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Trace Chemistries of Fire: A Source of Chlorinated Dioxins

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Summary. New, highly specific and sensitive analytical methodology has been applied to the determination of chlorinated dibenzo-*p*-dioxins in particulate matter. The results show that the dioxins are present in particles from many types of combustion sources and in dust and soil in the vicinity of combustion sources. The data indicate that chlorinated dioxins may occur in particulate matter from the combustion of most types of organic material, and suggest the hypothesis that chlorinated dioxins result from trace chemical reactions occurring in fire.

Polychlorinated dibenzo-*p*-dioxins have been found in fly ash from municipal incinerators by Olie *et al.* (*1*) in the Netherlands, by Buser *et al.* (*2*) in Switzerland, and by Eiceman *et al.* (*3*) in Canada, Japan, and the Netherlands. Buser also reported finding them in fly ash from an industrial heating facility. In all these studies the findings were qualitative and the presence of the dioxins was considered to be most probably caused by condensation of chlorophenols. Olie, however, suggested that a thermal synthesis from inorganic chloride and organic material was possible, and this route was supported by the presence of relatively large amounts of chlorinated benzenes on the particulate matter. Eiceman suggested that these compounds are formed during incineration processes.

This article presents quantitative data on particulate matter from a wide variety of combustion processes. These data cannot be satisfactorily explained in entirety by attributing the presence of polychlorinated dibenzo-*p*-dioxins to condensation of preexisting polychlorinated phenols.

The findings reported here are not offered as comprehensive or exhaustive results. Limiting factors include the small number of scientists specifically trained in the required methodology and the highly sophisticated instruments needed to conduct the work. In addition, the subject involves a large number of variables over which the investigators had no control.

Samples were not always taken by statistical design, and results are not intended to represent anything other than the sample analyzed. The analytical methodology developed so rapidly during this investigation that later results cannot always be directly compared to earlier ones. The analytical methodology including sampling has been reviewed by a group of scientists (*4*), however, and found to represent the state of the art. The results as a whole verify scientific observations that are now emerging worldwide.

Discovery

Chlorinated dioxins appear to be ubiquitous. Their ubiquity is due to the existence of natural phenomena, trace chemistries of fire which consist of numerous chemical reactions occurring during combustion at concentrations as low as 10^{-10} percent. We include two major pathways in these trace chemistries of fire, involving (i) chemicals present in higher concentration and reacting at very low yields (10^{-10} percent) and (ii) chemicals present in trace concentration and reacting at higher yields (10^{-4} percent).

A variety of research organizations have addressed themselves to the investigation of combustion processes. However, virtually all of their work has been concerned with the kinetics and thermodynamics of the fuels, oxidants, major intermediates, or major products. Mention should be made of several recent reviews of these investigations (*5*), although none of them discuss either pathway described above.

In an attempt to determine the source of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) that we detected in some fish from the Tittabawassee River (*6*), we examined the local as well as more distant environments and found that a large number of sources emit chlorinated dioxins into the environment. Samples were gathered from incinerator stacks as well as from chemical tar burners and a fossil-fueled power plant, vehicle mufflers, fireplaces, chimneys, cigarette smoke, and portions of charcoal-broiled steaks.

Chlorinated dioxins were found in each sample. However, those on particulate matter taken from the air emissions of a wide variety of commercial and domestic combustion processes are especially significant. Combustion processes must be more than 99.9 percent efficient to ensure reduction of the concentration

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Table 1. Chlorine content of fuels [summarized from (7)].

Fuel	Chlorine (ppm)
Coal	1300 (mean)
Refuse	2500 (average)
Paper	300 to 1600
Leaded gasoline	300
Unleaded gasoline	1 to 6
Fuel oil	N.A.*

*N.A., not available. Data were not available for the chlorine content in fuel oil. However, measurements indicated that 500 pounds of hydrogen chloride would be produced per day per 100,000 persons whose homes were heated by oil-fired furnaces.

of the dioxin from 1 part per million (ppm) to 1 part per billion (ppb). Common combustion processes are not adequate (5).

