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Dioxins and Furans

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The term “dioxins” refers to chlorinated dibenzo-*p*-dioxins (CDDs) and “furans” to chlorinated dibenzofurans (CDFs). Sometimes “dioxin” also refers to the most studied and toxic of the dioxins, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). CDD/CDFs are not created intentionally, but are produced inadvertently by a number of human activities including chemical manufacturing and incomplete combustion, as well as by natural processes such as forest fires and volcanoes.

CDD/CDFs are among the most studied chemicals in terms of their formation processes, environmental occurrence, and toxicity. Chemical fingerprinting studies have been published for the purposes of identifying potential sources of CDD/CDFs in air, soil, sediments, water, and tissue samples.

In this chapter, the physical and chemical properties of CDD/CDFs and the toxicity equivalent (TEQ) methods are reviewed. We describe the historical development of analytical methods and present some of the pitfalls of using historical data in chemical fingerprinting. We provide an overview of the natural and anthropogenic sources of CDD/CDFs then outline the general approaches used in forensic studies illustrated with two case studies.

14.1 PHYSICAL AND CHEMICAL PROPERTIES

CDDs and CDFs have a triple-ring structure that consists of two benzene rings connected by either one or two oxygens (CDFs and CDDs respectively). For CDDs, the benzene rings are connected by two oxygen atoms; CDFs are connected by one (Figure 14.1.1). These molecules have eight possible positions where substitution by a halogen such as chlorine can occur. Of environmental interest are the CDD/CDFs with four or more chlorines and specifically, those molecules with chlorine atoms on the 2,3,7, and 8 ring positions because of their toxicity. CDD/CDF homologues refer to compounds with the same number of chlorine atoms, regardless of position. For example, as shown in Table 14.1.1, there are 22 possible tetrachlorodibenzo-*p*-dioxin (TCDD) compounds or homologues. Only one of these, the 2,3,7,8-TCDD isomer, is considered toxic. The term “congener” refers to any individual CDD/CDF compound, regardless of homologue class. There are 75 possible congeners of CDDs and 135 possible CDF congeners.

CDD/CDFs are strongly lipophilic with very low water solubility. They have similar physical and chemical properties and are typically found as complex mixtures. They are primarily associated with particles and organic matter in the water column and with organic matter in soils and sediments. Once sorbed to soil, CDD/CDFs exhibit little potential for significant leaching or volatilization. In the atmosphere, CDD/CDFs partition between the particles and the gas phase, with higher vapor pressure congeners (i.e., the less chlorinated congeners) found to a greater extent in the gas phase. CDD/CDFs are very stable compounds under most environmental conditions, with the exception of atmospheric photooxidation and photolysis of nonsorbed species in the gaseous phase or at the soil or water–air interface.

CDD/CDF concentrations are often expressed as 2,3,7,8-TCDD TEQ concentrations by multiplying the concentration of each of the 17 2,3,7,8-substituted congeners by its respective toxicity equivalent factor (TEF) as shown in Table 14.1.2. Studies conducted in the 1990s, and even some current laboratory studies, use the so-called “international toxicity equivalent factors” (I-TEFs) adopted by the US Environmental Protection Agency (EPA) in 1989 (US EPA, 1989) to calculate TEQs (designated as I-TEQs). In 1998, the TEFs were revised by a consensus scientific committee sponsored by the World Health Organization (WHO). These TEFs (van den Berg *et al.*, 1998) are recommended by US EPA, (2003) and the resultant TEQs are termed “WHO-TEQs” in this chapter. For a comprehensive review of the literature on the environmental chemistry of CDD/CDFs, the reader is referred to a 2003 draft publication by EPA titled *Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) and Related Compounds*.

14.2 ANALYTICAL METHODS

When measuring CDD/CDFs, the motion of the field of analytical determinations has not been a linear succession of simple steps so much as it has been, and continues to be, a stimulating evolution (Buser, 1991). Initially, exposure-focused interests centered on a single molecule, 2,3,7,8-TCDD, as did the measurement techniques. Over the years, as an appreciation for the significant role played by other compounds developed, a shift in the scope of the analytical methodologies occurred to include dioxin-like

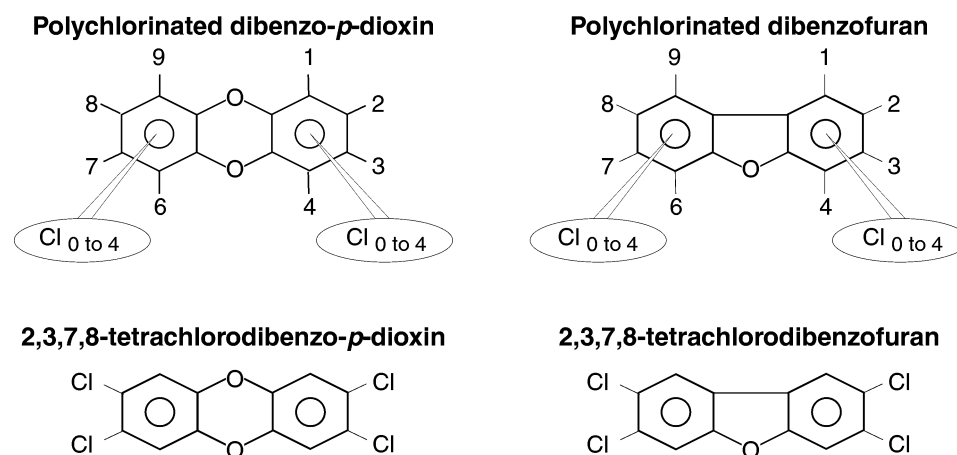


Figure 14.1.1 Molecular structure and numbering system of polychlorinated dibenzo-*p*-dioxins and dibenzofurans.

Table 14.1.1 Homologue Classes of CDD/CDFs

Homologue Class	Abbreviation	Chlorines	Number of Congeners
Polychlorinated Dibenzo- <i>p</i> -dioxins (CDDs)			
Monochlorodibenzo- <i>p</i> -dioxin	MCDD	1	2
Dichlorodibenzo- <i>p</i> -dioxins	DCDD	2	10
Trichlorodibenzo- <i>p</i> -dioxins	TrCDD	3	14
Tetrachlorodibenzo- <i>p</i> -dioxins	TCDD	4	22
Pentachlorodibenzo- <i>p</i> -dioxins	PeCDD	5	14
Hexachlorodibenzo- <i>p</i> -dioxins	HxCDD	6	10
Heptachlorodibenzo- <i>p</i> -dioxins	HpCDD	7	2
Octachlorodibenzo- <i>p</i> -dioxin	OCDD	8	1
			75
Polychlorinated Dibenzofurans (CDFs)			
Monochlorodibenzofuran	MCDF	1	4
Dichlorodibenzofurans	DCDF	2	16
Trichlorodibenzofurans	TrCDF	3	28
Tetrachlorodibenzofurans	TCDF	4	38
Pentachlorodibenzofurans	PeCDF	5	28
Hexachlorodibenzofurans	HxCDF	6	16
Heptachlorodibenzofurans	HpCDF	7	4
Octachlorodibenzofuran	OCDF	8	1
			135

Table 14.1.2 2,3,7,8-Congeners, TEFs, and Homologue Classes

2,3,7,8-Congener	NATO-89 I-TEFs	WHO-98 TEFs	Figure Order ^a	Homologue Class	Figure Order ^a
2,3,7,8-TCDD	1	1	1	Total TCDDs	1
1,2,3,7,8-PeCDD	0.5	1	2	Total PeCDDs	2
1,2,3,4,7,8-HxCDD	0.1	0.1	3	Total HxCDDs	3
1,2,3,6,7,8-HxCDD	0.1	0.1	4	Total HpCDDs	4
1,2,3,7,8,9-HxCDD	0.1	0.1	5	OCDD	5
1,2,3,4,6,7,8-HpCDD	0.1	0.01	6	Total TCDFs	6
OCDD	0.001	0.0001	7	Total PeCDFs	7
2,3,7,8-TCDF	0.1	0.1	8	Total HxCDFs	8
1,2,3,7,8-PeCDF	0.05	0.05	9	Total HpCDFs	9
2,3,4,7,8-PeCDF	0.5	0.5	10	OCDF	10
1,2,3,4,7,8-HxCDF	0.1	0.1	11		
1,2,3,6,7,8-HxCDF	0.1	0.1	12		
1,2,3,7,8,9-HxCDF	0.1	0.1	13		
2,3,4,6,7,8-HxCDF	0.1	0.1	14		
1,2,3,4,6,7,8-HpCDF	0.01	0.01	15		
1,2,3,4,7,8,9-HpCDF	0.01	0.01	16		
OCDF	0.001	0.0001	17		

Notes: TEF—toxicity equivalence factor

NATO-89—refers to the so-called “international TEFs” (I-TEFs) reported in NATO/CCMS (1988)

WHO-98—refers to the World Health Organization TEFs (WHO-TEFs) reported in Van Den Berg *et al.*, (1998)

^a Figure order refers to the order of these congeners and homologue classes shown on the horizontal axes of Figure 14.4.1.

compounds (DLC), which included the co-planar polychlorinated biphenyls (PCBs). When a subset of the DLCs attracted special attention from an exposure standpoint, the TEQ concept emerged. By the time this concept was introduced, most of the toxic CDD/CDF congeners had been synthesized in both native and ¹³C fully labeled forms.

