POLYCHLORINATED DIBENZO-*p*-DIOXIN AND DIBENZOFURAN RESIDUES IN ESTUARINE AND COASTAL NORTH SEA SEDIMENTS: SOURCES AND DISTRIBUTION

ERIK H.G. EVERS,*† HANS J.C. KLAMER,† REMI W.P.M. LAANE†
and HARRIE A.J. GOVERS‡

†Ministry of Transport, Public Works and Water Management,
Institute for Marine and Coastal Management/RIKZ (Tidal Waters Division),
P.O. Box 20907, 2500 EX The Hague, The Netherlands
‡Department of Environmental and Toxicological Chemistry, University of Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Abstract—Sediments from two depositional zones of the North Sea (the Wadden Sea and Oyster Grounds) and from the estuaries of the rivers Rhine, Meuse, Scheldt, Ems, and Humber were analyzed for polychlorinated dibenzofurans (PCDFs) and dibenzo-*p*-dioxins (PCDDs) using a congener-specific procedure. A simple grain-size correction procedure was utilized for the comparison of PCDF and PCDD concentrations in sediments from different origin. This procedure, which applies wet sieving of fresh sediment and isolating and analyzing the <63-μm grain-size fraction, was found to be appropriate for comparing levels of PCDFs and PCDDs in different estuarine and coastal sediments. PCDFs were more widely encountered than PCDDs in all sediments, except for the Ems-Dollard and the Humber estuary. The highest concentrations were found in the outflow sediments of the rivers Rhine and Humber. Concentrations up to 2,980 ng/kg PCDFs, principally 1,2,3,4,6,7,8-HpCDF and OCDF, and up to 1,760 ng/kg PCDDs, principally OCDD, were determined in the River Rhine sediments. Principal component analysis was used to visualize the compositional changes of PCDD and PCDF profiles in the sediments. Two-dimensional projections based on sample scores from the principal component models showed a marked influence of the River Rhine on the presence of these compounds in the western Wadden Sea and the Oyster Grounds. Based on a chemometric evaluation of chromatographic profiles of these coastal, estuarine and related freshwater sediments, we have deduced that these compounds originate primarily from industrial operation discharges, related to the production of chloroaliphatic compounds and the chloralkali industry along the River Rhine. The atmospheric deposition of combustion-generated PCDDs and PCDFs appeared significant only for remote marine environments.

Keywords—Chlorinated dioxins   Chlorinated furans   Sources   Sediments
Principal component analysis

INTRODUCTION

The North Sea is a semienclosed shelf sea of approximately 6×10^5 km^2 surrounded by land carrying dense and highly industrialized human populations. It is extremely important for transport and belongs to the most productive fishing areas in the world. Based on measurements of water currents, vertical salinity gradients, and various micropollutants, it has been established that the water quality of the Dutch coastal zone largely depends on the input of the River Rhine into the coastal zone and the interactions between river and seawater after flowing into the sea [1,2]. Therefore, suspended matter with associated hydrophobic contaminants from the Rhine, such as polychlorinated dibenzofurans (PCDFs) and dibenzo-*p*-dioxins (PCDDs), is partly deposited in the Wadden Sea, an intertidal coastal sea adjacent to the North Sea [3]. Rhine water also finds its way toward the Wadden Sea, following the inland route of the River Rhine, the River IJssel, and Lake IJssel.

Residues of PCDFs and PCDDs in Dutch inland waters originate from the transboundary pollution of the rivers Rhine [4,5] and Meuse [5] and by atmospheric deposition of combustion-generated compounds [6]. They enter the aquatic environme⌐

as unintentional by-products of two major sources. First, effluents and products of industrial processes applying chlorine or chlorinated solvents at elevated temperatures for the manufacture of a wide range of chemicals — especially chlorinated aromatic compounds — contain PCDFs and PCDDs at various levels and have been identified as key chemical sources of these compounds found in the environment [7-9]. Second, they are transferred throughout terrestrial and aquatic media after being emitted into the atmosphere from the incineration of municipal [10] and chemical [11] wastes and numerous other combustion processes such as fossil fuel combustion, the burning of natural materials (wood or straw) [12], and the use of leaded gasoline in combustion engines [13,14].

In addition, accidental fires involving chlorine-containing dielectric fluids such as polychlorinated biphenyls (PCBs) [15] and industrial calamities of the production of chloroaromatics [16] can result in serious contamination of relatively small areas. Another, probably natural, PCDD and PCDF source has recently been found in laboratory experiments [17]. Chlorophenols, which can originate from the catalyzed chlorination of humic material by haloperoxidases [18], can be converted into PCDDs and PCDFs by peroxidase-mediated reactions. Until now, however, natural chlorination reactions have not been proven in the environment.

The two major sources mentioned above can be subdivided into more specific combustion and industry-related sources whose emissions potentially end up in the North Sea, as shown in Table 1. Some of these sources emit distinctly different PCDD and PCDF congener patterns into the environment. The production of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and its sodium salt characteristically results in the formation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) [7]. The use of pentachlorophenol (PCP) causes a significant input of octachlorodibenzo-p-dioxin (OCDD) and other highly chlorinated dioxins and furans into the application area [19-21]. Both the manufacture of 1,2-dichloroethane (ethylene dichloride, EDC) using a copper chloride-catalyzed oxyhydrochlorination process at temperatures of 225 to 325°C [9,22,23] and the electrolytic production of chlorine using graphite electrodes [24] have been identified as sources emitting PCDDs and PCDFs with a typical "chlorination pattern" [25]. These sources are characterized by the presence of huge amounts of octa- and heptachlorodibenzofurans (OCDF and HpCDFs, respectively). During pulp and paper bleaching, mainly 2,3,7,8-chloro-substituted tetra-

and pentachlorodibenzo-p-dioxins and dibenzofurans are formed ("bleaching pattern") [26]. Combustion [10,27], metal reclamation [28], and steel [29] processes emit virtually all PCDD and PCDF congeners, with the two octachlorinated compounds as major contaminants ("combustion pattern").

As a consequence, PCDDs and PCDFs have contaminated landfills [30,31] and have entered sediments of lakes [32,33], rivers [4,21,34], estuaries [35-38], and marine waters [39-41]. Over the past few years results of numerous investigations indicated that PCDDs and PCDFs also occur ubiquitously in marine and estuarine organisms [42-51]. From these studies it appeared that PCDFs, which in Dutch inland sediments generally dominated over PCDDs [4], might be a greater global pollutant than PCDDs [42], but their principal sources were less well documented than the sources of PCDDs [52].