Building Blocks for Chlorinated Dioxins

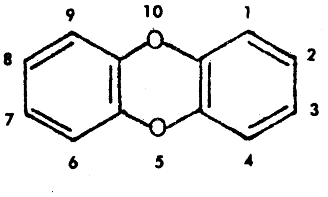
Refuse and fossil fuels are extremely complex mixtures of many chemicals and compounds, some of which are present at low concentrations. The chlorine content of various materials used as fuels for combustion has been examined by a committee sponsored by the National Academy of Sciences (7). Table 1 summarizes the result of that survey. The National Academy of Sciences estimated that "311 ppm of chlorine, mostly hydrogen chloride, is in flue gas from burning normal base refuse." Some of this chlorine is found on the fly ash accompanying the flue gas.

Fly ash from a municipal incinerator in Amsterdam was examined for chlorinated aliphatic and aromatic hydrocarbons by Lahaniatis *et al.* (8). More than 77 gas chromatography (GC) peaks, representing concentrations of 5 to 250 ppb, were obtained with an electron capture (EC) detector. Mass spectrometry (MS) provided identification of 27 of these peaks and empirical formulas for 22 more. Lasiewicz and Logensda (9) reported the following percentages of solid and gaseous products in emissions from oil-fired heating and power plants: sulfur dioxide, 1 to 6; sulfuric acid, 1 to 6; carbon monoxide, 0.1 to 0.2; nitrogen oxides, 0.5 to 1; dust, 0.2 to 1; vanadium compounds, 0.005 to 0.01; nickel oxide, 0.001 to 0.003; and soot, 0.1 to 0.5. Particles emitted from coal-fired boilers were shown by Kobayashi and Ibezawa (10) to contain 3,880 to 38,700 ppm vanadium, 1,810 to 98,500 ppm nickel, 1,440 to 19,200 ppm iron, and about 270 ppm manganese.

The data show that the myriad of initial pyrolysis products formed during combustion are jumbled at low concentrations in a sea of chemical reactions including pyrolysis, oxidation, reduction, and acidolysis which result from interaction of ions, electrons, free radicals, and free atoms. Up to now, the behavior of this chemical potpourri has been studied only in terms of the major products of combustion—water and carbon dioxide—and those generally described as minor—carbon monoxide, hydrogen chloride (7), sulfur oxides (11), and nitrogen oxides (12). This situation is further complicated by the use of water to quench or scrub the combustion gases. Donaldson (13) points out that water treated for domestic consumption contains about 1000 ppb organic chemicals. Commonly used waters often contain higher amounts of organic chemicals. When the chemicals in scrubber waters come in contact with the gaseous reacting chemicals, many more trace chemicals may form.

One trace-level combustion product, benzo[*a*]pyrene (14), has been studied in some detail. Like chlorinated dioxins, it is found on particulate matter. It is formed in higher concentrations during inefficient burning, has a high melting point, and readily photodegrades in solution. It is highly stable on particulates and has a very low solubility in water. The best estimates (14) showed that in 1971 benzo[*a*]pyrene was produced in the United States by refuse burning, heat and power generation, coke production, and automobiles and trucks in amounts of 600, 500, 200, and 20 tons, respectively.

The term chlorinated dibenzo-*p*-dioxins, or more simply chlorinated dioxins, refers to 75 compounds or any combination of the 75. Dibenzo-*p*-dioxin has the molecular structure



It is said to be chlorinated if one or more of the hydrogen atoms at the 1, 2, 3, 4, 6, 7, 8, and 9 positions is replaced by a chlorine atom. The 75 different chlorinated dioxins, each of which has its own special properties, are listed in Table 2. In only a few cases have these compounds been synthesized and their chemical and physical properties studied. Only TCDD has been examined comprehensively for its toxicological effects (14).

Table 2. Chlorinated dioxins.