From a regulatory point of view, the early rules were primarily based on 2,3,7,8-TCDD. Regulations evolved in parallel with regulatory and scientific interests and the simultaneous evolution of methodologies. Today, most international standards are TEQ based. To support the various international rules and regulations, a number of

analytical protocols describing sampling, sample preparation, analysis, and validation procedures were developed throughout the 1980s and 1990s (U.S. EPA, 1986, 1994, 1999a, b; Ballmacher, 2001; Environment Canada, 1997; JIS, 1999). Their current form benefited from years of research and development, as well as refinements with contributions from scientists, who over the past two decades, assisted with important developments in sample preparation and analytical techniques. Thus far, the best analytical results are achieved when pre-analytical sample cleanup, high-resolution gas chromatography (HRGC), and high-resolution mass spectrometry (HRMS) are combined. These developments were necessary for meeting new demands

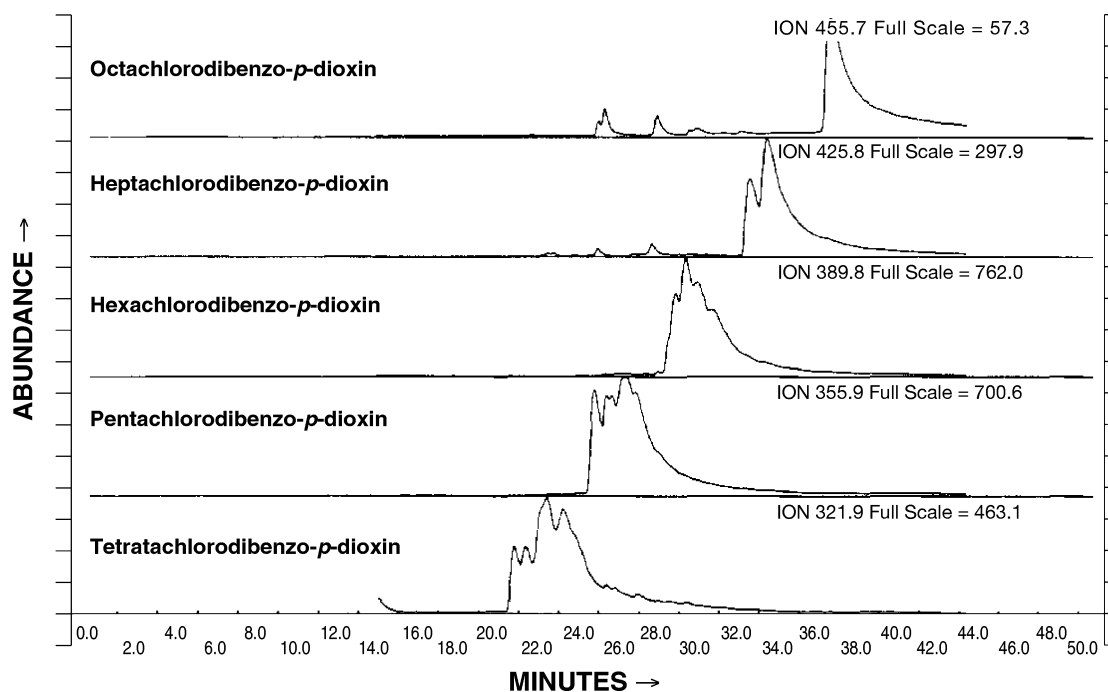


Figure 14.2.1 Example of low-resolution gas chromatography column technology. Source: Eiceman *et al.*, (1980). Reprinted with permission. Copyright (1980) American Chemical Society.

for improved sensitivity and specificity, which were mostly driven by risk assessment requirements.

Sophisticated and elaborate cleanups involving chemical treatments, gravity flow, and low-pressure chromatography columns became integral parts of the analytical methods. Their function is to isolate the target analytes from co-extractants while removing potential interferences to ensure that extremely small quantities of “dioxins” can be reliably analyzed. When not removed during sample fractionation, for instance, polychlorinated diphenylethers coeluting with CDFs are a source of positive bias even under high-resolution mass spectrometric conditions.

Early studies regarding sample introduction to the gas chromatograph were conducted using packed gas chromatographic column technology. Low-resolution GC (Figure 14.2.1) is unable to achieve isomer specificity and is therefore unsuited for TEQ determinations. As the risk assessment-driven need for isomer specificity increased, capillary columns (Figure 14.2.2) became widely accepted. Currently, no single GC column is capable of achieving isomer-specificity for each of the relevant 2,3,7,8-substituted congeners. Thus, at least two separate GC/MS analyses are required for accurate congener determinations.

Current improvements in chromatographic separations and time-saving procedures will become the norm in the future. For example, the application of molecular recognition technologies (e.g., molecular cavities, baskets, and other nests or hosts in which molecules or “guests” fit and bind selectively and reversibly) and molecularly imprinted polymers as chromatographic phases might become routine analytical tools in standard protocols. Other approaches, based on two-dimensional (2D) GC \times GC and comprehensive 2D GC (Ligon and May, 1984; Marriott *et al.*, 2003), provide advanced separation between congeners

while considerably reducing the run time to achieve powerful separations as illustrated in Figure 14.2.3. These new technologies will also require powerful computation, more effective data acquisition, and faster GC/MS systems.

In addition to sample preparation and introduction techniques, detection methods have also evolved from the electron capture detector (ECD), which was hampered by interferences, to the current use of the mass spectrometer (Richardson, 2001). At first, MS was used for confirmatory purposes. Eventually, the success and appeal of combining GC with MS elevated the technology to the method of choice for the analysis of organic pollutants by EPA; a consequence of the 1976 consent decree between EPA and environmental activists, and the need for more scientifically and legally defensible data.

The practice of analytical chemistry evolved from the development of instrumentation into more of a multidisciplinary and interactive, problem-solving discipline. In particular, by means of its versatility for interfacing with other analytical methods, MS turned into a universal method of analysis. It plays a central role in the work surrounding “dioxins,” helping the scientific community develop a better understanding of pollution and its consequences, and identifying prevention and treatment options.

The foundations of MS were laid more than a century ago by the pioneering research of J.J. Thomson, who envisioned it as a tool for investigating the structures of molecules. Early GC/MS methods for “dioxins” were based on low-resolution MS (LRMS) using full-scan or selected ion recording techniques. Although early methodologies represented the state-of-the-art technology, their limitations were quickly recognized. For instance, risk assessors were not satisfied with the high detection limits obtained with GC-LRMS (e.g., part per trillion in water; part per billion in soil). LRMS is also susceptible to false positives and

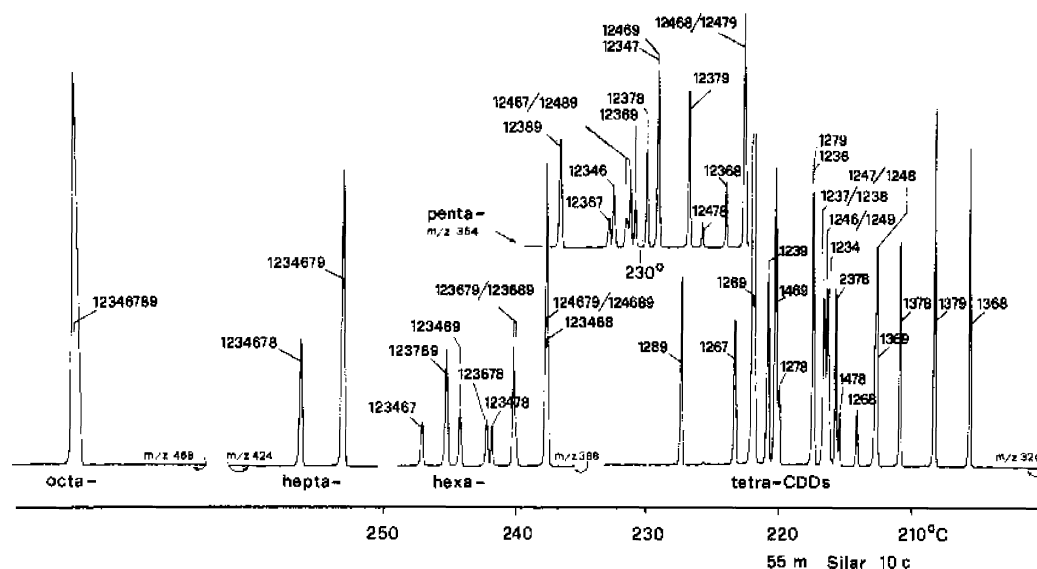


Figure 14.2.2 Example of high-resolution gas chromatography (GC) based on capillary GC column technology. Source: Buser and Rappe (1984). Reprinted with permission. Copyright (1984) American Chemical Society.

false negatives (Figure 14.2.4). The lack of mass separation further hinders the use of critical standards to monitor the extraction-fractionation efficiencies of specific toxic congeners. For instance, the use of ^{13}C -labeled HxCDF is not likely to be detected with LRMS because of interferences caused by native HxCDFs, which can behave differently from their HxCDD counterparts during sample fractionation. Finally, LRMS does not offer the means to monitor the GC/MS system performance each and every second of the analysis, which can be done in high-resolution GC (HRGC) through the use of the quality control check ions and selected ion current traces (Tondeur *et al.*, 1984).

Baughman and Meselson (1973) demonstrated the value of HRMS for the detection of 2,3,7,8-TCDD in fish tissue extracts. The sample extract was introduced via a solid probe while performing a voltage sweep with the mass spectrometer over the molecular ion region of TCDD. A separation between TCDD and DDT/PCB (commonly found interferences) was possible with a resolving power of 10,000.

The optimization of GC/MS protocols is currently based on the integration of sample extraction and fractionation procedures, sample introduction techniques, and the operation of the mass spectrometer at high resolutions. When considered in the context of stable isotope dilution, these key elements are the basis for the high level of accuracy and reliability as well as the low detection limits (e.g., 1 to 5 pg/L or parts per quadrillion in 1 L water; sub-pg/g in 10 g soil; 0.5 to 5 pg/g lipid-based in 20–30 mL human serum; and 0.01 pg/g in 25 g fish tissue) characteristic of today's methodologies.