The objective of the present study was to provide the first data on levels, congener profiles, geographical extent, and origin of the PCDD and PCDF contamination of estuarine and coastal North Sea sediments. The results were visualized and statistically interpreted by the use of principal component analysis (PCA) of PCDD and PCDF congener patterns of sediments, effluents, and wastes from or related to industrial and combustion sources. Various authors recognized the possibility to identify dominant sources of PCDDs and PCDFs for biota [33,53,54] and sediments [22,37,41,55] through the application of chemometric methods. Data from the analysis of measured PCDD and PCDF congeners in environmental samples may form data clusters that are structurally related to such factors as specific industrial sources and discharges, combustion processes, or other contaminating sources [55]. The relevance of direct (industrial discharges along the rivers and their estuaries) and indirect or diffusive (atmospheric deposition of combustion-generated compounds) sources is discussed. Furthermore, a simple grain-size correction procedure was tested for its applicability to make comparisons between concentrations of PCDDs and PCDFs in coastal sediments from different origins.

METHODS

Sediment collection

The Rhine and Humber samples were collected in June and August 1990 during cruises with the Rijkswaterstaat research vessel MS *Argus* and the RRS *Challenger*, respectively, of the Natural Environment Research Council (NERC), United Kingdom. The other samples were collected as a part

Table 1. Major sources and source characteristics of PCDDs and PCDFs

Source	Major emission into compartment/pollution type	Characteristic congeners	Key refs.
Combustion			
Municipal/hospital/chemical waste incineration	Air/diffusive and point source	All congeners present; levels of HpCDDs/Fs and OCDD are usually highest; equal amounts of PCDDs and PCDFs	[10,75]
Automobile fuels	Air/diffusive	(see "Waste incineration")	
Recycling processes, e.g., metal reclamation	Air/point source	All congeners present; usually $\Sigma(PCDF) > \Sigma(PCDD)$	[30,31]
Industrial processes			
Production of chloroaromatics			
Chlorophenols and products, e.g.,			
2,4,5-T; 2,4,5-trichlorophenol,	Soil and water/diffusive	2,3,7,8-/1,3,7,8-TCDD	[7,8]
2,4-Dichlorophenoxyacetic acid	Soil and water/diffusive	1,3,6,8-/1,3,7,9-TCDD; 2,4,6,8-TCDF	[7,8]
Pentachlorophenol	Water/diffusive	1,2,4,6,8-PnCDF; 1,2,3,4,6,8-, 1,2,4,6,7,8-, 1,2,4,6,8,9-HxCDFs; 1,2,4,6,7,9/8,9-, 1,2,3,6,7,9/8,9 HxCDDs; HpCDDs/Fs + OCDD/F	[19]
Polychlorinated biphenyls	Landfills and water/point source resp. diffusive	Only PCDFs present; pattern dependent on PCB preparation; dominant congeners 1,2,4,7-/1,3,6,7-, 1,3,4,6/1,2,4,8-, 1,2,3,9-/2,3,4,7-, 2,3,7,8-/2,3,4,8-TCDF; 1,2,4,7,8-/2,3,4,7,8-PnCDF; 1,2,3,4,7,8-HxCDF	[76,77]
Production of chloroaliphatics, e.g., 1,2,-Dichloroethane (oxyhydro-chlorination of ethylene)	Water/point source	Nearly all tetra- through octa-CDF congeners present; high levels of OCDF/D and HpCDFs; no tetra- and penta-CDDs; ratio $\Sigma(PCDF)/\Sigma(PCDD) > 10$; congeners show a typical chlorination pattern	[9]
Electrolytic production of chlorine using graphite anodes	Water/point source	(see "Production of chloroaliphatics") congeners show a typical chlorination pattern	[24,25]
Pulp and paper bleaching	Water/point source	2,3,7,8-TCDF/D; 1,2,3,7,8- and 1,2,3,7,8,9-HxCDD; some HpCDD and OCDD; no HxCDFs, HpCDFs, and OCDF; congeners show a typical bleaching pattern	[26]
Production of nonferrous metals			
Magnesium Nickel refinery	Water/point source	1,2,7,8-, 2,3,7,8-, 1,3,7,8/9-TCDF; 1,2,3,6,8,-/1,3,4,7,9-, 1,2,3,4,8/7,8-, 1,2,4,7,8-PCDF; nickel refinery gives different congener distribution of PnCDFs; ratio $\Sigma(PCDF)/\Sigma(PCDD) > 10$	[54,71,72]

of the Dutch contribution to the Joint Monitoring Programme (JMP) and North Sea Task Force (NSTF) baseline monitoring survey with the Rijkswaterstaat research vessel MS *Holland*. The JMP/NSTF was established in 1978 within the framework of the Oslo (1972) and Paris (1974) conventions for the prevention of marine pollution.

Sediment samples were collected by means of subsampling the upper 5-cm layer of sediment cores obtained with a stainless steel box corer of 50- × 50-cm surface area. The western Wadden Sea samples were taken manually with a nylon shovel on a tidal flat during the sampling campaign in June 1987 within a distance of several meters from each other. These cogenetic samples, which showed a gradient in the clay content, have been used to examine the distribution and standardization of both inorganic and organic micropollutants among several sediment grain-size fractions [56].

Analytical procedures

Specific grain-size fractions ($<1,000$ and $<63 \mu m$) were obtained by wet sieving the sediment with filtrate water (to disintegrate aggregates of fine material) over a specially designed nylon sieve with a pore size of 63 μm [56]. The collected fine fraction was frozen on board the ship, freeze dried, and stored at ambient temperature in the laboratory until further analysis. Full details of the grain-size distributions of the JMP/NSTF sediments are given by Akkerman et al. [57]. The dry weight and OC content of the sediments were determined gravimetrically after heating subsamples at 105°C for 4 h, and spectrophotometrically after wet oxidizing subsamples by potassium dichromate in hydrochloric acid at 120°C [58], respectively. The grain-size distribution of the sand fraction from the OC- and limestone-cleared sediments was determined using the Malvern analyzer (Master Particle Sizer® M3.1; Malvern Instruments, United Kingdom). The percentage of loss on ignition (% LOI) was determined gravimetrically after heating at 600°C during 45 min.

The quantification of the PCDD and PCDF amounts in the sediments was based on a slightly modified analytical procedure developed by Lamparski and Nestrick [59]. This method has been described in detail elsewhere [4] and is summarized below. The cleanup procedure involved Soxhlet extraction of freeze-dried sediment with toluene (Janssen Chimica, Beerse, Belgium); sample enrichment by sulfuric acid–, sodium hydroxide–, and silver nitrate–coated silica gel; and alumina adsorption column chromatography (Merck, Darmstadt, Germany). Separation of the tetra- through octachlorinated PCDD and PCDF congeners (except

for OCDF) from the total mixture of chloroaromatics was accomplished by application of the open-column eluates to reversed-phase HPLC with a Zorbax-octadecylsilane column (DuPont Instruments, Newton, CT; 250 × 9.4 mm i.d. at 45°C) using methanol as an isocratic eluent (flow velocity 2.0 ml/min). OCDF was collected in a separate fraction to avoid decomposition in the injection port and adsorption on specific active spots in the polar capillary GC column [60,61].