Chlorine substitution	Acronym	Number of positional isomers
Mono-	MCDD	2
Di-	DCDD	10
Tri-	T_3CDD	14
Tetro-	TCDD	22
Penta-	PCDD	14
Hexa-	HCDD	10
Hepta-	H_7CDD	2
Octa-	OCDD	1

Analytical methods for the determination of TCDD or other chlorinated dibenzo-*p*-dioxins have been evolving. We used primarily GC-MS for these determinations (6). By means of several liquid chromatographic (LC) cleanup procedures, we developed specific methods for the determination of each of the tetra-, hexa-, hepta-, and octa- compounds in environmental samples. Details of these methods are being published in a series of three comprehensive papers (15). Since some of the procedures were developed during the course of this work, we report results here under the general heading TCDD, which includes 2,3,7,8-TCDD and other isomers as outlined below:

1) Analytical method ML-AM-73-97 (LC plus GC-MS) discriminates 2,3,7,8-TCDD plus 16 other isomers (16).

2) Analytical method ML-AM-78-63 [high-pressure liquid chromatography (HPLC) plus GC-MS] discriminates 2,3,7,8-TCDD plus 11 other isomers (17).

3) Analysis by HPLC plus capillary GC-MS discriminates 2,3,7,8-TCDD plus two other isomers.

The data from the various investigations of environmental samples are summarized in Table 3. The samples are described in the following sections.

Soil and Dust

All soil samples listed in Table 3 were collected at the surface from open, undisturbed areas, 10 by 10 centimeters square and 1 centimeter deep; an effort was made to exclude grass and other debris. They were placed in clean bottles and sealed until they were analyzed. The first 13 samples collected in the Midland area were analyzed qualitatively. Octa- and heptachlorodibenzo-*p*-dioxins were detected in all the samples, hexachlorodibenzo-*p*-dioxins were detected in nine, and tetrachlorodibenzo-*p*-dioxins were found in only four. A second set of soil samples was taken from areas previously sampled. Five of these, including four corresponding to the samples that previously showed TCDD, were analyzed by analytical method ML-AM-78-63, which permitted separation of 2,3,7,8-TCDD from all but about 11 of its 21 isomers.

Interference was sometimes noted in the analysis of reagent blanks. To determine whether this was caused by contamination, dust samples were collected from the tops of bookcases, solvent storage cabinets, and hoods, and at the air intake of the Dow Chemical laboratory. Analytical method ML-AM-78-63 was used. Dust samples to be used as controls were also collected from Midland and Detroit and analyzed by method ML-AM-73-97. The concentration reported for TCDD includes 16 other isomers. The results of this random sampling did not satisfy the need for control samples. Samples of soil and dust were therefore collected from Chicago, Illinois, and from East Lansing and Gaylord, Michigan. A few of the TCDD results for Lansing and Chicago were confirmed by GC combined with high-resolution MS.

Other sources of environmental particulate material include "urban particulate matter," collected in St. Louis, Missouri, and distributed by the National Bureau of Standards as SRM 1648, and Milorganite, a sludge fertilizer from Milwaukee, Wisconsin. The results of these analyses are also shown in Table 3.

Incineration

The European findings of chlorinated dioxins in fly ash together with the results of our analyses of dust and soil led us to examine particulate matter from incinerators and a powerhouse.

Dow operates two major waste incineration systems within the Midland complex. The first is a stationary tar burner operating at 72 million Btu's per hour, which was constructed and started in 1970. This unit represents one of the most advanced designs in liquid tar incineration and is one of the largest in the world. It is equipped to burn supplemental natural gas automatically, should the burning quality of the tars be insufficient to maintain the desired combustion temperature. The other Dow system is a rotary kiln incinerator capable of incinerating solids and liquids and operating at 70 million Btu's per hour. Supplemental fuel is also burned in this unit in the rotary kiln and the secondary combustion chamber to maintain the desired combustion temperatures. Samples of particulate matter were taken from the stacks of both units, using a procedure based on Environmental Protection Agency (EPA) methods (*18*). The data

Table 3. Chlorinated dioxins in the environment.

