Chemometric Analysis of Potential Sources of Polychlorinated Dibenzo-p-Dioxin and Dibenzofuran Residues in Surficial Sediments from Newark Bay, New Jersey

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Introduction

The identification of polychlorinated-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in environmental matrices and investigations of the sources and fate of these compounds in the environment are important issues. The results of numerous studies indicate that these compounds are widely distributed in soils, sediments, and air from industrialized and heavily populated environments at low part per trillion concentrations[1,2,3].

Newark Bay, New Jersey is an enclosed estuary formed by the confluence of the tidal Passaic River and Hackensack River in the north and the Arthur Kill and the Kill Van Kull in the south. The estuary is surrounded by the New York City, NY and Newark, NJ metropolitan areas, the largest industrialized region in the eastern United States. It has been adversely impacted more than a century of industrial and domestic pollution[4]. Despite evidence indicating numerous point and nonpoint sources of PCDD/Fs to the environment[4,6,7], some researchers have suggested that the majority of PCDD/Fs found in sediments and biota are associated with a single source located near the confluence of the lower Passaic River and Newark Bay[8,9].

In earlier studies, the concentrations of 2,3,7,8-substituted PCDD/F residues and congeners were determined in surficial sediments from the estuary; several unique fingerprint patterns were identified using principal components analysis and cluster analysis[10], multivariate statistical techniques used increasingly in pattern recognition studies[2,3]. The isomeric fingerprint patterns in sediments from the lower Passaic River and Newark Bay were similar to those found in sediments from other waterways located within industrial or heavily populated areas[11]. In this study, the distributions of the congener groups and 2,3,7,8-substituted residues in surficial sediments were compared to those reported in various known or suspected industrial and municipal sources using principal components analysis. The objectives were to: (1) determine whether the distributions of PCDD/Fs in surficial sediments from Newark Bay are similar or different from those associated with known or suspected environmental sources; (2) determine whether more than one potential source could explain the presence of these compounds in sediments from Newark Bay; and, (3) determine if other sources are continuing to contribute PCDD/Fs to sediments.

Methods

The clean-up and quantification by high resolution gas chromatography / high resolution mass spectrometry, analytical results, and statistical correlations of the measured PCDD/F residues in sediments were reported in detail elsewhere[10,11]. The concentrations of PCDD/F congeners and 2,3,7,8-substituted isomers in industrial process residues, contaminated soils, urban air, chemical formulations, and municipal sludges and effluents were collected from published literature. In most cases, researchers reported all ten congener groups and fifteen 2,3,7,8-substituted PCDD/Fs, as well as method detection limits for residues or congeners identified as non-detect (ND). For

2,3,7,8-substituted residues identified as ND, the detection limit from each individual sample analysis or the highest detection limit reported among isomers within the same congener group was included in the data set. For a congener group identified as ND, the highest detection limit reported among the 2,3,7,8-substituted isomers measured within the congener group was assumed.

Principal components analysis was conducted using the statistical software program Pirouette (Version 1.0, Infometrix Inc., Seattle, WA). The data were scaled to minimize any statistical bias associated with the orders of magnitude differences in chemical concentrations. In accordance with Schwartz and Stalling[12] involving chemometric analyses of PCB residue profiles, the data were normalized to minimize the influence of concentration-dependent information on the first principal component. The concentrations of the 2,3,7,8-substituted isomers were normalized as a percentage of the combined sum of the concentrations of the fifteen residues. The concentrations of the congeners were normalized as a percentage of the combined sum of the ten congener groups. Congeners and 2,3,7,8-substituted isomers identified in the database as ND were assumed to be present at the limit of detection limit.

