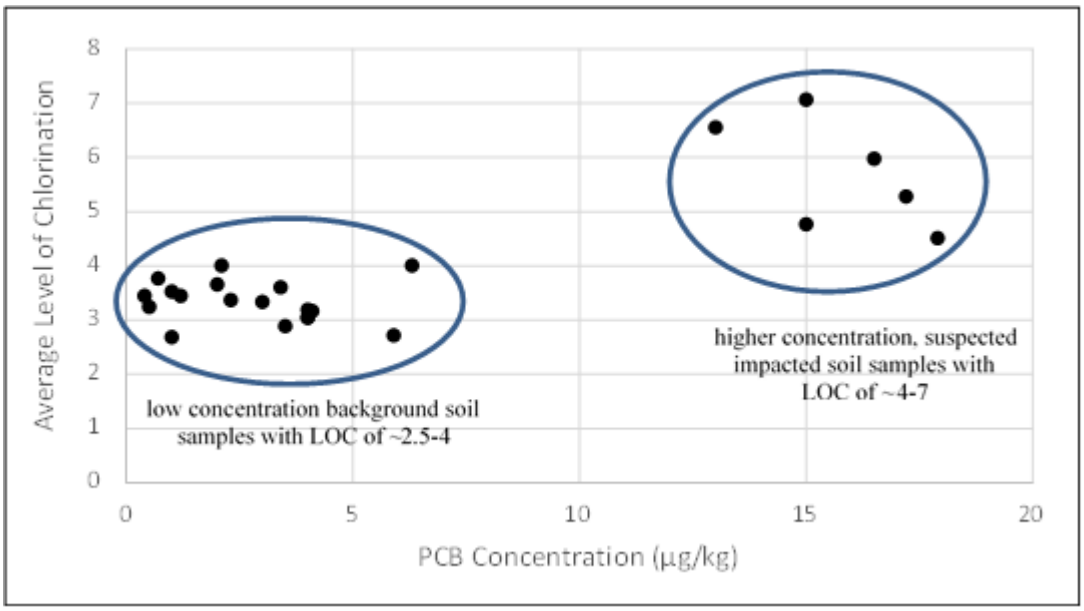


Figure 7-6. Low PCB concentration background soil samples have a lower LOC composition than suspected impacted site soil samples.
Source: A. Uhler, NewFields Companies LLC (unpublished).

- PCB congener histograms. Similar to LOC histograms, PCB congener composition histograms provide a graphical depiction of the PCB composition of samples. Histograms analogous to those shown in Figure 7-4 can be prepared for all samples, showing the relative PCB congener concentrations in congener number order by increasing LOC (Douglas et al. 2007). Qualitative PCB compositional characteristics of background and potentially impacted soil samples can be observed and categorized using this technique.
- Multivariate numerical analysis of LOC and PCB congener datasets. PCB datasets containing LOC or congener data are amenable to a variety of numerical data analysis techniques that provide a means to categorize PCB

compositional data using multivariate techniques. An excellent review of multivariate data analysis methods for forensic evaluation is provided by Johnson et al. (2007). Examples of multivariate data analysis techniques available to the investigator include:

- Principal component analysis (PCA). A mathematical method used to reduce the dimensionality of large datasets by transforming a large set of variables into a smaller one that still contains the majority of the information of the original data (Bro and Smilde 2014). PCA transforms a number of (possibly) correlated variables into a (smaller) number of uncorrelated variables called principal components. The principal components are rank-ordered by the amount of variance in the data they explain. Principal components represent the directions of the data that explain a maximal amount of variance among the data. Factor scores plots are visual projects of the principal component analysis. Factor scores that plot close to one another share similar chemical variability; sample scores that plot distant have different chemical variability (composition). Compositional characteristics of samples can be inferred from the factor scores and corresponding component loading charts.
- Polytopic vector analysis (PVA). A statistical pattern recognition technique that allows determination of compositional end-members and proportions of end-members found among samples (Noémi, Goovaerts, and Adriaens 2004). The PVA method generates three basic parameters: 1) the number of end-members (sources), 2) the composition of each end-member (signature of each source), and 3) the relative proportions of each end-member (source) in every sample.
- Soft independent modeling of class analogy (SIMCA). PCA is performed on a reference dataset, and reference class characteristics are identified. Unknown samples are then analyzed and compared to the reference data and classified according to best fits to the reference data, or mixtures thereof (Dunn, Stalling, and Wold 1984).