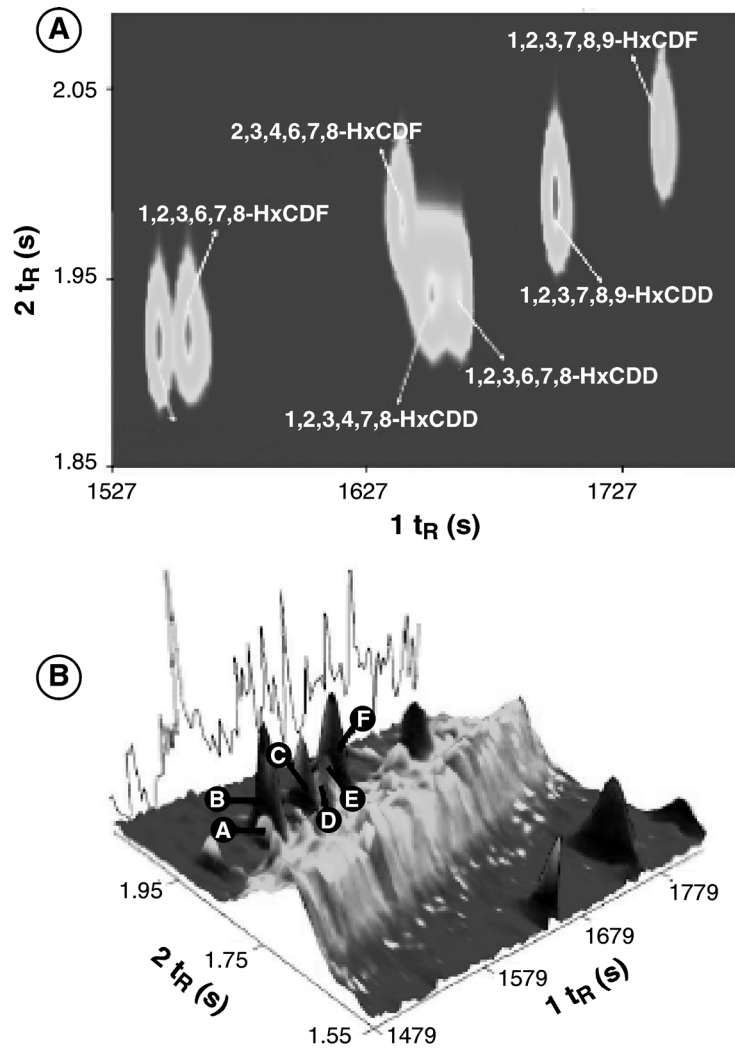
Risk assessment drives the need for improved sensitivity, specificity, and selectivity, as well as accuracy and reliability of CDD/CDF analyses. Despite its high cost, isotope-dilution HRMS remains the method of choice. Other techniques based on tandem MS/MS have been shown valuable in some specific applications where the accuracy of HRMS was challenged (Charles *et al.*, 1989). Other MS technologies have been recently described for CDD/CDFs (e.g., quadruple ion storage and time-of-flight) (Focant *et al.*, 2004).

The past several years have seen a renewed interest in rapid and low-cost screening bioassays (e.g., Denison *et al.*, 2002). Even though the significance of bioassays as an analytical tool was first recognized in the 1960s when antibodies were used to measure insulin in plasma by radioimmunoassay, they never achieved the status of recognition and adoption that has occurred following the 1999 Belgian dioxin scare over the contamination of livestock from tainted animal feed. Food safety has special requirements that are not comparable to conventional environmental testing of soil/sediment and wastewater matrices. Time, frequency, and cost are understandably of the essence; thus, the observed push for rapid screening tools. A cost-effective and reliable food safety monitoring program requires a balanced combination of screening and confirmatory assays because bioassays cannot provide molecular-level information. Furthermore, bioassays are incapable of accounting for actual losses of target compounds occurring during the extraction and fractionation procedures of a particular sample. Other limitations are associated with the ongoing assessment of co-extractants that bind the aryl hydrocarbon receptor as well as dioxin antagonists.

14.3 NATURAL AND ANTHROPOGENIC SOURCES

The presence of CDD/CDFs has been documented in "... practically all media including air, soil, meat, milk, fish, vegetation, and human biological samples" (Travis and Hattemer-Frey, 1991). The widespread occurrence of these persistent compounds is likely to be the result of atmospheric dispersion and deposition of particles resulting from combustion processes, from forest fires to waste incineration to auto exhaust. CDD/CDFs are also unwanted by-products in the manufacture of chlorinated organic compounds such as herbicides and wood preservatives.

The environmental forensic scientist investigating the potential sources of CDD/CDFs must understand the wide variety of sources as well as the range of "normal background" concentrations that would be expected in environments similar to those being evaluated. The purpose of this



Note:

(A) Expanded section of a GC x GC contour plot of a standard solution containing 1 ng of HxCDD/Fs. The deconvoluted ion current (DIC) is based on the sum of the molecular ions corresponding to H x CDD/Fs (m/z 390 + 374). (B) Expanded section of the HxCDD/F region of a GC x GC shade surface plot after injection of the cleanup fraction containing PCDD/Fs isolated from a real fish sample. DIC based on m/z 390 and 374. Concentrations are in the range of 2–3 $\mu\text{g } \mu\text{L}^{-1}$ (A: 1,2,3,4,7,8-H x CDF; B: 1,2,3,7,8,9-HxCDF; C: 2,3,4,6,7,8-H x CDF; D: 1,2,3,4,7,8-HxCDD; E: 1,2,3,6,7,8-HxCDD; F: 1,2,3,7,8,9-H x CDD).

Figure 14.2.3 Example of two-dimensional gas chromatography contour plots. Source: Focant *et al.*, (2004). Reprinted with permission. Copyright (2004) Elsevier.

section is to provide a summary of sources and to present a range of background concentrations reported in environmental media.

There have been many excellent literature reviews and compilations of CDD/CDF sources (e.g., Fiedler *et al.*, 1996; Rappe, 1994; U.S. EPA, 1997, 2000, 2003). US EPA (2005) at the time of writing had updated their “Inventory of sources and environmental releases of dioxin-like compounds in the United States” with data through the year 2000. This is the most comprehensive resource of CDD/CDF sources currently available, with more than 800 references cited, although at the time of this writing the document was available only as an “external review draft” and

the final report may include additional data provided during the peer review and public comment process. The final report and future updates will be posted on EPA’s National Center for Environmental Assessment (NCEA) Web site (<http://cfpub.epa.gov/ncea/>).

The ranking of sources from the 1987, 1995, and 2000 inventories is shown in Figure 14.3.1. The number one category in 2000 was emissions from backyard burn barrels (US EPA, 2005), accounting for approximately 32% of estimated emissions, followed by medical waste incinerators (24%) and municipal waste combustors (5%).

The EPA also maintains a downloadable database of CDD/CDF sources (Table 14.3.1) on the NCEA website.

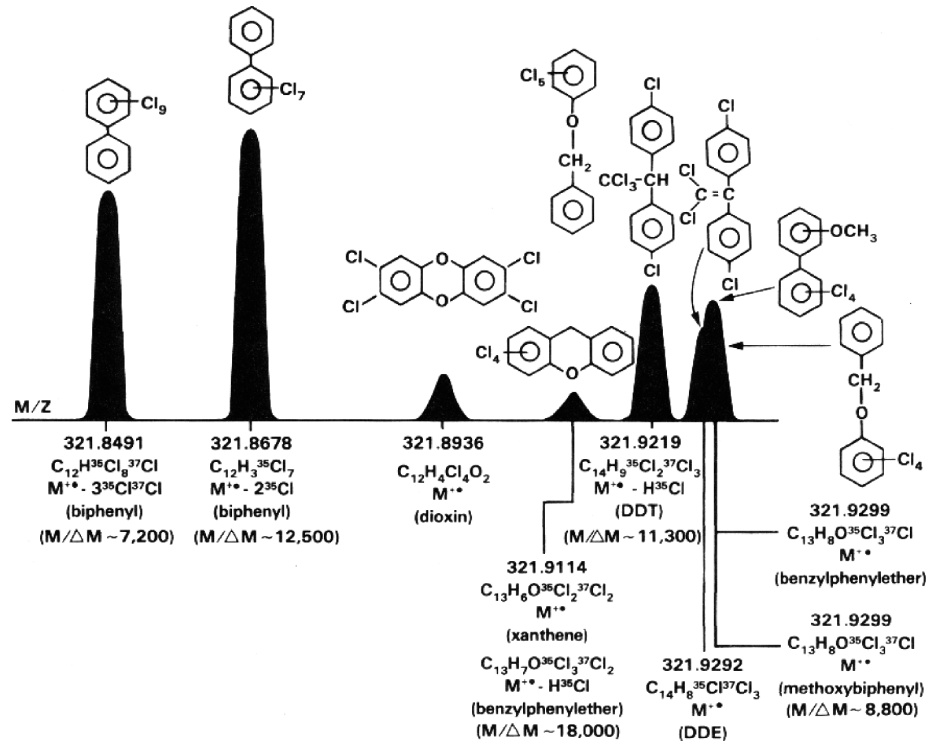


Figure 14.2.4 Commonly encountered interferences for TCDD when poor separation techniques are employed (e.g., insufficient and ineffective cleanups combined with GC/LRMS). The structures, elemental compositions, and resolving powers necessary to resolve TCDD from the interferences are given. Source: Tondeur et al., (1987). Reprinted with permission. Copyright (1987) John Wiley and Sons, Ltd.