Sample	Number of samples	Apparent dioxin content, ng/g (ppb)*					
		TCDD			HCDD	H_7CDD	OCDD
		Other isomers	2,3,7,8-	Total			
Soil							
Rural (Gaylord, Michigan)	5			N.D.†	N.D.	N.D.-0.05	N.D.-0.2
Urban (Lansing and East Lansing, Michigan)	5			N.D.	0.03-1.2	0.03-2	0.05-2
Major metropolitan (Chicago, Illinois)	8			0.005-0.03	0.03-0.3	0.1-3	0.4-22
Dow Chemical (Midland, Michigan)	5	0.8-18	0.3-100	1-120	7-280	70-3,200	490-20,000
Dust							
Dow Chemical laboratory	6	0.5-2	0.7-3	1-4	9-35	140-1,200	650-7,500
Midland, Michigan	2			0.03-0.04 (0.02)	0.2-0.4	2-4	20-30
Metropolitan (Detroit, Michigan)	4			N.D.-0.03	N.D.-0.3	0.3-4	0.1-4
Metropolitan (St. Louis, Missouri)	1	0.16	0.12	0.3	2	34	210
Metropolitan (Chicago, Illinois)	2			0.04 (0.04)	N.D.-0.3	0.6-3	3-8
Wastewater treatment sludge							
Commercial sludge fertilizer (Milwaukee, Wisconsin)	1	0.29	0.02	0.31	2	30	180
Incinerators, powerhouse							
Dow powerhouse	1	38 (20)	N.D. (10)	38 (20)	2	4	24
Dow rotary incinerator stack (present normal operation with supplemental fuel)‡	5			N.D. (2)	1-5	4-100	9-950
Dow stationary tar burner stack (normal operation with supplemental fuel)	5	N.D.	N.D.	N.D.	1-20	27-160	190-440
U.S. municipal incinerator (electrostatic precipitator) (Nashville, Tennessee)	1	7.3	0.4	7.7	14	28	30
European municipal incinerators				2-20	30-200	60-130	40-120
Mufflers							
Diesel truck muffler	2	0.02	0.003	0.023	0.020	0.100	0.26
Auto muffler	4	N.D.-0.004	N.D.-0.004	N.D.-0.008	N.D.	0.003-0.01	0.02-0.07
Other sources							
Home fireplace soot	2	N.D.-0.3	N.D.-0.1	N.D.-0.4	0.2-3	0.7-16	0.9-25
Home electrostatic precipitator	1	0.4 (0.4)	0.6	1.0	34	430	1,300
Cigarette smoke	2	N.D.	N.D.	N.D.	0.004-0.008	0.009	0.02-0.05
Charcoal-broiled steak	4	N.D.	N.D.	N.D.	N.D.	N.D.	0.03 (0.03)

*Where multiple samples were analyzed from similar sources, the range of observed values is shown. †N.D. indicates that the signal observed was less than 2.5 times noise. Limits of detection generally observed were TCDD, 0.001 to 0.01 ppb; HCDD, 0.01 to 0.05 ppb; H_7CDD, 0.005 to 0.03 ppb; and OCDD, 0.01 to 0.05 ppb. Limits of detection not within these ranges are shown parenthetically after the value reported for signals between 2.5 and 10 times noise. ‡Data without supplemental fuel not included here because this practice has been eliminated.

for the rotary kiln incinerator are given in Table 4. There is a dramatic difference in chlorinated dioxin concentration between runs with supplemental fuel and without supplemental fuel. The data for the stationary tar burner are summarized in Table 3.

An examination of particulate material collected by the electrostatic precipitator on a municipal refuse incinerator in Nashville, Tennessee, also confirmed the presence of chlorinated dioxins. Table 3 presents the results of this analysis. The performance of this and other currently licensed municipal incinerators has been described in a recent article on refuse fuel recovery (*19*).

Data on samples taken from the stack of a Dow Midland powerhouse operating under normal conditions with fuel oil and coal are presented in Table 3. Approximate data for the European municipal incinerators are also shown for comparison.

Table 4. Chlorinated dioxin content of particulate matter from the rotary kiln incinerator.