Results

Three dimensional principal components scores plots of the normalized 2,3,7,8-substituted residues and congener groups are shown in Figures 1 and 2, respectively. The distributions of PCDD/Fs found in surficial sediments from Newark Bay (R1-19) were similar to those found in several industrial, commercial, and residential sources that are typically present in urban environments. The congener and 2,3,7,8-substituted PCDD/F fingerprint profiles were similar to those found in municipal sewage sludge (SS1-16), o-chloroanil (OC1-4), pentachlorophenol (PC1-3, NPC1-3), chimney soot from oil burning furnaces (OL1-20), trichlorobenzene (TB), and MSW fly ash (ASH8-10), and paper mill black-liquor recovery furnaces (BL1-9). The 2,3,7,8-substituted profile in sediments collected from the Hackensack River (R3 and R18) and in one sample from the lower Passaic River (R4) were very similar to that generated by the pyrolysis of polyvinylchloride (PV1-6).

Other comparisons indicated that the 2,3,7,8-substituted residue profiles in sediments were similar to those found in ambient urban air particulates collected from urban areas in Hamburg, Germany and Bridgeport, CT USA, soils from semirural areas in the United Kingdom, air in automobile traffic tunnels, and soils from scrap metal reprocessors.

The variations among the congener and 2,3,7,8-substituted fingerprint patterns could be largely explained by the distributions of TCDD, TCDF, and the higher chlorinated PCDD/F congener groups (Figure 2 inset). For example, pattern similarities between lower Passaic River sediments and municipal sewage sludge, pentachlorophenol, and effluent from paper mill black-liquor recovery furnaces were attributed to similar distributions of 2,3,7,8-TCDF, 2,3,7,8-TCDD, total PeCDF, total HxCDF, total HpCDD, OCDF, and OCDD. These isomers and congeners also were responsible for the different profiles found in PCB Arochlor (PCBa1-6) and Kannechlor (PCBk1-6) formulations, graphite electrode sludge (GE1-3), and soot from coal burning furnaces (CL1-5).

Discussion and Conclusions

In recent years, there has been considerable discussion about the historical release of PCDD/Fs in Newark Bay. It has been suggested that a single source is responsible for the presence of 2,3,7,8-TCDD and 2,3,7,8-TCDF in sediments[9]. Although it is clear that the concentrations of 2,3,7,8-TCDD are higher near one or more point sources, there is no evidence that a single source can be responsible for the contamination. The results of this study show that the fingerprint patterns in Newark Bay were closely related to those generated by several different chemical manufacturing processes and municipal activities. The profile similarities and differences suggest that the presence of 2,3,7,8-substituted residues in surficial sediments are likely due to many sources. Several of these potential sources, including scrap metal refineries, pulp and paper mills, copper smelters, chemical manufacturing plants, municipal sewage treatment plants, and industrial / municipal incinerators, have been in operation along the shores of the estuary for

several decades[4,6,7].

Anthropogenic PCDD/Fs have substantially increased in the environment since the 1940's[1,2,13]. Releases from the combustion of diesel and leaded fuels are significant sources in urban environments, where automobile and shipping traffic increased with post-World War II economic expansion[1,14]. PCDD/F congener profiles in emissions from municipal solid waste incinerators and coal-fired power plants further implicate combustion as a major source[14]. Atmospheric deposition has been identified as the predominant source of PCDD/Fs in post-1940 dated sediments from relatively remote waterbodies[13]. The dramatic increased usage of pentachlorophenol and a variety of chlorinated organic chemicals since 1940 also has contributed to an increased background level in soils and sediments[1,2,3,11,13].