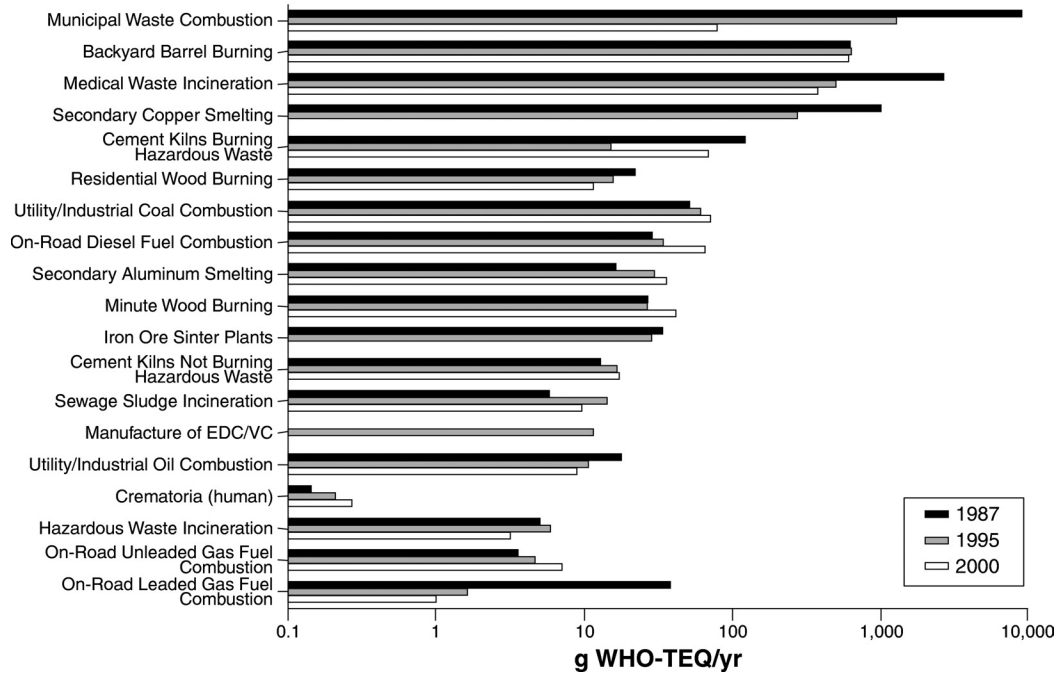


Figure 14.3.1 Estimates of annual air emissions of CDD/CDF (WHO-TEQ) for 1987, 1995, and 2000. Source: Figure 1.9 from US EPA (2005).

Table 14.3.1 Sources of CDD/CDFs Emissions and Emission Included within EPA's Database as of March 2001

Bleached chemical pulp and paper mills	Power generating facilities
Cement kilns burning hazardous waste	Coal-fired electric generating plants
Inlet temperature to APCD >4, 500°F	Oil-fired electric generating plants
Inlet temperature to APCD <4, 500°F	Primary ferrous metal smelting
Cement kilns not burning hazardous waste	Sinter production
Crematoria	Coke production
Drum and barrel reclamation facilities	Primary non-ferrous metal smelting
Ferrous foundries	Petroleum refining catalyst regeneration
Hazardous waste incinerators	Residential oil combustion
Industrial boilers burning hazardous waste	Secondary non-ferrous metal smelting
Kraft black liquor recovery boilers	Secondary aluminum smelting
Motor vehicles	Secondary copper smelting
Powered with unleaded gasoline	Secondary lead smelting
Powered with leaded gasoline	Sewage sludge incineration
Diesel powered heavy duty trucks	Scrap electric wire recovery
Municipal solid waste incinerators	Tire combustion
Medical waste incinerators	Industrial wood combustion

Source: US EPA, (2001)

The availability of this electronic database is a valuable resource for source identification studies, but the primary articles should be obtained and reviewed so that the original data can be evaluated for variability of profiles, handling of detection limits, and potential problems (e.g., coelution of isomers in older data sets). Several of the key source categories are discussed later with an emphasis on combustion.

14.3.1 Metals Smelting, Refining, and Process Sources
CDD/CDFs can be formed during various types of ferrous and non-ferrous smelting (both primary and secondary). US EPA, (2005) provides congener profiles for emissions from secondary aluminum, copper, and lead smelters, iron ore sinter plants, a scrap wire incinerator, and a drum incinerator.

14.3.2 Manufacturing Sources

Trace amounts of CDD/CDFs can form as by-products from the manufacture of chlorine-bleached wood pulp, chlorinated phenols (e.g., pentachlorophenol [PCP]), PCBs, phenoxy herbicides (e.g., 2,4-dichlorophenoxyacetic acid [2,4-D] and 2,4,5-trichlorophenoxyacetic acid [2,4,5-T]), and chlorinated aliphatic compounds (e.g., ethylene dichloride). Congener profiles are provided in US EPA, (2005) for pulp, sludge, and effluent from mills using chlorine bleach process, for technical grade PCP, for 2,4-D salts and esters, and for sewage sludge.

14.3.3 Combustion

Combustion is the primary source of CDD/CDFs to the global environment. CDD/CDFs are generated in waste incineration (e.g., municipal solid waste, sewage sludge, medical waste, and hazardous wastes), fuel combustion (e.g., oil, gasoline, diesel, coal, and wood), other high-temperature sources (such as cement kilns), and poorly controlled or uncontrolled combustion sources (e.g., forest fires, building fires, and open burning of wastes).

Cleverly *et al.*, (1997) reported that combustion sources typically emit all 2,3,7,8-substituted CDD/CDFs, although the relative congener concentrations vary. These authors found that 2,3,7,8-TCDD is usually 0.1 to 1% of total CDD/CDFs in combustion source emissions, with the exception of stack emissions from industrial oil-fired boilers,

where the available data indicate that 2,3,7,8-TCDD constitutes an average of 7% of total CDD/CDF emissions.

In evaluating congener profiles for the EPA inventory of sources, Cleverly *et al.*, (1997) noted that OCDD is the dominant congener in some, but not all, combustion emissions. OCDD dominates emissions from mass-burn municipal waste combustors (MWCs) that have dioxin emission controls. It also dominates emissions from industrial oil-fired boilers, industrial wood-fired boilers, unleaded gasoline combustion, diesel fuel combustion in trucks, and sewage sludge incinerators. These authors reported that the dominant congeners for other combustion sources are 1,2,3,4,6,7,8-HpCDF in emissions from mass-burn MWCs equipped with hot-sided electrostatic precipitators, hazardous waste incineration, and secondary aluminum smelters; OCDF in emissions from medical waste incineration and industrial/utility coal-fired boilers; 2,3,4,7,8-PeCDF in cement kilns burning hazardous waste; and 2,3,7,8-TCDF in cement kilns not burning hazardous waste.

Congener profiles for the following combustion sources are provided in US EPA, (2005): MWC, medical waste incinerators, furnaces burning hazardous waste, crematoria, sewage sludge incinerators, a tire combustor, vehicle exhaust, wood combustion, power boilers (coal, wood, and oil), cement kilns (burning hazardous and non-hazardous waste), petroleum catalytic reformer units, black liquor recovery boilers, cigarette smoke, landfill flares, and forest fires.

Open burning of yard waste and household trash is not only the number one source of CDD/CDFs in the national inventory (US EPA, 2005), but can also be a source of locally elevated CDD/CDFs immediately downwind from the burn barrel (Wevers *et al.*, 2003). CDD/CDF source identification studies in rural communities should include emissions from backyard burning as a potentially significant cause of elevated CDD/CDF concentrations in soils and house dust.

Unlike combustion of diesel or municipal solid waste in a controlled incinerator, the types of waste and combustion conditions in a backyard burn barrel are extremely variable. Therefore, it is difficult to predict what the CDD/CDF concentrations and profile would be in the surface soils or indoor dust of a house next to a burn barrel or a burn pit.

Available studies of CDD/CDF congeners in emissions from backyard burning (Gullet *et al.*, 2001; Lemieux *et al.*,

2003; Wevers *et al.*, 2003; Ikeguchi and Tanaka, 2000; U.S. EPA, 2005) indicate a wide range of congener patterns and more than four orders of magnitude range of TEQ concentrations. For example, in Wevers *et al.*, (2003), the congener patterns for burning garden waste and household waste were both dominated by OCDD and HpCDD, but the household waste emissions were also characterized by high relative concentrations of the low to mid-weight CDFs and one HpCDF. In contrast, the profiles from Lemieux *et al.*, (2003) were very low in OCDD and HpCDD.

According to Lemieux *et al.*, (2003), “[m]any possible parameters could have a significant influence on CDD/CDF emissions from burn barrels. Many of these parameters could be caused by variations in practice-related variables that would vary from homeowner to homeowner. Some of these parameters include physical condition of waste in the barrel (e.g., fullness of the barrel, degree of compression of the waste, distribution of waste components within the barrel), chemical composition of the waste (e.g., wetness, trace metal content, Cl content, organic vs. inorganic Cl), and combustion conditions resulting from variations in the previously mentioned physical and chemical characteristics.”

In the US EPA, (2005) review of burn barrel data, the authors state that “. . . the wide variability in test results (from less than 10 to more than 6000 ng I-TEQ_{DF}/kg) also indicates that a high degree of CDD/CDF emission variation can be expected due to factors that are not wholly related to waste composition or burning practice, such as waste orientation.”

14.3.4 Background Levels

One of the first steps in CDD/CDFs source evaluation studies is to determine if the concentrations in the media of concern are actually above background levels. Site-specific background samples are always preferred, but often unavailable. If site-specific background data are not available, the concentrations need to be compared to published values. US EPA, (2003) provides a comprehensive review of background data for soil, sediment, ambient air, water, fish tissue, and a variety of food items as summarized in Table 14.3.2. In addition, background data for indoor house dust from urban neighborhoods (Berry *et al.*, 1993; Saito *et al.*, 2003; Wittsiepe *et al.*, 1996) indicate a WHO-TEQ range of 2.1–270 ng/kg for 27 samples, with an arithmetic mean of 45 ng/kg (undetected results set to one half the detection limit).

14.4 FORENSIC TECHNIQUES

Environmental forensic investigations are most effective when they rely upon multiple tools. Chemical fingerprinting is one tool and is often useful in identifying (or eliminating) potential sources. However, there must be a plausible transport pathway from the source to a receptor in order to conclude that a fingerprint is a result of that source.

Chemical fingerprinting is a well-established technique for distinguishing different sources of contamination in the environment. It is particularly well suited for work with families of organic compounds that occur together, such as PCBs, polycyclic aromatic hydrocarbons, and CDD/CDFs. This is because (1) these classes contain many individual compounds, which together comprise a compositional pattern, also referred to as a “profile,” a “signature,” or a “fingerprint” and (2) the relative concentrations and/or ratios of an individual profile can be used as a marker of the original source material. However, because organic compounds can be transformed in the environment through chemical weathering and biological degradation, segments of the original

patterns can be altered. Another complicating factor is that multiple sources often mix together and mask the individual signatures.