The advantages of these multivariate numerical methods are that they provide a convenient means to analyze large datasets and reduce the output into relatively straightforward graphical output that can then be interpreted, such as for identifying the compositional features of background soil samples and comparing those chemical signatures to potentially impacted soil samples.

7.5 Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans (PCDD/F)

Please refer to the USEPA Dioxin website as a resource for technical information pertaining to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs).

PCDD/Fs are complex mixtures of chlorinated congeners of two benzene rings connected by either one or two oxygen molecules (PCDFs and PCDDs, respectively). These molecules can contain one to eight chlorine atoms (Figure 7-7). Arrangement of the one to eight chlorine atoms around each molecule yields 75 possible PCDDs congeners and 135 possible congeners of PCDF (Shields et al. 2006).

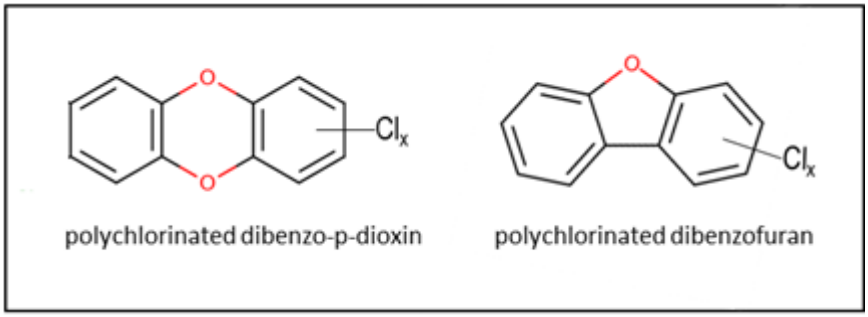


Figure 7-7. Generalized structures for polychlorinated dibenzo-p-dioxins and dibenzofurans. The number of chlorine atoms (x) can range from one to eight.

Source: A. Uhler, NewFields Companies LLC (unpublished).

Of the 210 possible congeners of PCDD and PCDF, 17 are commonly measured in environmental investigations, along with the summed total of the congeners of the same level of chlorination for the tetra- through hepta-chlorinated compounds (Table 7-3). The USEPA recommends the use of the consensus toxicity equivalency factor (TEF) values for 2,3,7,8-tetrachlorodibenzo-p-dioxin and dioxin like compounds published in 2005 by the World Health Organization (USEPA 2021). The concentration of the 17 PCDD/Fs congeners is commonly converted to a 2,3,7,8-TCDD (“dioxin”) toxicity equivalent (2,3,7,8-TCDD TEQ) by multiplying each of the 17 congener concentrations by a congener-specific TEF, which is a fraction of

the measured toxicity of 2,3,7,8-TCDD, the most toxic of the 17 PCDD/F congeners. The individual results of this transformation are then summed to form the 2,3,7,8-TCDD TEQ and used to facilitate risk assessment of exposure to the mixture of multiple PCDD/Fs. The TEFs listed in Table 7-3 are those published by the World Health Organization (2005). Among the benefits of converting raw dioxin concentration data to TEQ is the ability to compare measured TEQ concentrations with published benchmarks for media, including soil. This section discusses specific environmental forensics for assessing background in soils. Please refer to USEPA (2003) and Shields et al. (2006) for details regarding background knowledge about PCDD/F that may be helpful for some readers who are not familiar with this information.