Before high-resolution capillary gas chromatography- (HRGC-) electron impact mass spectrometry (MS) using the selected ion mode, the hexane extracts were evaporated to near dryness and redissolved in 10 μl nonane in microglass vials. Using a "cold-on-column" technique, 2.0 μl of the concentrated extract was injected into a Hewlett Packard (HP; Avondale, PA) 5890-A GC connected to a HP 5970 mass selective detector (MSD) at 70 eV. Specific GC conditions: Supelco (Bellefonte, PA) fused-silica capillary column (60 m SP-2331, ϕ 0.32 mm, film thickness 0.2 μm), using helium as a carrier gas (linear flow velocity 25 cm/s). Chromatographic conditions were similar for all analyses of the tetra- through octachlorinated PCDD and PCDF congeners, except for OCDF. The initial temperature of 160°C, was programed at 40°C/min to 200°C, then was programed at 4°C/min to a final temperature of 250°C. The OCDF fraction was analyzed separately using the same GC-MSD system equipped with a 60-m J & W Scientific (Folsum, CA) DB-5 capillary GC column, programing the initial temperature of 160°C, at 70°C/min, to a final temperature of 300°C. Three ions were monitored for each peak of interest. If the observed isotope ratio was not within 10% of the theoretical ratio or if the peak area was not above the threshold amount, then the calculated concentration was reported as below the detection limit.

An MS Chemstation® HP 59970 microcomputer, interfaced with the MSD, acquired data generated by the MSD. The quantitative values were corrected for losses during the analytical work by including a mixture of eleven $^{13}C_{12}$-labeled compounds as PCDD and PCDF surrogates for each chlorohomolog group (tetra- through octachloro-) and an external standard ($[^{13}C_6-]1,2,3,4$-TCDD). The recoveries of ^{13}C-labeled internal standards ranged from 62 to 84%. Detection limits ranged from 2 ng/kg for the individual lower chlorinated congeners to about 50 ng/kg for OCDD.

Data analysis

The data were transferred to an Olivetti M24 computer operating in an MS DOS environment ei-

ther manually or by way of a serial RS-232 link between the HP Chemstation and the Olivetti-PC, using a BASIC computer program. The transferred data were preprocessed and organized into a series of ASCII files, using a commercial spreadsheet program and combined with data from previous studies [4,9,22,55]. These files were loaded into the SIMCA-3B (Soft Independent Modelling of Class Analogy; Sepanova AB, S-12243 Enskede, Sweden) package with the module FIN-ASCII.

The congener-specific analysis of PCDDs and PCDFs in abiotic samples results in extensive data sets, often with a relatively low object- (sample-) to-variable (e.g., measured congener concentrations) ratio. To explore the different levels of information contained in the data sets, the SIMCA-3B method has been used to calculate and analyze principal components (PCs) [62–64]. This method reduces the comprehensive data set to a few PCs and performs especially well with many variables and few objects, compared to traditional methods of multivariate data analysis [63]. PCs are linear combinations of the original (n) variables constructed orthogonally to each other in the n-dimensional space. Essentially, PCA can be viewed as a projection method in which the intention is to preserve the maximum amount of variance and relations among samples and variables, while projecting down on to as few principal axes as possible. Interpretation of object grouping and variable correlation is made on object score and variable loading plots, respectively. For congeners that could not be analyzed above the limit of detection, the amount corresponding to half the detection limit has been used. To avoid any statistical bias associated with the differences of chemical concentrations in the samples [65], the data have been normalized by expressing the concentration of individual congeners as a percentage of the combined sum of all measured PCDD and PCDF congeners.

The SIMCA concept of disjoint modeling of classes has been used to construct PC models for sediments and air particulates with a known pollution history. The object standard deviation of the residuals (RSD) directly corresponds to the distance between objects and the classes. From the spread of the object points around the class model a tolerance interval for any probability level, usually 95%, can be calculated.

Literature data of sediments exposed to effluents containing PCDDs and PCDFs from chlorination processes (Chemieharbour [22]) and waste combustion (St. Laurensharbour [22]) near Rotterdam in The Netherlands, and sediments from the lower stretch of the River Rhine downstream of the industrialized Ruhr area in Germany [4,5] and West European air particulates [66], were added to the present estuarine and coastal sediment data. Four class models were constructed and graphically represented by residual or Coomans plots that can be used for the classification of (other) abiotic environmental samples [55].

RESULTS AND DISCUSSION

Characteristics of the sampling sites and sediments

The geographical position of the sampling locations and some sediment characteristics (percentage of sediment < 63 μm, and OC content) are summarized in Table 2. The sampling locations in the estuaries, the Wadden Sea, and the North Sea were selected in such a way that, besides taking account of important ecological areas, the influence of polluted riverborne material would be reflected in the sediments. All locations were situated in depositional zones that accumulate particle-associated contaminants transported within the natural water systems.

In its present shape the Rhine-Meuse estuary is completely artificial, changed by harbor works, dams, canalization, dredging, and reclamation of marshes and flats. Therefore, permanent deposition of sediments will hardly occur. The Scheldt estuary is a coastal plain estuary situated in the southwest of The Netherlands and the northwest of Belgium. Both the fluvial and upper estuary are polluted as a result of large wastewater discharges. The Oyster Grounds, large depressions in the southern North Sea, are muddy areas of approximately 4.7×10^3 km^2, with an annual sedimentation of $\pm 2 \times 10^9$ kg mud [67]. The Oyster Grounds contain a high benthic biomass and are important spawning areas for fish. Deposition of mud in the Wadden Sea, one of the largest wetlands of western Europe, occurs mainly on the tidal watersheds, along the inner margins, and particularly in the large embayments. The Humber estuary, on the English side of the North Sea, is a major estuary extending 62 km from the confluence of the Yorkshire River Ouse and the River Trent to the North Sea. The catchment area draining to the Humber is the largest of any estuary in the United Kingdom. It covers 27×10^3 km^2 and contains a wide variety of industry.

Results of sediment analysis

The analytical method resulted in the quantification of 104 congeners or congener groups. The most toxic 2,3,7,8-chloro-substituted congeners, except 1,2,3,7,8-PnCDF and 1,2,3,4,7,8-HxCDF, could be

Table 2. Locations, salinity, percentage of particles smaller than 63 μm, and OC content (in the <63-μm fraction) for the sampling areas[a]