Environmental transformations must be considered. The environmental forensic scientist needs to take these “real world” factors into account when interpreting chemical source fingerprints. For example, the chemical fingerprint of a sample from an environmental medium such as soil, sediment, or indoor house dust typically represents many decades of input of CDD/CDFs that may have been chemically transformed during transport from their original source and after deposition and/or mixed with other sources.

Comparison of weathered environmental samples to fresh industrial sources can sometimes be made. A comparison of these weathered mixed profiles (e.g., soil, sediment, indoor dust) to published profiles of an industrial material or unweathered emission samples taken from another location can be made in some situations. If a known industrial source is the dominant source and the profile of emissions from that source is well established, stable over time, distinct from ambient background, and not subject to significant transformations en route from source to receptor, then it can be quite useful in source identification. For example, Peek *et al.*, (2002) found that the CDD/CDF profile of stack emissions from a pulp mill distinctly matched the soils in an adjacent forested hillside. However, that profile did not match soils from nearby residential areas, which were subject to other more immediate sources such as burn barrels, as well as background soils in the area. The authors concluded that the forest was affected by only one source and the source profile was so distinct from other sources (i.e., very low OCDD) that a plausible linkage could be made.

Analytical data must be reliable. Chemical fingerprinting methods, whether based on sample-specific comparisons of profiles, analyses of “diagnostic ratios,” or multivariate statistical analyses, are dependent on good quality analytical chemistry data and are thus vulnerable to data quality problems. Analytical data for the same compounds, but from different laboratories or derived by different methods, can introduce uncertainty in the comparisons. The frequency of “non-detects” in the data set and how these results below the method reporting limit are handled can sometimes be critical to the data analyses and can potentially bias chemical fingerprinting results, particularly when compounds, such as CDD/CDFs, occur at extremely low concentrations. Another analytical problem, particularly when older laboratory data are used, is “coelution” (i.e., when non-target analytes elute in a GC column at the same time as a target compound and are thus analyzed en masse), which can lead to the misidentification of analytes or inaccurate quantification. Coelution of certain CDD/CDF congeners was common in the analyses done in the 1980s before high-resolution techniques became more common. The problem of coelution led to increasing dependence on more definitive analytical methods such as HRGC.

Chemical fingerprinting methods range from simple to complex. There are many chemical fingerprinting methods, which range from simple profile comparisons of individual samples to sophisticated multivariate analyses. Individual profile comparisons can be useful when the profiles are clearly different. However, the human eye has difficulty detecting subtle patterns between histogram plots of 17 CDD/CDF congeners or, as an extreme example, the peaks of 80 semivolatile compounds on a gas chromatogram. Multivariate statistical analyses such as hierarchical cluster analysis and principal components analysis (PCA) are often used to condense and simplify a complex set of variables. These widely used and accepted techniques are scientifically defensible, although the underlying mathematics are complex.

14.4.1 Individual Profile Evaluation

The first fingerprinting step, and sometimes the only step, is the evaluation of individual samples by comparison of profiles of the relative concentrations of either the commonly reported 17 2,3,7,8-substituted congeners or the 10 homologue classes. Concentrations of CDD/CDFs found in environmental media can vary by orders of magnitude; therefore, standardization of the results is necessary so that the congener or homologue profiles from different locations and different media can be compared.

14.4.1.1 Standardization Methods

Four types of standardization methods are commonly used. We define them as the “2,3,7,8-sum,” “relative homologue,” “relative TEQ,” and “total homologue” methods. In Figure 14.4.1, profiles using these four standardization methods are shown for individual environmental samples (e.g., soil, dust, sediment, air) and source samples (e.g., various combustion sources, Kraft mill sludge, soils impacted by PCP, and sediments impacted by 2,4,5-T). As illustrated in Figure 14.4.1, samples of similar media or sources may have common 2,3,7,8-sum profiles, but very different profiles using the other standardization methods. Each of these methods provides a different, yet equally valid, view of the relative concentrations of the congeners and homologue classes. Consideration of multiple standardization methods for both visual comparisons and exploratory data analyses provides a more rigorous analysis than using just one standardization method. Each of these standardization methods is discussed in the following subsections.

14.4.1.2 “2,3,7,8-Sum” Standardization Method

Each reported 2,3,7,8-substituted congener is divided by the sum of the 2,3,7,8-substituted congeners reported. This is a common standardization method and is similar to dividing each congener by the total CDD/CDFs (US EPA, 2005) and takes advantage of the detail provided in the congener-specific results. However, there are two problems with this method: CDD/CDF profiles can be altered by weathering and bioaccumulation (this is partially addressed by “relative homologue standardization” method) and the profile comparisons can be limited by lack of detection of specific congeners (this is partially addressed by the “total homologue standardization” method). Another challenge is the problem of viewing the low concentrations that are masked when the relative concentrations of OCDD or others are extremely high. Presenting the relative concentrations on a logarithmic scale allows examination of the pattern of the low concentration congeners. However, if the scale is expanded too much to show the differences in the low-percentage congeners, the differences between the major contributing congeners are difficult to see.

14.4.1.3 “Relative Homologue” Standardization Method

Each 2,3,7,8-substituted congener is divided by its respective homologue class (e.g., 2,3,7,8-TCDD is divided by the total TCDDs, 1,2,3,4,7,8-HxCDF is divided by the total HxCDFs). OCDD and OCDF are divided by the total 2,3,7,8-substituted dioxins and furans, respectively. This method, first proposed by Hagenmaier *et al.*, (1994), somewhat neutralizes the effects of differential weathering and bioaccumulation resulting from the degree of chlorination (i.e., homologue class) among environmental samples (e.g., soil, sediments, and dust). Differences in weathering and bioaccumulation between 2,3,7,8-substituted congeners and non-2,3,7,8-substituted congeners with the same degree of chlorination probably also occur; yet fewer changes are likely within the homologue class than between them. This

method, however, does not address the radical shift in congener patterns resulting from ultraviolet radiation and subsequent photodechlorination that occurs in sunlight within minutes and hours after combustion or aerial spraying of herbicides containing trace amounts of CDD/Fs (Karch *et al.*, 2004; Podoll *et al.*, 1986).

14.4.1.4 “Relative TEQ” Standardization Method

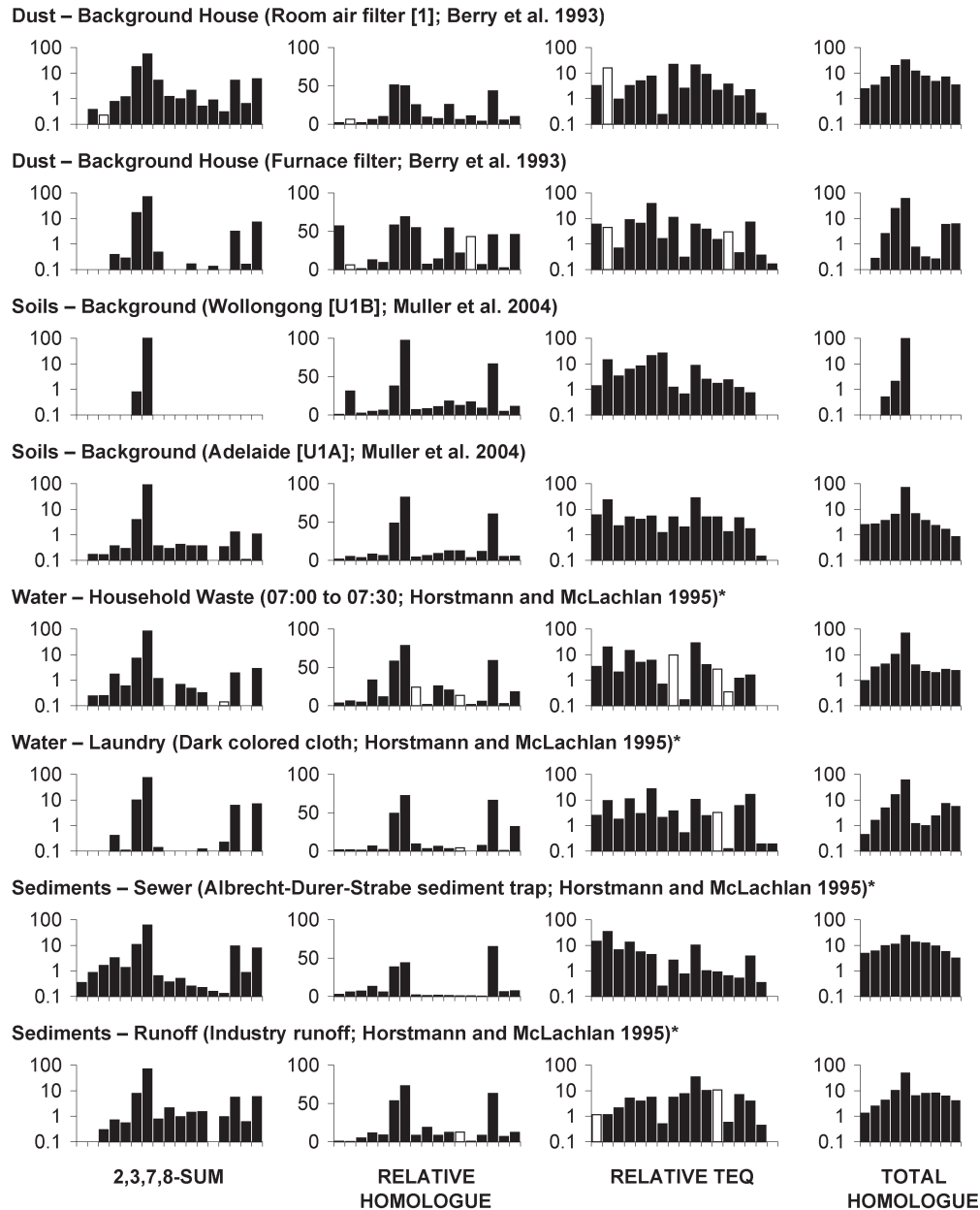
The TEQ for each reported 2,3,7,8-substituted congener is divided by the TEQ for the sample (Fiedler *et al.*, 1996; MDEQ, 2003). This standardization method takes advantage of the detail provided in the congener-specific results, and it also provides information on which congeners contribute to toxicity. Another advantage of this method is that the dominance of OCDD (often orders of magnitude greater than some of the lower chlorinated congeners) does not mask the patterns of the low-concentration congeners. However, this standardization method has the same two problems as the 2,3,7,8-sum method: CDD/F profiles of similar environmental media can be altered by weathering and bioaccumulation (this is partially addressed by the “relative homologue” standardization method), and the profile comparisons can be limited by lack of detection of specific congeners (this is partially addressed by the “total homologue” standardization method).