Table 7-3. Most commonly reported PCDD and PCDF congeners

Source: (Van den Berg et al. 2006).

Analyte	Toxicity Equivalency Factor (TEF)
Dioxin congeners	
2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0003
Furan congeners	
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.03
2,3,4,7,8-PeCDF	0.3
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1

2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.0003
Level of chlorination-sums	
Total tetrachlorodibenzo-p-dioxin (TCDD)	N/A
Total pentachlorodibenzo-p-dioxin (PeCDD)	N/A
Total hexachlorodibenzo-p-dioxin (HxCDD)	N/A
Total heptachlorodibenzo-p-dioxin (HpCDD)	N/A
Total tetrachlorodibenzofuran (TCDF)	N/A
Total pentachlorodibenzofuran (PeCDF)	N/A
Total hexachlorodibenzofuran (HxCDF)	N/A
Total heptachlorodibenzofuran (HpCDF)	N/A

7.5.1 Data screening and treatment of nondetects

Prior to forensic analysis, raw PCDD/F analytical data should be carefully screened to identify and censor data that are inaccurate or biased. This screening includes both candidate background and site investigation data. Data users should evaluate and exclude data that suffer from elevated detection limits; contain laboratory flags indicating that data may be affected by field or laboratory blank interferences, matrix interferences, or instrument detection limitations (detector saturation); or lack acceptable mass spectrometer second ion confirmation for reported PCDD/F congeners. Useful data quality assessment guidelines for PCDD/F analytical data are provided in the USEPA *National Functional Guidelines for High Resolution Superfund Methods Data Review* (USEPA 2016).

Many PCDD/F datasets contain nondetect results. Nondetects can be handled in a number of ways. Replacing the nondetect with either the detection limit or one-half the detection limit is a common approach and will standardize the influence of nondetects in subsequent data treatment (Shields et al. 2006). However, as the total PCDD/F concentration in a sample approaches the detection limit, a greater proportion of a sample's PCDD/F composition will be accounted for by nondetects, and the transformed PCDD/F congener results will be dominated by the substituted detection limit values. Data users should conduct sensitivity analysis to identify and exclude samples where the nondetects bias or skew the results of subsequent forensic analysis of PCDD/F congener patterns. In multivariate analysis or diagnostic ratio analysis, samples biased by detection limit substitutions are usually clearly evident and graphically cluster together, remote from samples based upon reliable PCDD/F data.

7.5.2 Forensic data analysis of PCDD/F in soil

Forensic analysis of PCDD/F in soils, including both those identified as candidate background samples and suspected impacted samples, involves data exploration techniques that combine evaluation of PCDD/F concentration and PCDD/F pattern analysis. Often, the results of diagnostic numerical analyses are paired with geospatial analysis to depict relative geographic locations of samples with similar (or different) PCDD/F compositional patterns.

Evaluation of the distribution of PCDD/F soil concentration data is used to identify subsets of data representative of background and of impacted conditions. The statistical methods to carry out that analysis are described elsewhere in this guidance. An excellent compilation of background investigations of PCDD/F in soil can be found in USEPA (2003).

Once candidate background and suspected impacted soil samples are identified, an evaluation of the pattern(s) of PCDD/F isomers for those classes of samples can be conducted. The steps involved in PCDD/F pattern analysis involve data pretreatment, followed by graphical analysis of diagnostic PCDD/F congener patterns that are descriptive of the composition of the samples, thereby allowing the investigator to describe and contrast the PCDD/F composition of both background and soils suspected of being impacted by PCDD/F. Selection of data evaluation methods and/or selection of diagnostic metrics used in forensic analysis is accomplished through critical exploration of the dataset under investigation. The goal of such initial data exploration is to identify compositional characteristics descriptive of the samples and, where the data allow, to distinguish PCDD/F compositional characteristics of background soil samples from those of impacted soils. Refer to USEPA (2003) and USEPA (2006) for information pertaining to PCDD/F patterns for background soils and for documented PCDD/F sources, respectively.