Sample no.	Sampling location	Geographical position		Sampling date	Salinity (‰)	<63 μm (%)	OC (%)	Remarks
		Latitude	Longitude					
1	Western Wadden Sea	52°54'20"	04°55'40"	June 1987	–[b]	—	1.0	Sandy; fraction <1,000 μm
2	Western Wadden Sea	52°54'20"	04°55'40"	June 1987	—	—	2.1	Sandy; fraction <63 μm
3	Western Wadden Sea	52°54'20"	04°55'40"	June 1987	—	—	2.8	Fraction <1,000 μm
4	Western Wadden Sea	52°54'20"	04°55'40"	June 1987	—	—	2.2	Fraction <63 μm
5	Western Wadden Sea	52°54'20"	04°55'40"	June 1987	—	—	4.3	Muddy; fraction <1,000 μm
6	Western Wadden Sea	52°54'20"	04°55'40"	June 1987	—	—	2.8	Muddy; fraction <63 μm
7	Middle Wadden Sea	53°24'07"	05°43'42"	October 1990	33.8	1.0	2.4	Sand 96.6%
8	Ems–Dollard estuary	53°20'08"	06°56'43"	October 1990	27.7	14.0	2.5	Sand 72.6%
9	Rhine estuary, Eemsharbour	51°53'50"	04°24'08"	June 1990	0.6		1.1	Sampled during low tide
10	Rhine estuary	51°53'53"	04°22'30"	June 1990	1.0		2.9	Sampled during low tide
11	Eastern Wester Scheldt	51°26'13"	04°00'56"	November 1990	23.7	2.6	2.6	Sand 91.6%
12	Western Wester Scheldt	51°26'08"	03°38'28"	September 1990	31.1	12.1	2.0	Sand 64.7%
13	North Sea, Oyster Grounds	54°08'93"	04°20'34"	September 1990	34.6	7.9	1.6	Sand 84.5%
14	Humber estuary	53°32'51"	00°06'52"	August 1990	—	24.8	2.3	Top layer; box core sample
15	Humber estuary	53°32'51"	00°06'52"	August 1990	—	—	2.1	Upper 10–20 cm; day grab

[a] See Akkerman et al. [57] for a complete description of samples 7 to 13, including concentrations of micropollutants of various kinds. These cogenetic samples were taken manually with a nylon shovel on the Balgzand tidal flat for examining the grain-size distribution of organic micropollutants [56].
[b] Salinity and percentage of particles <63 μm not measured.

identified individually. The concentrations of the seventeen 2,3,7,8-substituted PCDD and PCDF congeners and the total concentrations of the tetra- (TCDD/TCDF), penta- (PnCDD/PnCDF), hexa- (HxCDD/HxCDF), hepta- (HpCDD/HpCDF), and octa- (OCDD/OCDF) chlorinated homolog groups in the different sediment samples are listed in Table 3. Also shown is the total toxic equivalent concentration and the sum concentration of the PCDD and PCDF in the samples.

As shown in Figure 1, going north along the Dutch coast, the sediment concentrations of PCDDs and PCDFs exhibit a decline with increasing distance from the River Rhine outflow. Due to the mixing of suspended matter from the river with suspended matter transported into the estuary from the coastal sea, concentrations of micropollutants in particulate matter generally decrease with distance seaward.

PCDFs were more widely encountered than PCDDs in all sediment samples, except for the Ems-Dollard and one sediment sample from the Humber estuary. The highest concentrations were found in the outflow sediments of the rivers Rhine and Humber. Concentrations up to 2,980 ng kg^{-1} total PCDFs, principally 1,2,3,4,6,7,8-HpCDF and OCDF, and up to 1,760 ng kg^{-1} PCDDs, principally OCDD, were determined in the River Rhine sediments. Humber sediments contained levels of up to 6,917 ng kg^{-1} PCDF and up to 3,640 ng kg^{-1} PCDD, principally HpCDDs and OCDD. Expressed in terms of toxic equivalents (TEQs [68]), the concentrations ranged from 45 ng kg^{-1} TEQ in the Rhine estuary to 267 ng kg^{-1} TEQ in a single Humber sediment. Repeated recent measurements could only confirm the lower TEQ concentration in the surface sediment of the Humber (D.R. Sayers, personal communication).

The dominant congener in all sediments from locations situated in depositional zones of the River Rhine, namely, the Rhine estuary itself, the Wadden Sea, and the more offshore Oyster Grounds, was OCDF at concentrations ranging from 208 ng kg^{-1} in the Oyster Grounds to 1,722 ng kg^{-1} in the Rhine estuary. This feature seems to be characteristic for the PCDD and PCDF congener patterns found in
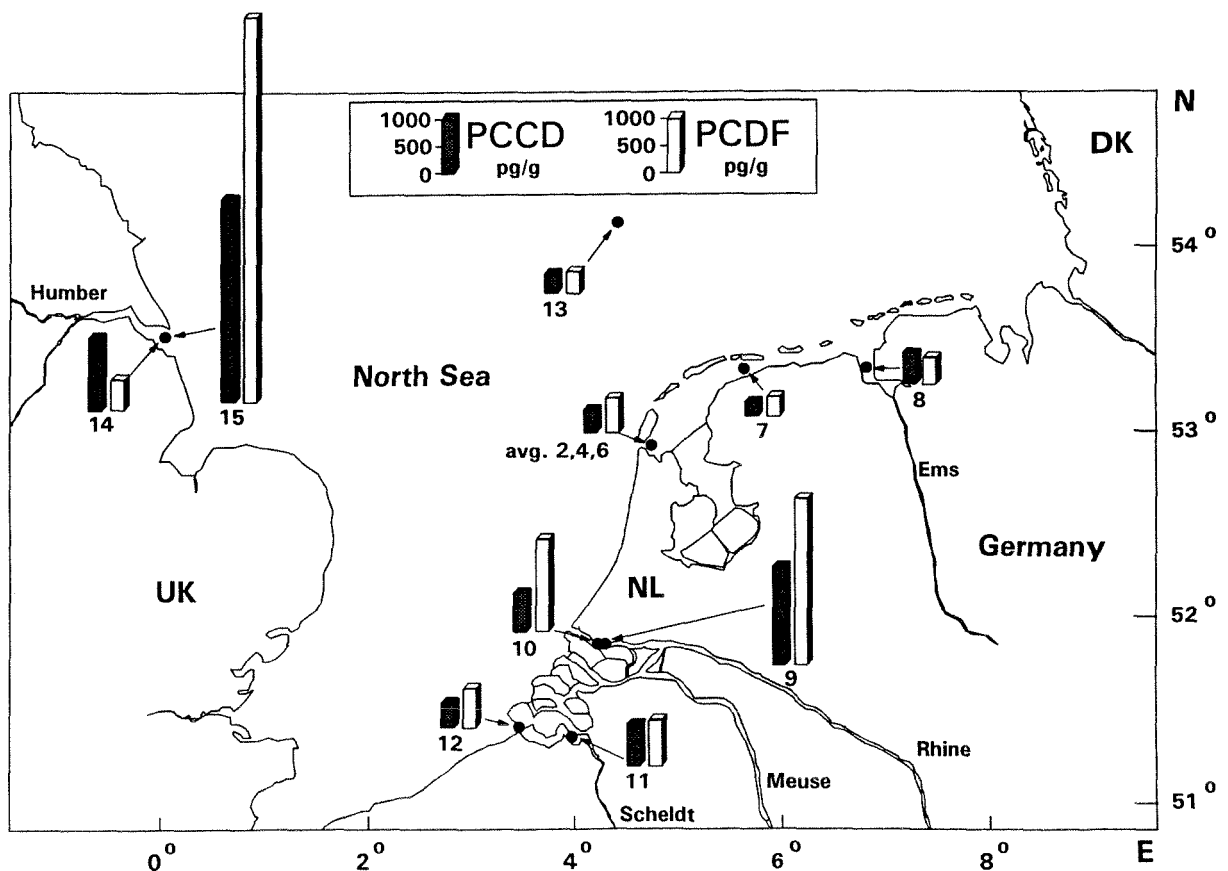

Fig. 1. Map of the study area showing locations and total concentrations of PCDDs and PCDFs of sediments (<63 μm) from the Wadden Sea; Oyster Grounds; and estuaries of the rivers Rhine, Scheldt, Ems, and Humber (see Table 2 for the exact sample locations).