14.4.1.5 “Total Homologue” Standardization Method

Each homologue class is divided by the total CDD/CDFs (e.g., total PeCDFs divided by the total CDD/CDFs). This is a common standardization method and a convenient way of showing gross differences in profiles. However, unlike the congener-specific methods, subtle but potentially important differences among the low-concentration congeners are not presented. Also, unlike the “relative homologue” method, it does not account for any significant dechlorination of environmental samples resulting from weathering or differential uptake by organisms.

14.4.1.5.1 Selected Ion Current Profiles (SICPs)

For the analysis of CDD/CDFs using HRGC/HRMS, SICPs are generated by the laboratory for each homologue class. These are analogous to the “mass fragmentograms” that Rappe (1994) presented for a variety of CDD/CDF homologue classes from different types of environmental samples and the HRGC patterns presented for different environmental and source samples by Swerev and Ballschmiter (1989). The SICP is a visual representation of the measurements of a particular family of organic compounds and provides information on the presence or absence of CDD/CDF congeners and other organic compounds within a given homologue class, not just the 2,3,7,8-substituted congeners. For example, only the three 2,3,7,8-substituted HxCDD congeners (i.e., 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, and 1,2,3,7,8,9-HxCDD) are usually reported, yet there are a total of 10 HxCDD congeners (Table 14.1.1). The responses of all HxCDDs that may be present in a sample are measured and a total HxCDD concentration would be reported by the laboratory as “Total HxCDD.” The SICP for HxCDD, for example, could potentially show a response (a peak on the graph) for any one or up to all 10 congeners if they were present above the instrument’s detection limit. Samples that have been influenced by different sources of CDD/CDFs would show different dominant peaks and patterns of peaks on the SICPs for certain homologues. For example, SICPs for HxCDDs are shown in Figure 14.4.2 for chimney soot, fly ash, PCP, and hexachlorocyclohexane. These SICPs provide the distribution pattern for all ten isomers and thus provide the investigator with a more detailed evaluation of pattern differences between individual samples than do



*Coelution of some congeners, see text for discussion

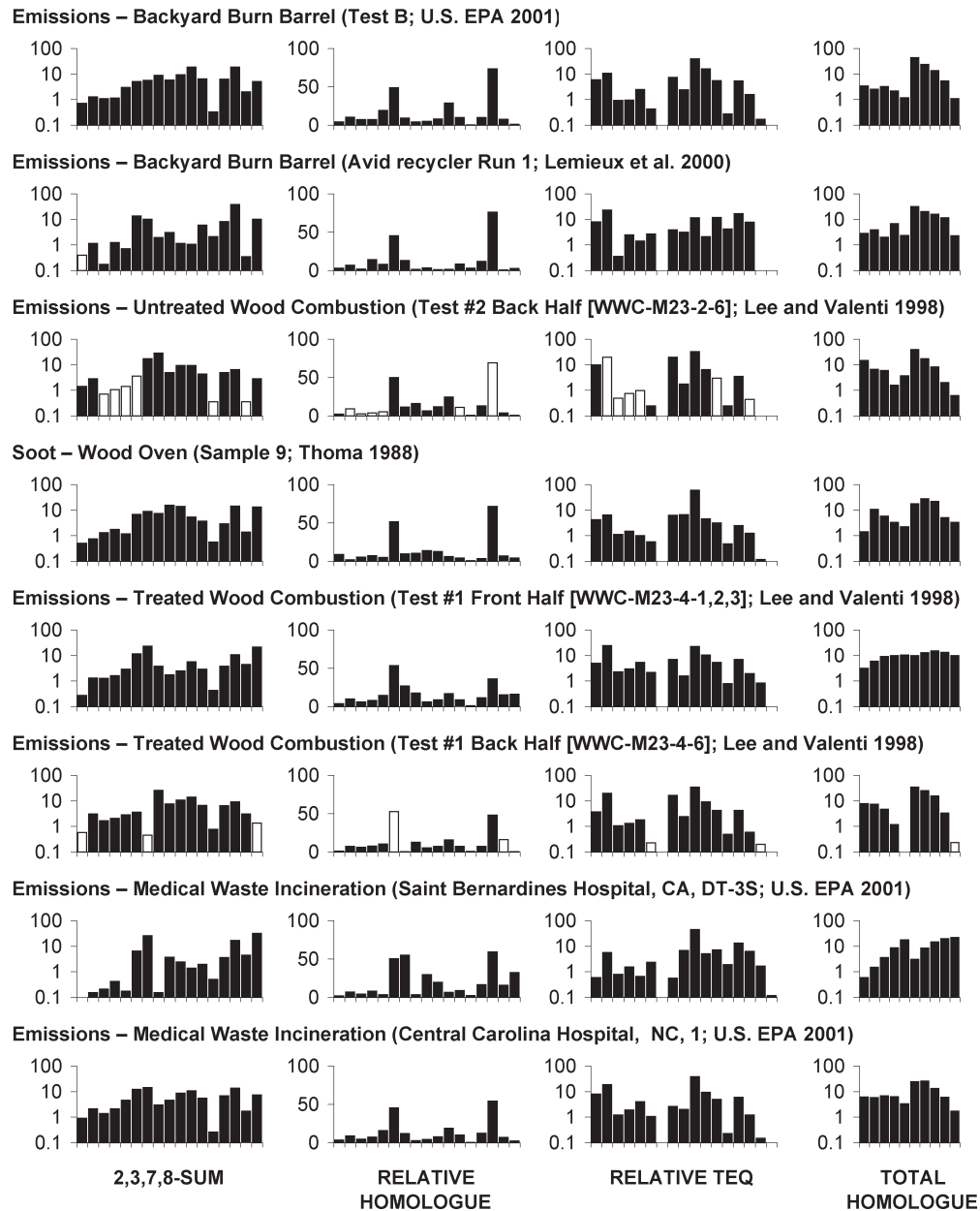
(a)

Figure 14.4.1 Congener and homologue profiles of individual environmental and source samples using four different standardization methods. All values shown on the vertical axes are percents. Refer to Table 14.1.2 for the order of congeners and homologues shown on the horizontal axes. Open bars represent calculations performed on non-detects using 1/2 detection limit.

the standard profiles of the 17 target 2,3,7,8-substituted congeners that are usually reported. The SICPs are most useful in evaluating samples collected at the same time, submitted to the same laboratory, and analyzed under the same conditions.

14.4.2 Exploratory Data Analysis

To complement visual comparisons and/or ratio analyses described above, exploratory data analyses can be used to evaluate sources. Mathematical methods can be used to identify patterns (similarities and differences) in groups of



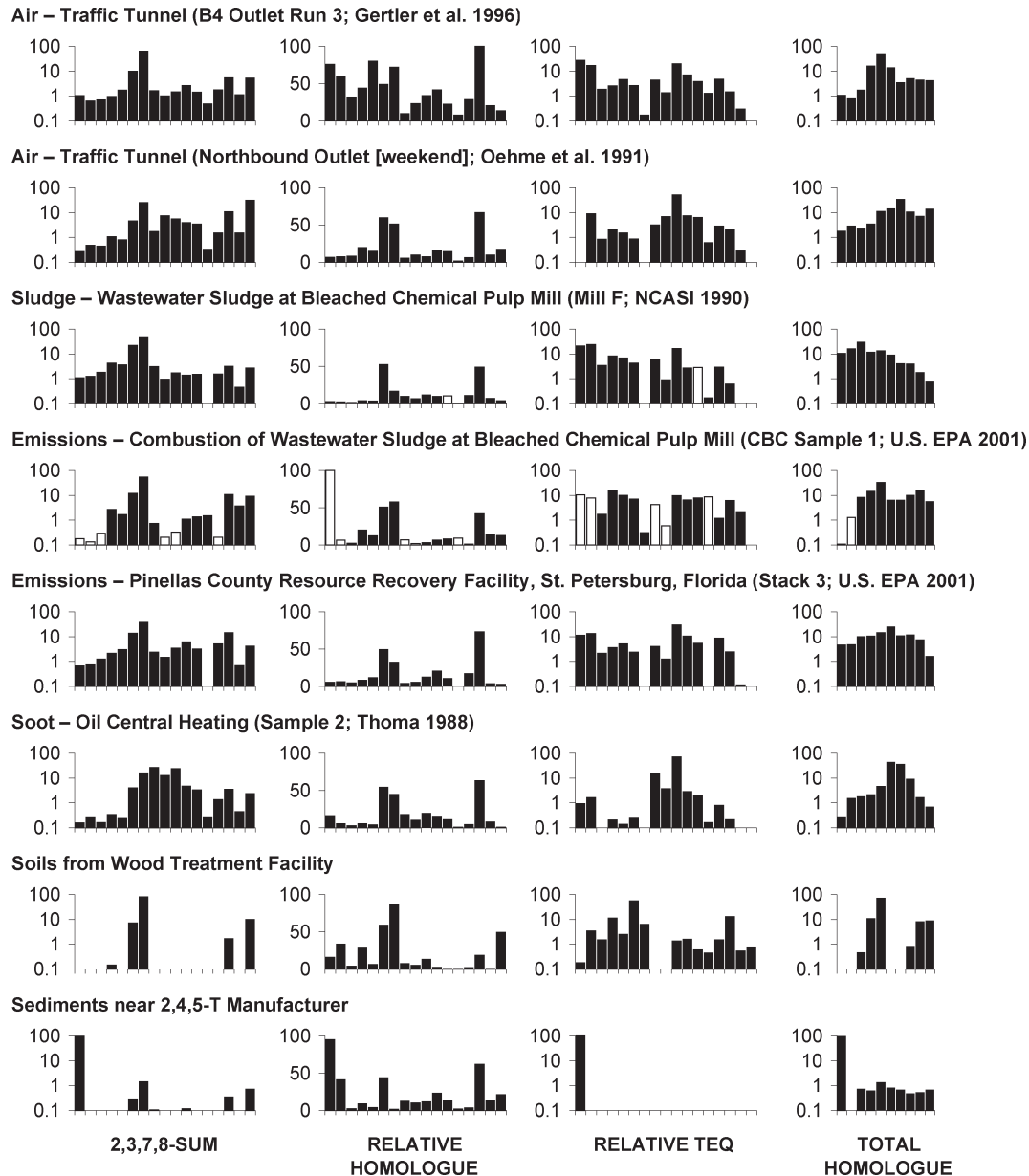
(b)