PCDD/F patterns based on congener concentration data alone can be used for initial data exploration of candidate background soil samples and suspected impacted soil samples to evaluate obvious chemical patterns that describe and/or distinguish certain samples or groups of samples. Depiction of PCDD/F congener concentration data in basic graphical format such as bar charts or radar plots allows the investigator to quickly evaluate key PCDD/F compositional features of samples. Examples of such bar charts include those shown in Figure 7-8.

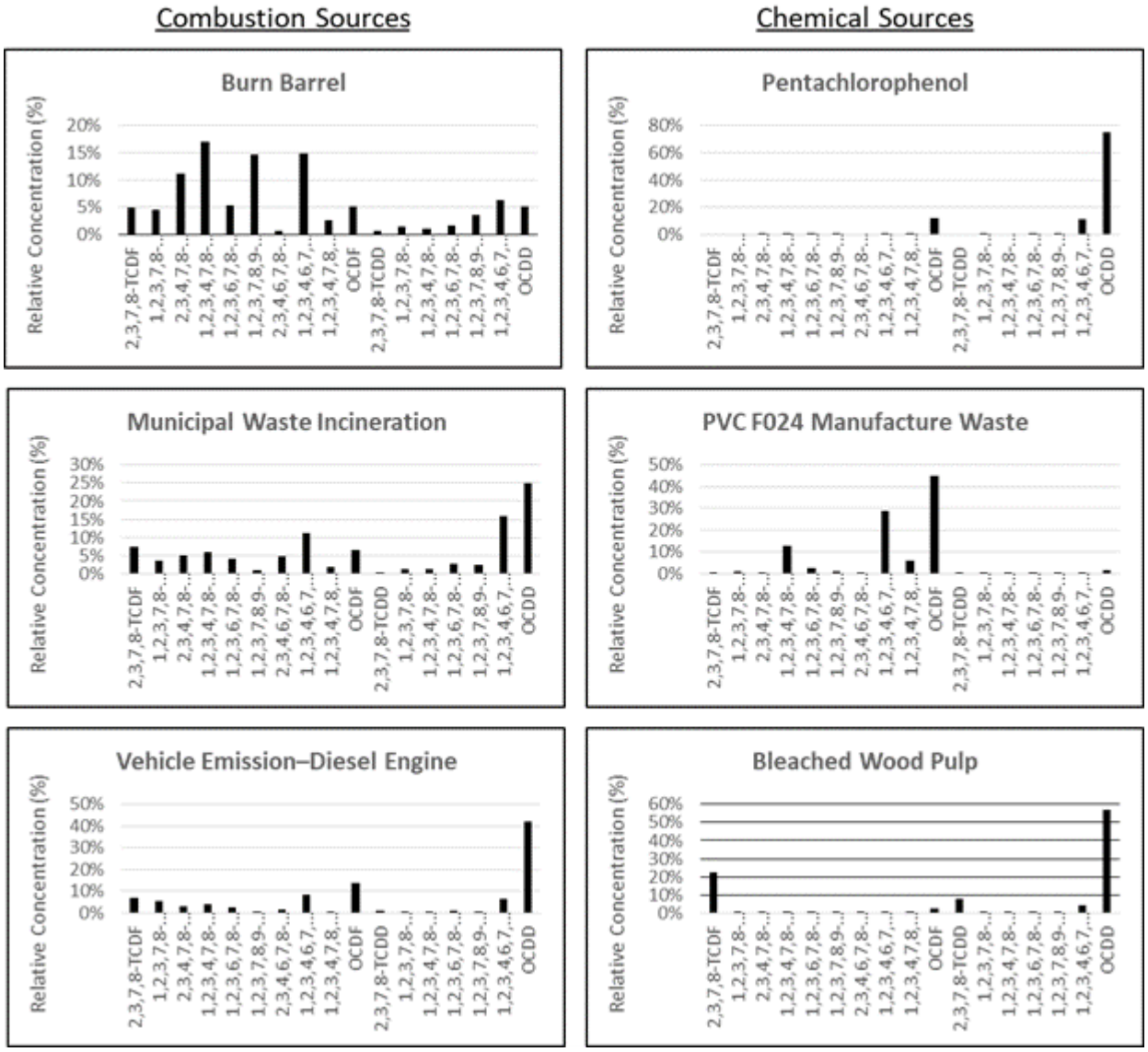


Figure 7-8. Examples of combustion and chemically produced PCDD/F congener distributions.
Source: (USEPA 2006).

Soil data from PCDD/F investigations often contain samples of highly varied total concentration. In addition, the relative concentration of PCDD/F congeners within a sample can vary by several orders of magnitude. Both total concentration and disparity in relative PCDD/F congener concentration can lead to significant biases during data analysis. Hence, forensic evaluation of PCDD/F compositional features benefits from pretreatment of the data prior to exploratory analysis.

Data normalization helps attenuate the effect of these potential concentration-driven biases. Shields et al. (2006) describes a number of data pretreatment steps that are useful for forensic evaluation of PCDD/F patterns and are applicable to evaluation of data related to soil samples. These include:

- Sum standardization. The concentration for each of the commonly reported 17 PCDD/F congeners is divided by the sum total concentration of the 17 congeners and multiplied by 100. This normalizes the relative PCDD/F concentrations on a scale of 0–100 for all samples, eliminating any concentration bias that may be introduced into compositional analysis. This approach does not adjust for significant differences in relative concentration among congeners, and the user must be aware of the limitations of this approach for certain types of data analysis—for example, correlation analysis.
- Relative homologue standardization. The concentrations of the commonly reported 17 individual PCDD/F congeners are divided by the respective total homologue concentration and multiplied by 100. This approach attenuates some differences in relative concentration among PCDD/F congeners. It is a useful data processing step for initial analysis of the data using certain multivariate data analysis techniques such as PCA or hierarchical cluster analysis, the latter of which identifies structure (similarity) among groups of samples within a dataset (McKillup 2012).