Table 3. PCDD and PCDF concentrations (ng kg⁻¹ dry wt.) in the <63-μm sediment fraction of the sampling locations

Compound	Western Wadden Sea						Middle Wadden Sea	Ems–Dollard	Rhine		Wester Scheldt		North Sea	Humber	
Sample no.	1ᵃ	2	3ᵃ	4	5ᵃ	6	7	8	9	10	11	12	13	14	15
2,3,7,8-TCDD	<3	<4	17	22	10	<8	<5	<7	27	<24	<4	<3	<4	<38	<25
Total TCDD	<3	<4	17	22	10	<8	<5	<7	27	<24	<4	<3	8	<38	<25
1,2,3,4,7,8-PnCDDD	<2	<8	<5	<8	<7	<3	<6	<10	<8	<11	<6	<5	3	<30	39
Total PnCDD	6	<8	15	<8	9	4	6	<10	<8	18	<6	14	16	63	261
1,2,3,4,7,8-HxCDD	<4	2	4	<13	<10	<5	<5	<15	<10	<11	<4	2	2	<50	101
1,2,3,6,7,8-HxCDD	<4	2	7	<13	<10	<5	7	8	<10	26	7	5	5	<50	59
1,2,3,7,8,9-HxCDD	<4	<16	8	<13	7	10	<5	7	<10	17	6	5	7	<50	77
Total HxCDD	24	34	66	49	69	61	44	69	39	161	76	61	60	224	822
1,2,3,4,6,7,8-HpCDD	26	50	56	60	66	62	37	55	68	160	78	53	44	145	653
Total HpCDD	62	98	108	122	134	124	78	128	131	309	161	111	93	296	1,217
OCDD	86	216	173	251	190	256	128	342	503	1,268	492	260	172	725	1,340
2,3,7,8-TCDF	8	20	9	23	28	16	8	11	20	29	12	13	8	34	148
Total TCDF	57	39	146	48	53	16	16	24	20	238	144	100	19	34	1,403
1,2,3,4,8-/1,2,3,7,8-PnCDF	5	8	5	<7	9	<5	10	6	19	12	13	12	10	<17	192
2,3,4,7,8-PnCDF	3	9	9	11	12	11	5	4	9	18	9	10	7	15	170
Total PnCDF	38	95	113	57	126	59	71	72	131	218	115	94	61	94	1,692
1,2,3,4,7,9-/1,2,3,4,7,8-HxCDF	18	19	26	21	15	15	9	13	48	23	22	20	10	17	450
1,2,3,6,7,8-HxCDF	<2	13	15	7	8	10	7	10	22	107	19	14	7	<16	183
1,2,3,7,8,9-HxCDF	<2	<10	4	<7	<3	3	<7	<7	<8	16	5	4	2	<16	42
2,3,4,6,7,8-HxCDF	<2	<10	11	12	15	12	8	8	15	37	9	8	7	<16	281
Total HxCDF	35	81	131	82	53	87	53	66	145	390	114	90	58	17	2,358
1,2,3,4,6,7,8-HpCDF	31	118	100	98	125	104	72	74	191	332	115	124	46	97	969
1,2,3,4,7,8,9-HpCDF	8	<7	13	<9	10	14	<15	<12	56	27	9	<8	<5	<28	49
Total HpCDF	55	138	142	110	169	149	72	92	328	412	144	134	46	132	1,152
OCDF	86	257	225	302	354	362	142	213	1,026	1,722	295	282	208	261	312
Total PCCDs	178	348	379	444	412	445	256	539	700	1,756	729	446	349	1,308	3,640
Total PCDFs	271	610	757	599	755	673	354	467	1,650	2,980	812	700	392	538	6,917
Total TEQᵇ	5	13	32	36	26	15	8	10	48	43	16	15	12	16	267

ᵃFraction <1,000 μm has been analyzed.
ᵇInternational NATO/CCMS toxic equivalents; see Van Zorge et al. [68].

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the Dutch aquatic environment [55] and is in good agreement with results of PCDD and PCDF measurements in recently deposited Dutch freshwater sediments [4,69] and suspended matter from the River Rhine at the monitoring stations at the Dutch-German border near Lobith [5]. Sediments from the River Rhine downstream of the highly industrialized Ruhr area in Germany typically show a chlorination pattern. The same pattern has recently been found in sediments from the River Lippe in Germany and the Chemieharbour in The Netherlands, in both cases near large vinylchloride monomer-producing plants [22,23]. The only industrial processes known until now that can account for this profile are oxyhydrochlorination processes of aliphatic compounds and electrolytic processes for producing chlorine from sodium chloride (see Table 1). These processes are used by a wide variety of vinylchloride monomer production facilities [9] and chlorine-producing and -applying industries [24]. Recently, Meyer et al. [70] and Oehme et al. [71] found similar patterns in sediments from New York state community water systems and from the Frierfjord area in Norway, respectively. Although no data have been published on HpCDF and OCDF levels in waste effluents from magnesium plants, reaction conditions of the production of magnesium, in which chlorine, coke, and magnesium oxide are involved at 70 to 800°C, also seem favorable for the formation of PCDDs and PCDFs having a chlorination pattern [72].

Grain-size effect

As shown previously, both trace metals and organic contaminants tend to concentrate in the finely grained clay-rich sediment fractions [56,73], partly due to a larger specific surface area and a higher OC content. The analysis of organic contaminants in the clay and silt fraction (fraction <63 μm) to evaluate their concentrations in sediments of various textures and origins for this purpose is supported by the International Council for Exploration of the Sea (ICES) and has already been applied in the monitoring programs of the JMP/NSTF.

The value of <63 μm was chosen for various reasons. First, it can easily be separated from the sediment by wet sieving. Second, very fine particles (<2 μm) show a relatively low abundance in the North Sea and the Wadden Sea. Therefore, the collection of that fraction is very time-consuming and remobilization of contaminants cannot be excluded. Finally, there is also a hydrodynamic reason, as nearly all material transported in suspension in the water column belongs to the <63-μm fraction, in

contrast to the coarser sand fractions [3]. As can be inferred from the standard deviations given in Table 4, the concentrations of PCDDs and PCDFs in the total fractions (<1,000 μm) of three cogenetic Wadden Sea sediments vary widely, whereas their concentrations in the <63-μm grain-size fraction are fairly reproducible. The isolation and analysis of the <63-μm grain-size fraction has been proved to be most appropriate for comparing trace metal and organic micropollutant concentrations of marine sediments from different areas [56] and should therefore be recommended for this kind of research.