Figure 14.4.1 (Continued)

multivariate CDD/CDF congener data. Methods used to assist in source identification of CDD/CDFs include, but are not limited to, double ratio plots (Horstmann *et al.*, 1993), hierarchical cluster analysis (e.g., Hagenmaier *et al.*, 1994; Fiedler *et al.*, 1996; Gotz and Lauer, 2003), discriminant analysis (Peek *et al.*, 2002; Gotz and Lauer, 2003), PCA (Creaser *et al.*, 1990; Tysklind *et al.*, 1993; Wenning *et al.*, 1993a; Rappe, 1994; Fiedler *et al.*, 1996; Gotz *et al.*, 1998; Masunaga *et al.*, 2001; Fattore *et al.*, 2002; Abad *et al.*, 2003; Bakoglu *et al.*, 2005; Kim *et al.*, 2005; Lee *et al.*, 2005;

Watanabe *et al.*, 2005), neural networks (Gotz and Lauer, 2003), and polytopic vector analysis (PVA) (Wenning *et al.*, 1993b; Ehrlich *et al.*, 1994; Huntley *et al.*, 1998; Barabas *et al.*, 2004).

The statistical theory for these techniques is discussed elsewhere (e.g., Johnson *et al.*, [2002] for PCA and PVA; Morrison [1976] for discriminant analysis; SYSTAT [2004], S-Plus [2005], and StatMost [2002] for hierarchical and other cluster analysis; SPSS [1995] and StatSoft [2005] for neural networks). Some important practical considerations



(c)

Figure 14.4.1 (Continued)

when applying these methods to a variety of CDD/CDF data sets are as follows:

Data sets often have a large proportion of undetected congeners. The analyst needs to describe not only the screening criteria used to include or exclude these data but also, if included, what value was used to represent the estimated concentration. Typically, one-half the detection limit is used, but sometimes, zero, the full detection limit, or some other surrogate value is used. The analyst should conduct and describe sensitivity analyses with regard to differences and similarities in the conclusions depending on the data censoring method applied.

As shown in Figure 14.4.1, congener profiles can vary significantly depending on the standardization method. The multivariate analyses should be applied to all four common standardization methods if the data are available (sometimes only the 2,3,7,8 congeners are available and no homologue class data is reported; sometimes the converse is true). The results of the exploratory data analysis are more robust if they are consistent across different standardization methods.

Historical data must be carefully screened for high detection limits and coelution of key congeners. For example, there are very few reports of the specific congeners

Table 14.4.1 Summary of North American CDD/CDF WHO-TEQ Levels in Environmental Media and Food

Media	Units	Sample Size (n)	Mean ^a	Minimum	Maximum
Urban soil	ppt	270	9.3	2	21
Rural soil	ppt	354	2.7	0.1	6
Sediment	ppt	11	5.3	<1	20
Urban air	pg/m ³	106	0.12	0.03	0.2
Rural air	pg/m ³	60	0.013	0.004	0.02
Freshwater fish and shellfish	ppt	289	1.0	NA	NA
Marine fish and shellfish	ppt	158	0.26	NA	NA
Milk ^b	ppt	8 composites	0.018	NA	NA
Dairy ^c	ppt	8 composites	0.12	NA	NA
Eggs ^d	ppt	15 composites	0.081	NA	NA
Beef	ppt	63	0.18	0.11	0.95
Pork	ppt	78	0.28	0.15	1.8
Poultry	ppt	78	0.068	0.03	0.43
Vegetable fats	ppt	30	0.056	NA	NA

Notes:

CDD—chlorinated dibenzo-*p*-dioxin;

CDF—chlorinated dibenzofuran;

NA—not available;

TEQ—toxicity equivalent;

WHO—World Health Organization.

Source: From Table 1.4 in US EPA (2003).

^a Values are the arithmetic mean TEQs. Non-detects were set to one-half the limit of detection, except for soil and CDD/CDFs in vegetable fats for which nondetects were set to zero. CDD/CDFs in water were generally undetected except for a small proportion of samples with detected values of OCDD and OCDF.

^b Each composite for CDD/CDF was composed of 40+ US regional samples.

^c Dairy concentrations calculated from milk lipid concentrations and then assuming a fat fraction for dairy.

^d Each composite for CDD/CDF data was composed of 24 eggs.

found in historic PCP. The most commonly used data to represent PCP source profiles are congener concentrations for two PCP samples and two sodium pentachlorophenolate samples reported by Hagenmaier and Brunner (1987). However, the original report clearly shows that two of the 2,3,7,8-substituted congeners coelute with another congener. Specifically, 1,2,3,7,8-PeCDF coeluted with 1,2,3,4,8-PeCDF and 1,2,3,4,7,8-HxCDF coeluted with 1,2,3,4,7,9-HxCDF. Isomer-specific analyses of CDD/CDFs from the 1980s commonly had coelution problems for these congeners (e.g., Christmann *et al.*, 1989a, b; Buser, 1991). For historic data with such coelution problems, congener-specific analyses would not be reliable and the analyst should use the total homologue standardization method if these profiles need to be included for source determination.

To illustrate the use of several of these exploratory data analysis methods, we present two case studies. Case study 1 addresses the use of discriminant analysis to determine if aerial emissions from a power boiler at a pulp mill caused elevated CDD/CDFs in downwind drinking water supplies. Case study 2 presents the use of a variety of data analysis methods to determine the predominant sources of CDD/CDFs in the sediments of Hamburg Harbor and the Elbe River in Germany.

14.4.3 Case Study 1

Homes and small businesses downwind from a pulp mill used roof catchment systems to collect rainwater into cisterns for domestic uses including drinking water. Analyses of the sediments in some of these cisterns showed elevated CDD/CDF concentrations. Peek *et al.*, (2002) conducted air dispersion modeling and chemical fingerprinting to determine if the CDD/Fs in the cistern sediments resulted from historical deposition of stack emissions from the mill's power boiler. Dewatered chlorinated sludge and salt-water soaked wood and bark were combusted with fuel oil and thus the fly ash had elevated CDD/CDF concentrations.

Data evaluated included fly ash from the mill boilers when the mill was in operation, cistern sediment samples, soil samples from areas outside the impact of aerial deposition from the mill, and soil samples near the mill potentially impacted by aerial deposition. Also included were literature samples for several other potential sources, including auto exhaust, burn barrels, wood burning, oil heat, and fertilizers.

Data used in analysis were the homologue class concentrations divided by the total CDD/CDF concentrations (i.e., the "total homologue" standardization method).

Analyses included discriminant analysis and plots comparing the mean and standard deviation of each total homologue proportion between the different sources. A single plot for each homologue class allowed the different sources to be compared relative to the variability within each source.

In this application, discriminant analysis was used to generate linear functions of the relative homologue proportions that best separate the different groups or sources included in a "training data set" of source terms. These discriminant functions were then used to classify samples of unknown origin (e.g., offsite soils and cistern sediment samples) into one of these original groups. Additionally, the new variables generated by the discriminant functions, known as canonical variables, were plotted to show the relative positions of samples, similar to PCA. The advantage of this method over standard PCA is that the initial discriminating functions can be evaluated regarding their quality using the percent of samples correctly classified. Standard statistical output for discriminant analysis included *F*-statistic values for testing whether the initial groups could be distinguished from one another. These values were then compared to a critical *F*-value for a specified alpha level and converted to *p*-values using the appropriate degrees of freedom based on the number of groups and samples included.