- Relative TEQ standardization. The concentrations of the commonly reported 17 individual PCDD/F isomers are multiplied by the congener's respective TEF. This approach has the benefit of attenuating the dominance of relatively high PCDD/F congeners such as OCDD, OCDF, and other higher chlorinated congeners, yielding datasets that are reasonably well scaled and amenable to a variety of graphical and numerical analyses.
- Total homologue standardization. The concentration of each homologue class (for example, total tetrachlorodioxin isomers, TCDD) is divided by the sum of all homologue classes and multiplied by 100. Shields et al. (2006) reported that this approach reveals gross differences in PCDD/F composition. The technique is applicable for basic graphical analysis (for example, bar plots) and useful for comparing PCDD/F composition among samples.

Evaluating the compositional features of PCDD/F in soil can be accomplished by a number of approaches, ranging from basic to more complex:

- Graphical (PCDD/F isomer distribution) analysis. The most straightforward approach for evaluating PCDD/F compositional features for soil samples is through basic PCDD/F pattern analysis of PCDD/F composition using bar plots or star plots (Shields et al. 2006). Transformed data, using one of the techniques described above, yields PCDD/F compositional depictions that can be compared among samples. This technique is often useful for small datasets where the investigator is not encumbered by the need to inter-compare a large number of compositional plots.
- Diagnostic ratios. The composition of PCDD/F isomers arising from many types of both combustion and chemical sources often has distinct proportions of PCDD/F isomers, which lend themselves to diagnostic ratio analysis. This analysis involves cross-plotting diagnostic ratio pairs, or a single diagnostic ratio versus total PCDD/F concentration. In such cross-plots, samples of similar source character share similar Cartesian space, while samples containing PCDD/F of different chemical character plot remote from the otherwise similar samples ((Horstmann, McLachlan, and Reissinger 1993), (Townsend 1983)).
- Multivariate analyses. Mathematical, multivariate methods can be used to identify samples that contain PCDD/F with similar (or different) PCDD/F compositional patterns. A variety of multivariate techniques are available to the investigator and include principal components analysis (PCA), hierarchical cluster analysis, and other receptor-based models (Johnson et al. 2007). These methods are particularly well suited to large sample datasets, where otherwise simpler methods of analysis—for example, comparison of histograms—would be too unwieldy and time-consuming.