Detailed congener profile analysis

From the 104 measured tetra- through octachlorinated PCDD and PCDF congeners, 77 relevant and validated variables were selected. Tetra- and pentachlorinated PCDDs were omitted from the data set because their concentrations were mostly below the limit of detection.

The object score plot of the unsupervised analysis of the whole normalized data set is given in Figure 2A. The analysis of the 124 × 77 data tables shows that the systematic part of the data can be described by two significant (cross-validated) PCs. Together they explain 89% of the variance in the data set, and therefore their two-dimensional plot gives a good view of the major features of the data. The plot suggests the presence of at least three different classes — Chemieharbour sediments, St. Laurensharbour sediments, and River Rhine sediments. The Chemie- and St. Laurensharbour sediments showed the most uniform distribution of the PCDD and PCDF congeners among the class sediments and grouped tightly together. Sediments from the upper part of the River Rhine (near Strasbourg, Gambsheim, and Iffezheim, Germany [4]) were positioned in the upper left part of the PC plot close to two samples of commercial PCP formulations

Table 4. Grain-size distribution (ng kg^{-1} dry wt.) of PCDDs and PCDFs in three cogenetic sediments[a]

Compound	Fraction <63 μM (ng kg^{-1} dry wt.)		Fraction <1,000 μM (ng kg^{-1} dry wt.)	
	Avg.[b]	Range	Avg.[b]	Range
ΣPCDD	412 ± 45	348–445	323 ± 103	178–412
ΣPCDF	627 ± 33	599–673	594 ± 229	271–757

[a]Sediments originated from the Balgzand tidal flat (see Klamer et al. [56] and Table 2).
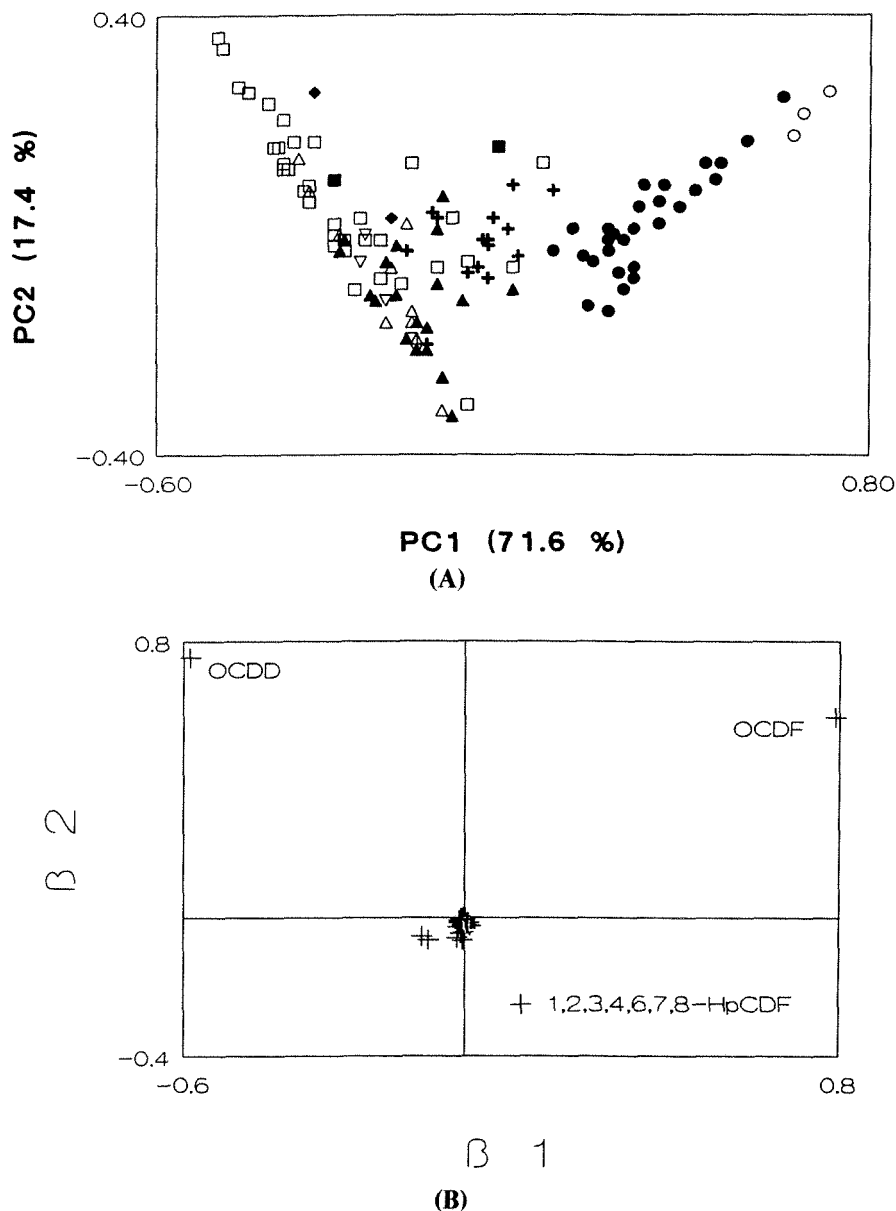[b]Mean ±SD for three determinations.

Fig. 2. (A) Principal components score plot of the various samples. The variance explained by each principal component is given in parentheses as a percentage. The symbols represent sediment samples from the Chemieharbour (●), the St. Laurensharbour (▲), the River Rhine (□), the North Sea and adjacent coastal areas (+; this study); and fly ash samples (△), air particulate samples (▽), solid waste from the oxyhydrochlorination process at the Chemieharbour (○), two sodium pentachlorophenate samples (◆), and suspended matter samples from the rivers Rhine and Meuse (■). (B) Corresponding variable loading plot.

[19]. This positioning is consistent with the results of Hagenmaier et al. [21], who demonstrated that sediments from southwestern Germany contained PCDD and PCDF congeners, especially OCDD and HpCDDs, that were indicative for the application of PCP and its sodium salt.

The significance of each congener in determining the positions of individual sediment samples and clusters of samples along the PC axes is illustrated by the PC-loading plot shown in Figure 2B. The isomers with the highest contribution to the differences observed between samples and among clusters are located farthest from the origin of the axes. Most variables are clearly grouped around and centered on zero value, which means that only five variables — OCDF, OCDD, 1,2,3,4,6,7,8-HpCDF, and both the heptachlorinated PCDD isomers — accounted for nearly all the variation along the corresponding PC axes. The determination of these congeners will therefore be sufficient to give the same information as the original data, albeit with a somewhat decreased precision. Regarding the ecotoxicologi-

cal relevance of the 2,3,7,8-substituted PCDD and PCDF congeners, pattern recognition can best be performed on these 17 congeners, as they also include the above mentioned 2,3,7,8-chloro-substituted congeners.