This method requires that there be sufficient samples to characterize each initial group or source available for the "training data set." Inclusion of too few or too many

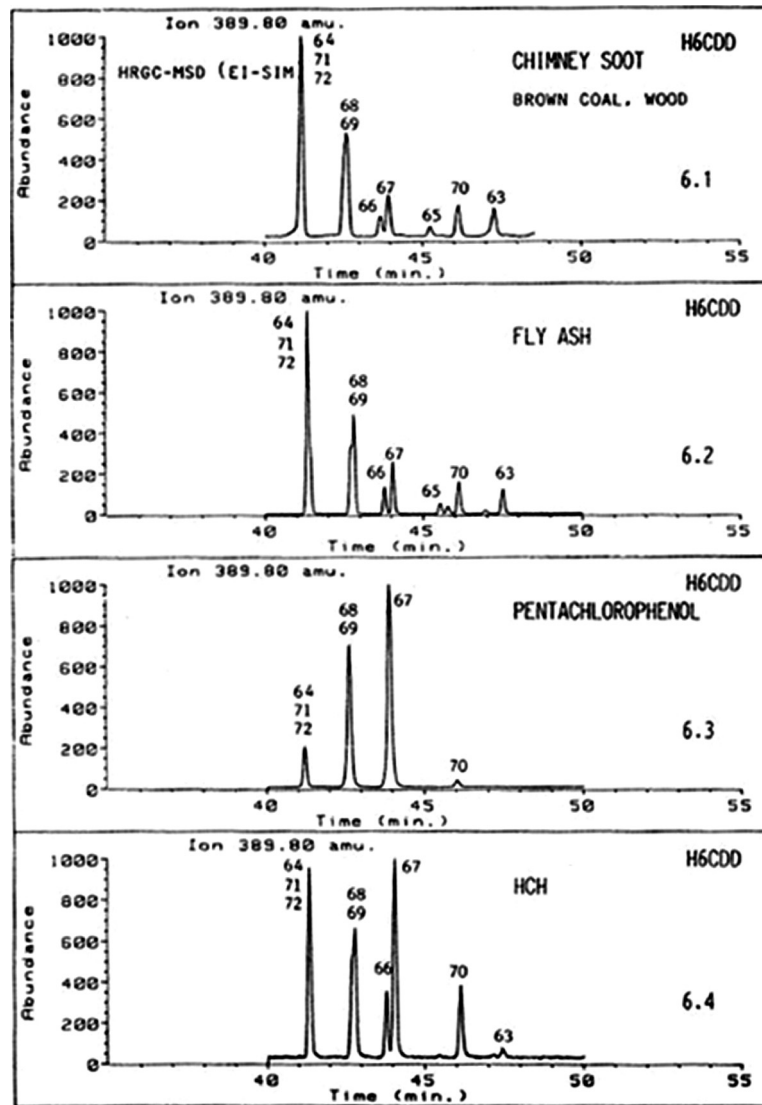


Figure 14.4.2 Selected ion current profiles of HxCDD isomers for chimney soot, fly ash, pentachlorophenol, and hexachlorocyclohexane (HCH). The 2,3,7,8-substituted isomers are shown as peak numbers 66 (1,2,3,4,7,8-HxCDD), 67 (1,2,3,6,7,8-HxCDD), and 70 (1,2,3,7,8,9-HxCDD) from the SIL 88 HRGC column. Source: Swerev and Ballschmiter (1989). Permission requested.

groups in the initial training data set can affect the final results. Too few initial groups or incomplete characterization of the included groups could result in the samples of unknown origin being incorrectly classified, because the method requires them to be classified as one of the initial groups. Too many groups included initially could result in misclassifications because the variability within groups overrides the differences between them. This ought to be detected during initial evaluations of the discriminant functions as a high rate of misclassifications between the overlapping groups. If the overlapping groups do not include a critical source and a background group, this may not affect the overall final conclusions.

The discriminant functions were developed based on the training data set of samples of the mill fly ash, background soil, and literature source samples including emissions

from trash burning, oil furnaces, wood burning, automobile exhaust, and fertilizers. All of these samples represented potential sources of CDD/CDFs to the cistern sediment. Plotting the resulting canonical variables showed the cistern sediment and soil from a nearby developed area as indistinguishable from the local background soil (see Figure 14.4.3). Onsite soils showed a mixture of fly ash and background soils indicating multiple sources. (Note that the symbols for the many onsite soils samples were removed from the original figure in Peek *et al.*, [2002] so that the remaining symbols could be clearly seen in Figure 14.4.3). The forest soils were strongly associated with fly ash. This was not surprising because these samples were collected in an undisturbed forest within the area of maximum deposition of the stack emissions (as shown by the dispersion modeling). The measured CDD/CDF concentration in the

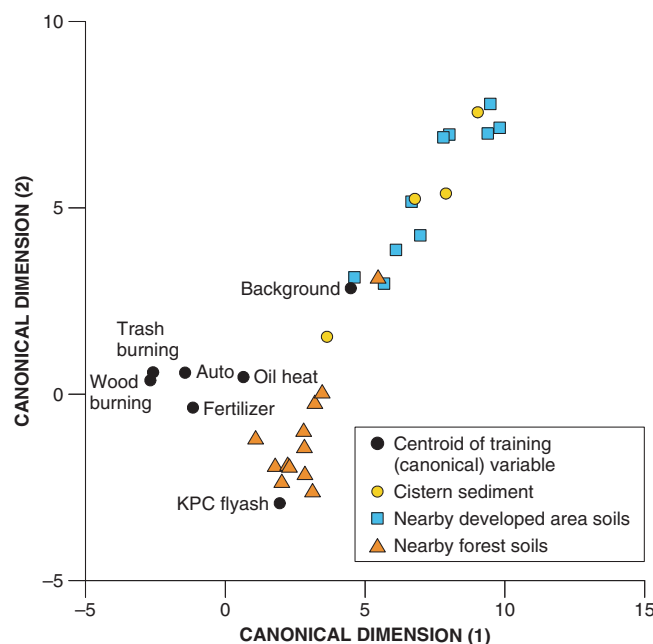


Figure 14.4.3 Canonical variable scores of the site data set. The first two canonical variables are shown. The centroid of the training data sets are shown as filled circles and labeled. The site test data are categorized by symbol. Note: Symbols for pulp mill area soils removed from figure for clarity. Source: Peek *et al.*, (2002). Reprinted with permission. Copyright (2002) American Chemical Society.

forest soils was consistent with the estimated deposition (Shields *et al.*, 1999). Additionally, a high percentage (10 of 12) of the forest soil samples from near the mill but within the aerial deposition plume were classified by the discriminant functions as fly ash.

14.4.4 Case Study 2

The Elbe River flows through Germany from the Czech border north into the North Sea. CDD/CDF concentrations are elevated in the sediments of the Elbe River, its tributaries, and the harbor of Hamburg. The objective of the investigation by Gotz *et al.*, (1998) was to test whether the industrial center of the former German Democratic Republic, the Bitterfeld region, contributed to the elevated concentrations. Analysis included multiple possible sources as well as other sampled media from the general area. The categories of data included represent possible external sources (PCP, pesticides, and chloralkali process); metallurgical processes; municipal waste incinerators and air samples; sewage sludge; sediment and suspended particulate from the Elbe River and Hamburg harbor, and soil samples from the flooding areas of the Elbe and Dove Elbe rivers; and sediment, suspended particulate, surface water, and soil from the Bitterfeld region. A total of 143 samples were included.

Data used in these analyses were the 2,3,7,8-congener concentrations divided by their homologue class concentration (i.e., standardized by the "relative homologue" method). OCDD and OCDF were each divided by the total CDD and CDF, respectively. Also included as a variable was the relative proportion of CDDs divided by the total CDD/CDFs.

In this case study, data were analyzed using several multivariate statistical methods, specifically hierarchical and *K*-means cluster analysis, factor analysis (i.e., PCA), and combinations of factor analysis with each of these clustering methods. Later analysis (Gotz and Lauer, 2003) also

included a Kohonen neural network analysis. The final cluster groups were interpreted with regard to the relationships between sources and sample types in addition to the similarities and differences between the multiple analytical methods.

Overall, the various methods used in this case study provide a similar story. Soil from the Bitterfeld region was the most significant source of CDD/CDFs to the sediments of the Elbe River and Hamburg harbor as well as to the other floodplain soils of the Elbe. Elevated CDD/CDFs in the Bitterfeld soils were attributed to both chemical production and metallurgical processes.

Results were presented for two of the linkage methods used with hierarchical clustering but the results are similar, as are the results using the *K*-means cluster analysis. PCP, PCB, organochlorine pesticide production, and chloralkali process samples each cluster separately. (Note that the PCP profiles are represented by the Hagenmaier and Brunner [1987] data with the coelution problem.) The metallurgical, Elbe River, Hamburg harbor, and Bitterfeld region samples cluster together, as do the samples from the flooding areas of the Elbe and Dove Elbe rivers. The *K*-means and the hierarchical clustering based on Ward's linkage method show a separation for the magnesium production samples and the flooding area of the Dove Elbe River. The remaining source samples and the upstream Elbe River samples group together to some degree.

The groupings identified in the plot of the first two factors from the factor analysis show the Elbe River, Hamburg harbor, Bitterfeld region, and metallurgical source samples closely grouped and the other external sources predominantly clustered away from these, the more specific sources more independently (PCP and the chloralkali plant, for example). Additionally, the upstream Elbe River samples were separate from the rest of the river samples. Hierarchical cluster analysis of the first three factors resulted in

much the same groupings, though the copper slag samples separated from the rest of the Bitterfeld region cluster, and the upstream Elbe River samples were considered a separate cluster from the other external sources. The groupings based on factor analysis are remarkably similar to the cluster analysis methods, especially considering that the first three factors account for only 48.3% of the original variability in the relative concentrations.

In a later analysis of data from the same area, Gotz and Lauer (2003) used neural networks, specifically a Kohonen network or self-organizing feature map. This method is classified as an unsupervised learning technique because it requires only input data, as opposed to "learning" relationships from a data set that includes both the input variables (i.e., relative homologue concentrations) and the correct classifications (sample groups). This method uses an iterative process to adjust a starting set of clusters to better reflect the structure of the data (StatSoft, 2005). Each iteration of the fitting process re-centers the group or cluster nearest a new sample to reflect inclusion of the new sample in that group. The final results are similar to a cluster analysis approach. An advantage of this method over cluster analysis is that the final structure can be used to classify future samples similar to discriminant analysis. The advantage of the neural network over discriminant analysis is that future samples can be classified as not belonging to any of the original source groups. Discriminant analysis requires a new sample to be classified as one of the original groups analyzed, whereas Kohonen networks allow an acceptance threshold to be set such that samples not meeting the criteria are classified as undecided with regard to their group membership.

Application of the Kohonen network to the larger Elbe River data set, augmented with data collected between the earlier publication and 2003, concluded much the same results as the earlier reported cluster and factor analysis. This analysis resulted in a Bitterfeld-Elbe cluster containing the Bitterfeld soil region, Elbe River, Hamburg harbor, and flooding area samples. All clustering was identical to the hierarchical cluster analysis conducted on the larger data set.

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