The goal of PCDD/F forensic analysis—regardless of the data analysis method used—is to identify the pattern(s) of PCDD/F isomers that are embodied by the statistically identified group of samples that is emblematic of background. The characteristic pattern or range of patterns assigned to background conditions can then be compared to samples suspected of being impacted by site-related PCDD/F. Differences in the chemical patterns between background and impacted samples lend insight into the nature and geographic extent of suspected PCDD/F impacts. An example comparing the PCDD/F compositional pattern for off-site background soil samples to PCDD/F impacted site soil samples is shown in Figure 7-9.

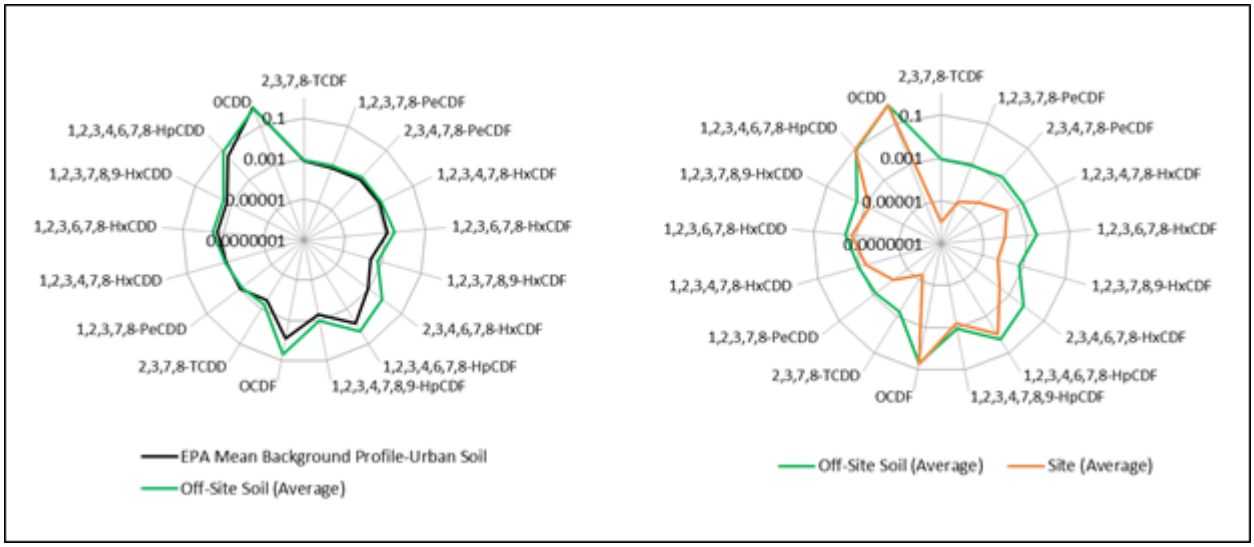


Figure 7-9. Sum-standardized star plots showing comparison of PCDD/F pattern for off-site background soil samples with the average PCDD/F pattern for impacted soils. The plot on the left shows the PCDD/F pattern for

off-site background soil samples that compare favorably with the pattern for USEPA mean urban background soil, while the plot on the right shows that the average PCDD/F pattern for impacted soils from the related industrial site exhibits a clearly different PCDD/F pattern compared to background.
Source: A. Uhler (unpublished).