Sample	Fuel*		Apparent dioxins, ng/g (ppb)				
	Kiln	Secondary	TCDD Other isomers	TCDD 2,3,7,8-	HCDD	H_7CDD	OCDD
			Without supplemental fuel				
R_1F_1	T, SW, G	T	1,800	2,800†	13,000	110,000	180,000
R_1F_2	T, SW, G		5,000	8,200†	65,000	510,000	810,000
R_2F_1	T, SW, G		3,300	110	1,300	2,000	3,000
R_3F_1	T, SW, G		12,000	N.D. (260)‡	5,600	37,000	59,000
			With supplemental fuel				
R_3	T, SW, G	O, G	N.D. (8.0)	N.D. (2.0)	1.4	13.0	30.0
R_4	T, SW, G		N.D. (7.0)	N.D. (5.0)	N.D. (1.0)	4.0	9.0
R_5	T, SW, G		N.D. (2.0)	N.D. (2.0)	N.D. (0.5)	6.0	15.0
R_6	T, SW, G	T, G	N.D. (2.0)	N.D. (4.0)	5.0	27.0	170.0
R_7	T, SW, G		N.D. (2.0)	N.D. (2.0)	4.0	110.0	950.0

*T, tars; SW, solid waste; G, gas; O, oil. †The high results reported for the 2,3,7,8- isomer are probably due to analysis by the nonspecific GC-MS packed-column method. Later results were obtained with a capillary column specific for 2,3,7,8-TCDD. The TCDD results from run 1 (R_1) are not comparable to those from runs 2 and 3. ‡Numbers in parentheses are limits of detection, as explained in a Table 3 footnote.

Table 5. Other identified chlorinated compounds.*

Sample source	Chlorinated dibenzofurans Hexa-	Chlorinated dibenzofurans Hepta-	Chlorinated dibenzofurans Octa-	Decachlorobiphenyl	Polychlorinated terphenyls
Dow research building	++	++	++		++
Midland city		+	+		+
Fireplace soot		+	+		+
All soil samples		+	+		+
Electrostatic precipitator		+	+		+
Metropolitan area dust (Detroit)					+
Urban area soil (Lansing and East Lansing)		+	+		+
Metropolitan area dust					
Chicago		++	++		++†
St. Louis		+	+		+
Metropolitan area soil (Chicago)		++	++	++	+†

*(+) Positive according to retention time on a liquid chromatogram, GC-MS not used; (++) positive by both LC and GC-MS. †Very large amount relative to other samples.

Table 6. Chlorinated dioxins in rotary kiln incinerator scrubber water.

Sample	Apparent dioxins, ng/g (ppb)				
	TCDD Other isomers	TCDD 2,3,7,8-	HCDD	H_7CDD	OCDD
Particulates filtered from scrubber water					
Without supplemental fuel	300	2,200*	3,400	26,000	42,000
With supplemental fuel	14	32*	200	970	1,200
Filtered scrubber water without supplemental fuel	0.0018 (0.01)	0.001* (0.0006)	0.005	0.024	0.026

*The analytical method did not separate 2,3,7,8-TCDD from 11 other isomers.

Combustion of Dioxins

Early in 1965 Dow analytical scientists showed that TCDD decomposes 99.95 percent at 800°C in a stream of air passing through an unpacked quartz tube containing the TCDD (*20*). Consequently, it was accepted that TCDD would be destroyed in a system such as a tar burner. A further study in 1970 (*21*) confirmed these results and also showed that the 2,3,7,8-tetra- isomer is stable below 800°C.

Another Dow study in 1970 (*19*) established that the combustion products of TCDD in a 150 percent excess of air are water, carbon dioxide, hydrogen chloride, and chlorine. The adiabatic flame temperature was calculated as 1025°C. At this temperature the HCl/Cl_2 mole ratio is 3.05/0.48. This study, coupled with the earlier studies, led us to conclude that, below 800°C, the destruction of TCDD is relatively incomplete.

In preparation for the incineration at sea of the mixture known as Agent Orange (*22*), the U.S. Air Force contracted with the Marquardt Company, Van Nuys, California, to conduct tests on the combustion of Agent Orange with firewall temperatures of 1150°, 1400°, and 1600°C and a minimum of 30 percent excess air. TCDD, a trace impurity in one of the components of Agent Orange, was not found in the particulate matter in either the stack or the scrubber water at limits of detection of 300 and 2 ppb, respectively. In these tests, the walls of the combustion chamber were preheated to the desired temperature (1400°C) and the Agent Orange was added without auxiliary fuel. The temperature of the flame was not measured.