More detailed information about the possible sources of these compounds based on isomeric similarities emerged from the classification analysis illustrated in residual or Coomans plots (Figs. 3 and 4). The isolated location of two point sources in the Europort area between Rotterdam and the North Sea provided homogeneous training data sets [55] that may serve as class models to identify and quantitate dominating sources of these compounds for related sediments. Class model 1, the chlorination model, was made up of 30 sediment surface samples contaminated by effluents from the production of ethylene dichloride (EDC) at the Chemieharbour, The Netherlands [22]. Class model 2, the combustion model, consisted of 20 surface sediments contaminated by drainage water that had runoff from an incinerator fly ash storage site alongside the involved municipal-chemical waste incinerator [22]. The similar distribution of PCDD and PCDF congeners in sediments from the lower stretch of the River Rhine downstream of the Ruhr area [4] also provided the possibility to construct a uniform class model that represented the Rhine congener pattern. This pattern may be found in coastal sediments that are influenced by River Rhine water. Broman et al. [41] demonstrated that the profile compositions of PCDDs and PCDFs associated with air particulates corresponded to a high extent to the congener profiles of settling particulate matter in offshore Baltic waters. Therefore, we also constructed a class model from published PCDD and PCDF concentrations of air particulates from regions close to the North Sea to compare the offshore marine sediment samples with particulates deposited from the air.

The results of the classification analysis are shown in Figures 3 and 4. The lines in the figures indicate the tolerance level at 5% ($p = 0.05$) around the class models. The tolerance interval is calculated from the residual variance in the class model by using an approximate F test with 95% confidence limits [63] (Table 5). Samples that cannot be described by the models will show up far away from the RSD lines. For all of the separate classes, at least one PC was significant.

Figure 3 shows that the waste samples from the EDC production plant belong significantly to class model 1, which was made up of the chlorination process–related sediment samples. Details of this latter study will be published elsewhere. Sediments from the Humber mouth (not depicted) did not show any similarity to the class models, which indicates a completely different types of source. The estuarine and coastal North Sea sediments could not be significantly described by any of the two class models of Figure 3. The test objects were also tested against class model 3 and 4, the River Rhine and air particulate class models (see Fig. 4). Here, several coastal and estuarine sediment samples showed a similarity to the River Rhine model. The settled sediments from the Rhine estuary (sediments 9 and 10), as well as the suspended sediment sample taken at the German Dutch border, belonged significantly to class model 3, the Rhine model. Sediments from the Dutch Wadden Sea (1–6) also showed more similarity to the River Rhine sediments than to air particulates, indicating a direct influence of the PCDD and PCDF load of this river on their presence in these coastal sediments. The RSD of these sediments was smaller than two times the Rhine class RSD and more than two to seven times the air particulates model. The sediment from the remote Oyster Grounds (13) and the western part of the River Scheldt (12) showed about the same distance to both class models and therefore might be influenced by both sources. Again, the sediments from the Humber mouth and the suspended sediments from the River Meuse could not be described properly by the two class models.

It has been suggested that the atmospheric input is dominant for these compounds in remote North Sea waters [74] and that water-carried particulate matter from coastal input is of secondary importance. Using a simple long-range Gaussian model with homogeneous meteorology and deposition characteristics, the relative contribution of the atmospheric input of, for example, PCBs to the contamination of the North Sea was calculated to be about 93% [74], because the bulk of the particles normally settles relatively close to the source (a river or outlet). Remote sedimentation areas that receive both atmospheric and water-phase input may not always retain the characteristics of the original point sources [20,41]. The contaminant profiles found in these sediments appear to result from the intervention of nonisomer-specific combinations of environmental processes such as redistribution of sediment-bound PCDDs and PCDFs [35], biological and chemical degradation, photolysis, volatilization, and physical transport of fine-grained material. Nevertheless, the remote Oyster Grounds sediments still show some similarity to sediment samples from the lower stretch of the River Rhine. The atmospheric input of PCDDs and PCDFs
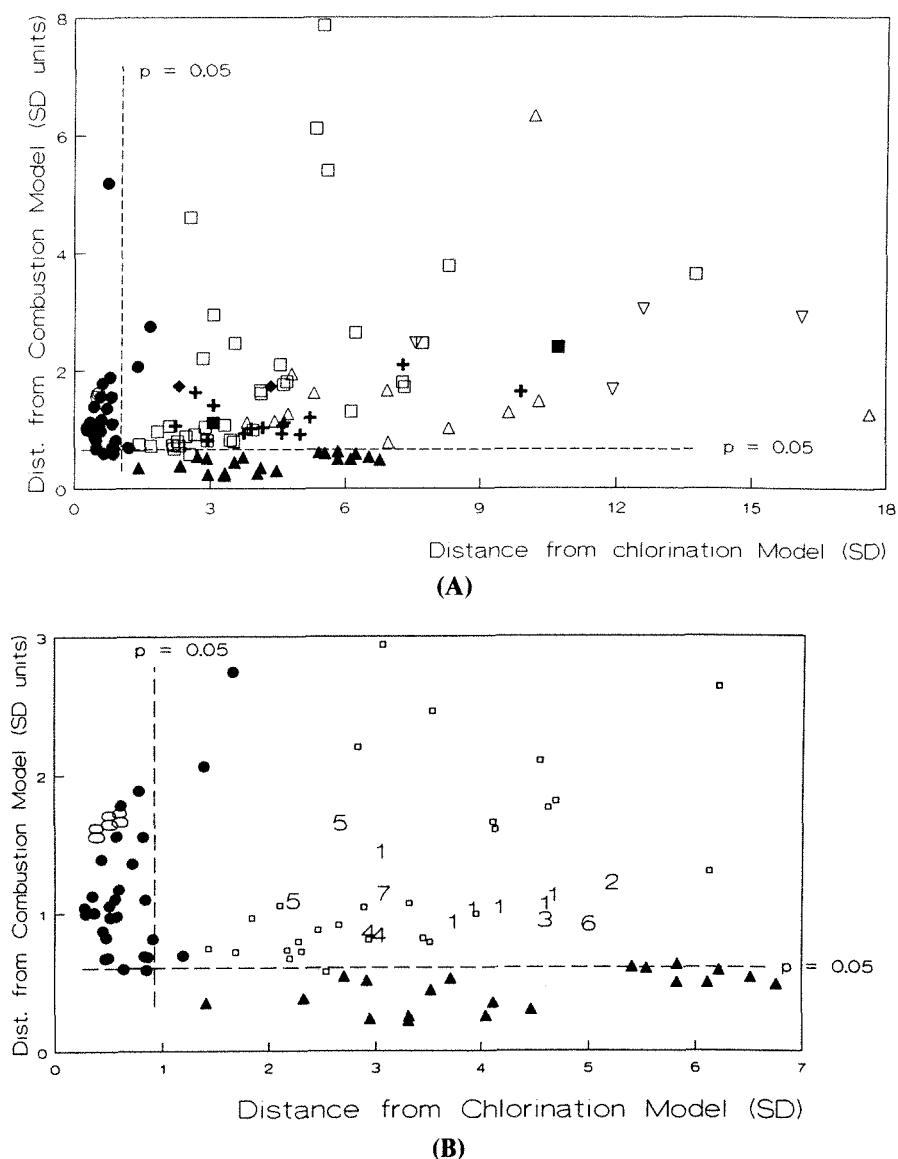
(A)