7.6 Perfluoroalkyl Substances (PFAS)

Per- and polyfluoroalkyl substances (PFAS) are synthetic fluorinated aliphatic compounds. They are more water-soluble than other classes of contaminants, such as PAHs and PCBs, and are therefore most commonly recognized as groundwater contaminants. However, some of the PFAS released to the environment will adsorb to solids, and PFAS are found in soils, which can act as a reservoir for groundwater contamination. A detailed discussion of the PFAS sources, physiochemical properties, environmental fate and transport, regulations, site characterization methods, sampling and analysis considerations, and treatment technologies is presented in the ITRC *PFAS Technical and Regulatory Guidance Document* (ITRC 2021). This section focuses on the measurement, data handling, and data analysis techniques that are relevant to forensic analysis of PFAS substances in background and site-impacted soils.

7.6.1 PFAS uses

The unique properties of PFAS have allowed them to find use in many different industrial and consumer applications. For example, PFAS are:

- key components of Class B fluorine-containing firefighting foams, including aqueous film forming foam (AFFF), fluoroprotein (FP), and film-forming fluoroprotein foam (FFFP)
- used as stain- and water-resistant coatings and treatments for textiles and leather
- used to treat paper products for packaging or serving food
- used in metal plating and etching, as they can maintain their efficacy under the high temperatures and acidic conditions
- used in wire manufacturing to coat wires and cables
- used to manufacture semiconductors in the photolithography process
- used in manufacturing, as industrial surfactants, to manufacture plastics and fluoropolymers, as mold release coatings, or in other applications
- used in consumer products, including as nonstick surfaces in cookware; to treat carpets or automotive upholstery; in outdoor textiles and sporting equipment; in cleaning agents and fabric softeners; in polishes and waxes; in medical products; in varnishes, dyes, and inks; and in personal care products such as shampoo, hair conditioner, sunscreen, cosmetics, toothpaste, and dental floss

In some cases, PFAS materials may be directly discharged to the environment (for example, as with firefighting with AFFF or atmospheric releases from manufacturing facilities). Given the range of industrial and consumer uses of PFAS materials, PFAS is also common in various waste streams; wastewater treatment plants and landfills are common sources of PFAS to the environment. For a more detailed description of the history and use of PFAS, see the ITRC's fact sheet entitled *History and Use of Per- and Polyfluoroalkyl Substances (PFAS)* (ITRC 2020) and Section 2.5 of the ITRC's online *PFAS Technical and Regulatory Guidance Document (ITRC 2021)*. This section discusses specific environmental forensics for assessing background in soils. Please refer to the ITRC fact sheet entitled *Naming Conventions and Physical and Chemical Properties of Per- and Polyfluoroalkyl Substances (PFAS)* (ITRC 2020) as well as Buck et al. (2011) or additional information regarding background knowledge about PFAS that may be helpful for some readers who are not familiar with this information.

7.6.2 Forensic PFAS compositional pattern analysis techniques

The field of PFAS forensics is in its nascent stages. The understanding of the concentrations of target PFAS or forensic signatures associated with source materials is evolving. Research is being conducted to understand fate and transport in the environment and to evaluate tools to investigate changes in PFAS composition for the purposes of source attribution. The reader is referred to Brusseau, Anderson, and Guo (2020) and Rauert et al. (2018) as examples of investigations pertinent to findings of PFAS in soils.

Benotti et al. (2020) have suggested a tiered approach for characterizing the PFAS signatures associated with source materials and have suggested that some or all aspects of this approach may be useful when evaluating PFAS contamination in soil or water samples. However, until a library of source materials is available, and until researchers understand the full scope of forensic information that may help elucidate source, the best approach for associating or dissociating environmental contamination from one or more sources is to compare PFAS information in a soil or water sample to similar

information from the site-specific source area/s. Information on PFAS forensics is provided in Section 10.5 of the ITRC's online *PFAS Technical and Regulatory Guidance Document (ITRC 2021)*.