The Air Force disposed of Agent Orange in the summer of 1977 by high-temperature incineration at sea on a Dutch-owned ship M/T *Vulcanus*. Although the walls of the combustion chamber were maintained at 1273°C on the average and the high flame temperature was measured optically as 1500°C, the EPA, which monitored this program, reported a combustion efficiency for TCDD of only about 99.9 percent (*23*).

Particulate Matter from Mufflers

Mufflers from gasoline-powered automobiles were collected at muffler shops in Pontiac and Detroit, Michigan (more than 100 miles from Midland), as they were removed from cars. The car owners voluntarily gave the mufflers and information about mileage and gasoline type used. The make, model, and mileage of each car were noted. The mufflers were transported to the Dow Analytical Laboratories sealed in plastic bags. Mufflers from diesel-powered trucks were collected at Auburn and Saginaw, Michigan. They were sealed and transported as above.

At the Dow Analytical Laboratories, the inside chambers of the mufflers were scraped and residue was collected from these chambers and analyzed for chlorinated dioxins by both GC with electron capture detection and GC-MS after liquid chromatographic separation. Results are summarized in Table 3. The discovery that there are chlorinated dibenzo-*p*-dioxins in particulate emissions from internal combustion engines indicated that these compounds may be ubiquitous in combustion processes.

Other Sources

Soot from fireplaces. The carbonaceous material on the walls of the metal firebox of a 25-year-old fireplace, whose flue had not been cleaned for 10 years, was sampled in a manner designed to avoid contamination. Birch, oak, willow, mountain ash, and applewood untreated with preservatives had been burned in this fireplace, along with some paper to start the fire. The residue on firebrick in a 12-year-old fireplace, whose chimney had never been cleaned, was also sampled. The fuel had been hardwood, mostly oak, none of it treated with any wood preservatives. These samples were analyzed as described for mufflers. The results are presented in Table 3.

Particulates from a home electrostatic precipitator. Particulate material was collected from a home electrostatic precipitator. The collection represents the material accumulated during six spring and summer months of operation of the precipitator. The results obtained are also reported in Table 3.

Charcoal-broiled steaks. New York strip steaks grilled over a charcoal fire were sampled at 13, 18, and 28 minutes. Grilling for these times produced rare, well-done, and overdone samples. Each of the three samples was immediately wrapped in aluminum foil, placed in a plastic bag, and then put in a freezer to await analysis. Analyses were performed by method ML-AM-78-63. The results are shown in Table 3.

Cigarette smoke. Smoke generated by the simulated smoking of cigarettes (an arbitrarily selected national brand without filters) was analyzed for trace levels of chlorinated dioxins. The smoke was collected on special collection matrices consisting of 100/120-mesh silica (coated in situ with 20 percent hexadecane by weight) contained in a disposable glass transfer pipette. The cigarette was attached to the pipette by cleaned latex rubber tubing and puffed by applying gentle vacuum with a rubber pipette bulb. Approximately 20 to 30 puffs nominally 2 to 3 seconds in duration were collected from each cigarette. An entire package of 20 cigarettes was combusted during each experiment. Combustion experiments were conducted in two different urban locations. Before use, the inlet end of each collection tube was spiked with 2.0 nanograms of ^{13}C-labeled 2,3,7,8-TCDD, which served as an internal standard for TCDD quantitation after residue cleanup. Each collection tube was extracted with hexane, followed by a multistep cleanup, including reverse phase LC, to remove interferences. The LC eluent was subjected to both low-resolution GC-MS and electron capture GC analysis. The results are given in Table 3.

The further discovery that chlorinated dibenzo-*p*-dioxins are the result of commonplace burning involving fireplaces, charcoal broilers, and cigarettes supports the conclusion that these compounds may be ubiquitous in combustion processes.

Other Chlorinated Compounds Identified

The following compounds were identified in many of the samples: hexa-, hepta-, and octachlorodibenzofurans, decachlorobiphenyl, and polychlorinated terphenyls. Since analytical standards were not available and recoveries are not known, no quantitative measurements were made. These observations are in Table 5. The samples also contained numerous unknowns that were not qualitatively identified.