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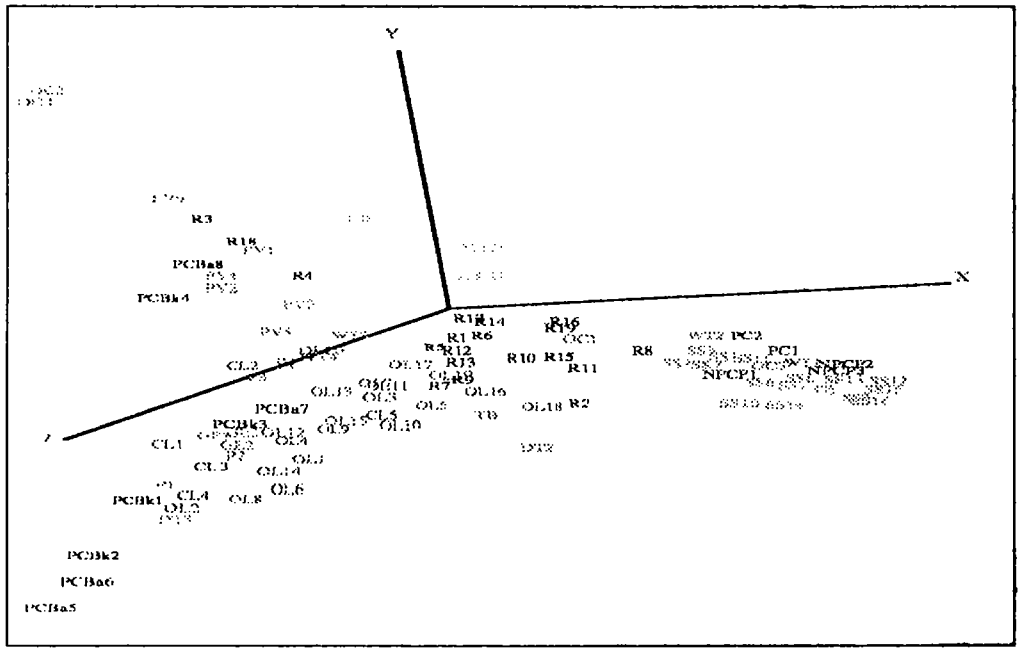

Fig. 1. Three dimensional principal components scores plot of normalized 2,3,7,8-substituted PCDD and PCDF isomer patterns in surficial sediments from Newark Bay (R1 - R19), industrial sludges and effluents, pyrolytic and combustion residues, and chemical residues.

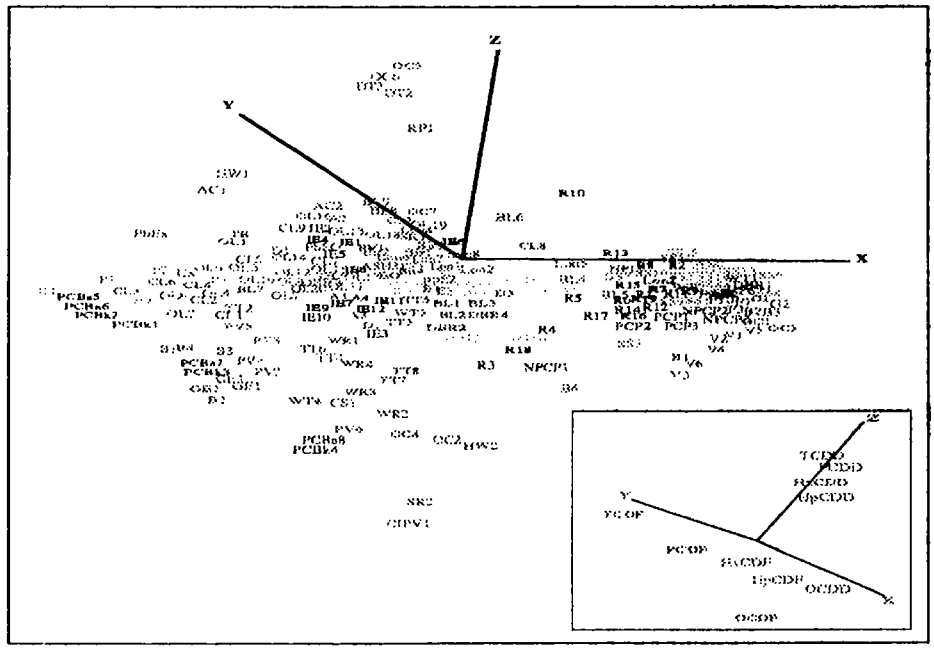

Fig. 2 Three dimensional principal components scores plot of normalized PCDD and PCDF congener patterns in surficial sediments from Newark Bay (samples R1 - R19) and various environmental sources. The loadings plot for the first three principal components is shown in the inset. Congeners located furthest from the origin are responsible for the differences between samples shown in the scores plot.