(B)

Fig. 3. Coomans plot from the disjoint class modeling of PCDD and PCDF compositional similarities of samples from this and other studies. The dotted lines represent the 95% C.I.s around the class models. (A) Coomans plot of class 1 (chlorination model; horizontal) and class 2 (combustion model). See Figure 2 for explanation of the symbols. (B) Inset from Figure 3A. The digits represent sediment samples from the western Wadden Sea (1), the middle Wadden Sea (2), the Ems-Dollard estuary (3), the Wester Scheldt (4), the Rhine estuary (5), the Oyster Grounds (6), River Rhine suspended sediments (7), and solid waste from the oxyhydrochlorination of EDC (8).

Table 5. SIMCA principal component models of the individual sample classes[a]

	Chemieharbour	Laurensharbour	River Rhine	Air particulates
No. of significant principal components	1	2	1	2
Amount of variance explained, %	24.1	48.1	24.8	61.4
F1	71	64	58	38
F2	76	75	75	75
RSD max ($P = 0.05$)	0.769	0.497	0.647	0.85

[a]F1 and F2 are the degrees of freedom, the RSD max is the maximum residual standard deviation. RSD max values have been used to draw dotted lines in the Coomans plot in Figure 3.
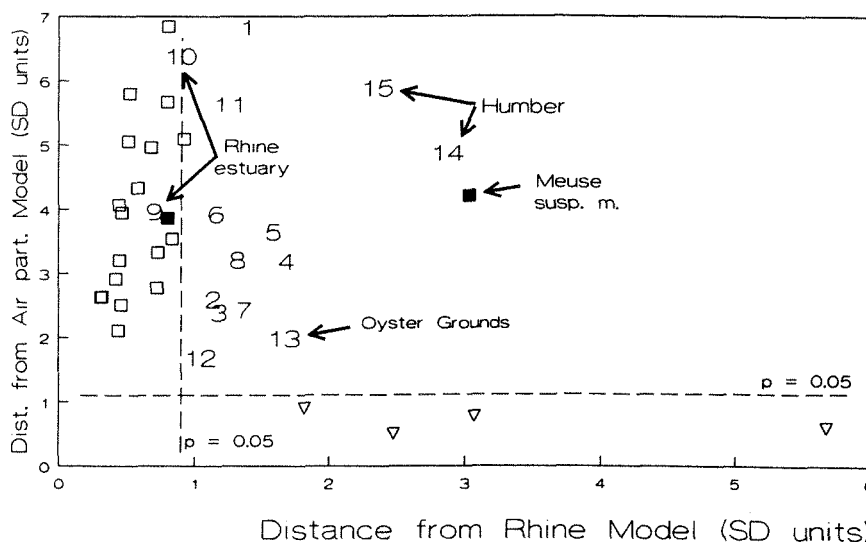
Fig. 4. Coomans plot from the disjoint class modeling of PCDD and PCDF compositional similarities of sediments from the lower stretch of the River Rhine (class 3, horizontal, □) and air particulates (class 4, ▽). See Figure 2 for further explanation of the symbols and Table 2 for explanation of the digits.

might therefore be less important than PCBs. If the atmosphere was the only significant source of PCDDs and PCDFs to the North Sea, we would expect statistically similar isomer compositions in remote sediments from the Baltic Sea and the North Sea. The observed patterns, however, suggest that atmospheric input cannot be the sole source for PCDDs and PCDFs in the North Sea. From the present study it is concluded that the congener-specific analysis of PCDDs and PCDFs, in combination with the multivariate analysis of the measured data, supports the chemical profile similarities between sediments from the industrialized Ruhr area, the lower stretch of the River Rhine, and the Wadden Sea. PC and classification analysis are useful tools for identifying sources of persistent compounds that contaminate the aquatic environment.

CONCLUSIONS

The concentrations of PCDDs and PCDFs in outflow surface sediments from the rivers Rhine and Humber were the highest among the examined estuarine and coastal sediments. Concentrations up to 2,980 ng kg^{-1} total PCDFs, principally 1,2,3,4,6,7,8-HpCDF and OCDF, and up to 1,760 ng kg^{-1} PCDDs, principally OCDD, were determined in the River Rhine sediments. One Humber sediment contained levels of up to 6,917 ng kg^{-1} PCDF and up to 3,640 ng kg^{-1} PCDD, principally HpCDDs and OCDD.

The concentrations of PCDFs dominate PCDDs in all sediments, except for the Ems-Dollard and one sediment sample from the Humber estuary. Sediments from locations situated in depositional zones of the River Rhine always contain OCDF as the major congener. Industrial processes in which OCDF is predominantly formed, among other congeners, such as the oxyhydrochlorination of ethylene and the electrolytic production of chlorine, have a strong influence on the levels and profiles of PCDDs and PCDFs in North Sea sediments. Such industries are located along the River Rhine in the Ruhr area, along some tributaries (River Lippe in Germany), and in the estuary (Chemieharbour in Rotterdam, The Netherlands) of the Rhine. The atmospheric deposition of combustion-generated PCDDs and PCDFs could not solely account for the presence of these compounds in remote North Sea sediments such as the Oyster Grounds.

The determination and report of PCDD and PCDF data should be on congener-specific measurements rather than homolog levels. Pattern recognition techniques based on isomer-specific congener profiles, coupled with particulate and PCDD/PCDF inventories as applied here, are appropriate methods of eliciting information on potential sources. Determination of PCDDs and PCDFs in the sediment fraction <63 μm is recommended if the purpose of the study is to compare estuarine or coastal sediments from different origins.

Waters Division, Haren, The Netherlands) for technical assistance in analysis of samples, and our colleague G. Groeneveld for help with the figures. We appreciate the reviews and suggestions rendered by P. de Voogt (University of Amsterdam). We are indebted to A. Morris and R. Howland from the Plymouth Marine Laboratory, United Kingdom, for permission to participate in the Humber Plume cruise, CH69/90, aboard RRS *Challenger*, which contributed to the North Sea Project of the UK-NERC, and to the crews of MS *Argus*, MS *Holland*, and RRS *Challenger* for their skillful assistance during the sampling campaigns.

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