Waterborne particulates from scrubbers. Composite scrubber water samples were taken from the rotary kiln incinerator during the sampling reported in Table 4. The particulate matter was separated by filtration and the chlorinated dioxins were determined by analytical method ML-AM-78-63; the results are reported in Table 6. The water filtrate from the scrubber water composite was also analyzed and the results are shown in Table 6. The data from Table 6 together with the relative weight of scrubber water show that more than 99.7 percent of the chlorinated dioxins are associated with filterable particulate matter.

Conclusions

The following conclusions are supported by this study:

1) Some refuse incinerators and fossil-fueled powerhouses are sources of airborne and waterborne particulates that contain chlorinated dioxins.

2) Some gasoline- and diesel-fueled automobiles and trucks are sources of airborne particulates that contain chlorinated dioxins.

3) Some fireplaces, charcoal grills, and cigarettes have been identified as sources of particulate matter that contains chlorinated dioxins.

4) Chlorinated dioxins enter the environment by way of airborne particulate matter from combustion sources and waterborne particulate matter from scrubbers, which are increasingly required for major combustion sources.

5) Additional chlorinated compounds were observed and apparently arise from combustion; they include chlorinated dibenzofurans, decachlorobiphenyl, polychlorinated terphenyls, and others that have not been identified.

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Multidimensional Scaling, Tree-Fitting, and Clustering

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Summary. American mathematical psychologists have developed computer-based methods for constructing representations of the psychological structure of a set of stimuli on the basis of pairwise measures of similarity or confusability. Applications to perceptual and semantic data illustrate how complementary aspects of the underlying psychological structure are revealed by different types of representations, including multidimensional spatial configurations and nondimensional tree-structures or clusterings.

Without any quantitative information about the physical properties of colors, tones, speech sounds, or words, we can learn something about how humans process such stimuli from an analysis of ratings of perceived similarity, frequencies with which the stimuli are actually confused with each other, latencies of discriminative responses, or, in the case of infants and other animals, magnitudes of the "orienting reflex" when one stimulus is substituted for the other (*1*, *2*). This purely psychological approach has advantages over a psychophysical one in the case of complex, naturalistic stimuli such as faces, for which the relevant physical dimensions are as yet poorly characterized, and it is essential in the case of symbolic stimuli such as words, for which the relevant semantic dimensions are not even present in the physical stimuli.

Early History

Proposals that stimuli be modeled by points in a space in such a way that perceived similarity is represented by spatial proximity go back to the suggestions of Isaac Newton (*3*) that spectral hues be represented on a circle, of Helmholtz and Schrödinger (*4*) that colors in general be represented in a curved Riemannian manifold, of Drobisch (*5*) that pure tones be represented on a helix, and of Henning (*6*) that odors and tastes be represented within a prism and a tetrahedron, respectively. However, little progress was made toward the development of data-analytic methods for the construction of such spatial representations on the basis of psychological data until the efforts of a group of psychometricians, beginning in the late 1930's at Chicago and subsequently moving to Princeton, culminated in the 1952 development by Torgerson of the first fully workable method of metric multidimensional scaling (*7*, *8*).

This method is called "metric" because it requires psychological estimates of metric distances between the stimuli. Either one had to assume that the data (for example, subjective ratings of dissimilarity) increased linearly with such distances (*9*), or one had to use some preliminary (for example, "Thurstonian") scaling procedure to convert the data into numbers that could then be assumed to increase linearly with distance (*8*). Even after such numbers had been obtained, the computation required several more stages in which one successively (i) estimated the "additive constant" and thus obtained a matrix of estimated distances between the points; and then, on the basis of a theorem of Young and Householder (*10*), (ii) computed a matrix of scalar products between the points (interpreted as vectors issuing from their common centroid), and (iii) factored this matrix into its eigenvalues and vectors to obtain explicit coordinates for the stimuli in a Euclidean space of a number of dimensions corresponding to the number of large eigenvalues.

Meanwhile, I had been approaching the problem of analyzing such measures of similarity by estimating the nonlinear form of the monotonic function, f_{mon},

$$s_{ij} = f_{\mathrm{mon}}(d_{ij}) \qquad (1)$$

where s_{ij} is the obtained measure of similarity between stimuli i and j and where d_{ij} is a distance between corresponding points i and j that satisfies quite general metric conditions. The conditions that I proposed were (i) the distance axioms of

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