7.7 Remote Sensing

7.7.1 Overview

Remote sensing isn't a single tool, but a collection of tools that can detect properties of materials without direct contact. The ones of primary interest to background evaluations are satellite imagery, aerial photography, optical or electromagnetic spectrum techniques, such as optical sensing with specific bands (for example, SPOT, ASTER, Landsat), optical sensing based on hyperspectral imaging (based on 100 or more contiguous spectral bands), and optical sensing using the thermal infrared band. For determining suitable background reference areas, the most useful remote sensing tools are historical imagery and delineation of contaminated soils by correlating soil attributes with spectral features across a range of spectral bands.

Remote sensing can include radar, satellite imagery, geographical information systems, sonar, imaging through spectral bands, and light detection and ranging (lidar). For a given material, the amount of solar radiation that is reflected, absorbed, transmitted, and emitted varies with wavelength. When this radiation or electromagnetic energy is plotted over a range of wavelengths, the resulting curve is called the material's spectral signature. Multispectral imaging, based on several spectral signatures, and image classification can be used to generate thematic maps. More information regarding remote sensing and sensors can be found in these references: ((ITRC 2019), (Gholizadeh et al. 2018), (Slonecker and Fisher 2014), (Singh 2016)).

7.7.2 Items to consider

The reflected or emitted radiation values observed by remote sensing tools are products of geophysical properties and conditions at or near the earth's surface (or shallow subsurface). Certain spectral signatures can be interpreted with multiple explanations and multiple metals and contaminants at a site can result in overlapping signatures that can be complex to sort out. It is important to have ground truthing of remote sensing data for proper interpretation.

Scale needs to be considered. For example, spatial resolution can vary from the millimeter scale (drone-based cameras) to meters (SPOT and Landsat) or greater, so the appropriate data source must be chosen to meet the needs of the project at hand. Remote sensing data are often in a raster format and the size of the pixels must be compared to the needs of the project. Modern advances, such as deploying remote sensing equipment with unmanned aerial vehicles (drones), may be helpful for smaller scale projects.

Satellite remote sensing data with lower spectral resolution may be inappropriate. Hyper- and super-spectral satellite sensors have recently been developed and may provide better tools for environmental data.

Remote sensing based on spectral reflectance techniques requires exposure to soils, so areas with extensive pavement or tarmac may not profit from these tools, unless the goal is to delineate extent of pavement or roads. The presence of vegetation may also impede the use of spectral reflectance techniques.

7.7.3 Application

Although there is no published research on using remote sensing techniques for establishing background concentrations or risk assessments, remote sensing is a tool that could be very helpful in assisting with such assessments, such as evaluating whether an area should be considered as background. An important use of remote sensing in establishing background concentrations is for examining images of the selected background reference area in the past. Historical satellite imagery and aerial photographs can be used to identify areas that currently appear barren or untouched by human activity but that historically were subject to activities that could have affected background concentrations in soil (for example, areas surrounding a closed or abandoned mine). This can occur both in a range of areas where vegetation growth is quick and broadly dispersed to areas that have remained undeveloped once historical structures were removed.

Remote sensing has been used for many years for evaluating spatial distribution of soil properties, such as soil texture and soil moisture, and for mineral exploration, but its use for environmental investigations has been sparse. Its strength is to provide spatial information over large areas.

The ability of remote sensing to delineate the spatial distribution of metals or other contaminants would help determine whether the concentrations at a site are locally restrictive, hence site-related, or extensive and more than likely background. The spatial relationship of potential contaminants, such as metals and PAHs in soil, can be useful in improving risk management.

Arsenic contamination in soils can be mapped by relating the reflectance spectrum of plants with arsenic content in soils and mapping those spectra (Asmaryan et al. 2014). Arsenic in soil can be predicted from hyperspectral imaging (Wei et al. 2020). Remote sensing is a fast-evolving field and may have greater use in the future for determination of chemical concentrations.