ELSEVIER

Chemosphere 62 (2006) 417–429

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Distribution of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in suspended sediments, dissolved phase and bottom sediment in the Houston Ship Channel

Monica P. Suarez [a], Hanadi S. Rifai [a,*], Randy Palachek [b], Kirk Dean [b], Larry Koenig [c]

[a] *Department of Civil and Environmental Engineering, University of Houston, 4800 Calhoun Rd, Room N107D, Houston, TX 77204-4003, USA*
[b] *Parsons Water & Infrastructure, Austin, TX 78754, USA*
[c] *Texas Commission on Environmental Quality, Austin, TX 78753, USA*

Received 23 August 2004; received in revised form 20 January 2005; accepted 17 April 2005
Available online 29 June 2005

Abstract

Spatial distributions of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in the water column and bottom sediments of the Houston Ship Channel in Texas were measured three times over a 1-year period. Total TEQ concentrations in water ranged from 0.01 to 0.25 pg/l for the dissolved phase and from 0.09 to 2.91 pg/l for the suspended phase, while TEQ concentrations in bottom sediments varied from 0.9 to 139.8 ng/kg dry wt. The dissolved concentrations were lower than their respective suspended concentrations, with average dissolved/suspended ratios between 0.11 and 0.59 for individual congeners. More than 89% of the total concentration of 2378-substituted PCDD/PCDFs was attributable to OCDD but 2378-TCDD was the major contributor to total TEQ for the three sampled media. Average logs of organic carbon-normalized suspended sediment–dissolved partitioning coefficients ($\log K_{oc}^{obs}$) varied between 4.92 and 8.59 l/kg-oc; while in the bottom sediment–dissolved interface, $\log K_{oc}^{obs}$ values ranged from 5.48 to 8.48 l/kg-oc. Observed $\log K_{oc}$values varied within a factor of 0.64–1.26 from equilibrium $\log K_{oc}$ values, suggesting fluxes of PCDD/PCDFs across the interfaces. It was found that in the HSC, on average, the tendency of a compound to move from the particulate phase to the dissolved phase decreases with increasing K_{ow}.

Keywords: PCDD/PCDFs; Partitioning; Spatial distribution; Water column; Bottom sediment

1. Introduction

Sampling for PCDD/PCDFs in water bodies has mainly focused on sediment and tissue because of the difficulty involved in sampling their very low concentrations in water. Typically, PCDD/PCDF concentrations in water are on the order of tenths of parts per quadrillion (ppq or pg/l), whereas their detection limits are on the order of 10 ppq and higher. Thus, researchers interested in quantifying PCDD/PCDFs in water have to use high-volume sampling technologies that allow concentrating the PCDD/PCDF from large volumes of water. The handful of studies in the literature that have used

---

[*] Corresponding author.

0045-6535/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2005.04.088

such technologies have focused on the partitioning relationships between the dissolved and particulate phases of PCDD/PCDFs in the water.

Broman et al. (1991), for example, analyzed dissolved and suspended samples from offshore locations in the Baltic Sea using a high-volume tangential-flow filtration system. They found that all PCDD/PCDF congeners except TCDFs, HxCDFs, OCDFs, and TCDDs were mainly associated with particulate matter and the distribution was dependent on the concentration of particulate lipids but not correlated to the particulate organic carbon (POC). They attributed this to the high POC values (~45%) that were present in their samples. Multivariate analysis allowed Broman et al. (1991) to conclude that the main source of PCDD/PCDFs in remote water areas was atmospheric deposition and that sources from coastal areas were of secondary importance. Gotz et al. (1994) used a filter/PUF (polyurethane foam) sampling system and found that more than 98% of the PCDD/PCDF concentration in the River Elbe water column was in the suspended particulate phase. They observed different fingerprint profiles for suspended and dissolved samples collected from the same location and analysis of isomeric patterns for HpCDF led them to conclude that the contamination was caused by combustion emissions and municipal and industrial effluents. Hashimoto et al. (1995) measured PCDD/PCDFs in non-polluted areas along the Japanese coast using a glass wool/XAD-2 resin sampling system and detected PCDDs but not PCDFs. They observed that the composition of PCDD in seawater was similar to that of ancient oceanic sediment, raising the possibility that PCDDs were produced in marine water.

Rantalainen et al. (1998) used semipermeable membrane devices (SPMDs) to sample the water column and sediments in the Lower Fraser River (B.C., Canada). They compared SPMD results against those obtained using a glass fiber-filter/XAD-2 resin unit; and in general observed good agreement between the two methods. PCDD/PCDF concentrations were higher in SMPDs exposed to sediment than in those exposed to the water column at the same locations but they showed similar congener patterns suggesting similar sources in the past and present. They concluded that levels of PCDD/PCDFs were relatively low for such an industrialized area. Lohmann et al. (2000) collected air and water samples simultaneously from the Raritan Bay/Hudson River Estuary and demonstrated flux of PCDD/PCDFs from water to air. They found that for the same number of chlorines, PCDDs were less associated with the particulate phase than PCDFs, with the exception of TCDD/Fs. The particle-bound fraction for PCDD/PCDFs increased with the degree of chlorination except for TCDDs.

While the aforementioned studies investigated the distribution of PCDD/PCDFs between dissolved and suspended phases in water, they did not study the distribution of PCDD/PCDFs among the dissolved, suspended sediment, and bottom sediment phases. This is a topic of great interest though, with respect to PCDD/PCDF in water bodies because the main pathway of exposure for humans is through the food chain. Fish, crab, and other organisms bioaccumulate the PCDD/PCDFs they are exposed to from the water body and it is not clearly understood whether the bioaccumulation occurs from the sediment or water. Additionally, and because of the cost and difficulty in sampling water concentrations, models that can predict water concentrations from sediment values are of interest. Finally, it is important to understand the distribution of PCDD/PCDF between the three phases in order to determine the origin of the PCDD/PCDFs and to develop appropriate source control strategies.

This paper addresses this deficiency and develops a unique database of water and sediment PCDD/PCDF concentrations for a heavily polluted water body in Texas. The main objectives of the paper are to scrutinize the levels and patterns of PCDDs and PCDFs in water from the Houston Ship Channel (HSC) and to assess their partitioning between the suspended sediment–dissolved and bottom sediment–dissolved phases. This dataset constitutes, to the best of the authors' knowledge, the most extensive PCDD/PCDF dataset of its kind and the first quantification of PCDD/PCDFs in water for the HSC.

Only one other study in the literature has undertaken this type of investigation. Persson et al. (2002) measured PCDD/PCDFs in a marine fjord in Norway. They describe PCDD/PCDFs as compounds whose solid–water partitioning and particle-driven dispersion is significantly affected by their interaction with soot-carbon in addition to organic matter (enhanced sorption).

In this study, a total of 33 stations are sampled concurrently for the 17 2378-substituted congeners and for total homologue groups in the dissolved phase and suspended sediments. The congener data from the study are analyzed spatially to establish trends. The data are then analyzed to calculate partitioning coefficients.

2. Methods

2.1. The Houston Ship Channel

The Houston Ship Channel (HSC), located in the San Jacinto River Basin, is comprised of a network of water bodies extending approximately 50 miles from the Port of Houston near downtown Houston to the Gulf of Mexico (see Fig. 1). The Channel is an estuarine system that is composed of the tidally-influenced Houston Ship Channel and San Jacinto River and free-flowing tributaries that become tidal as they approach the Channel. The

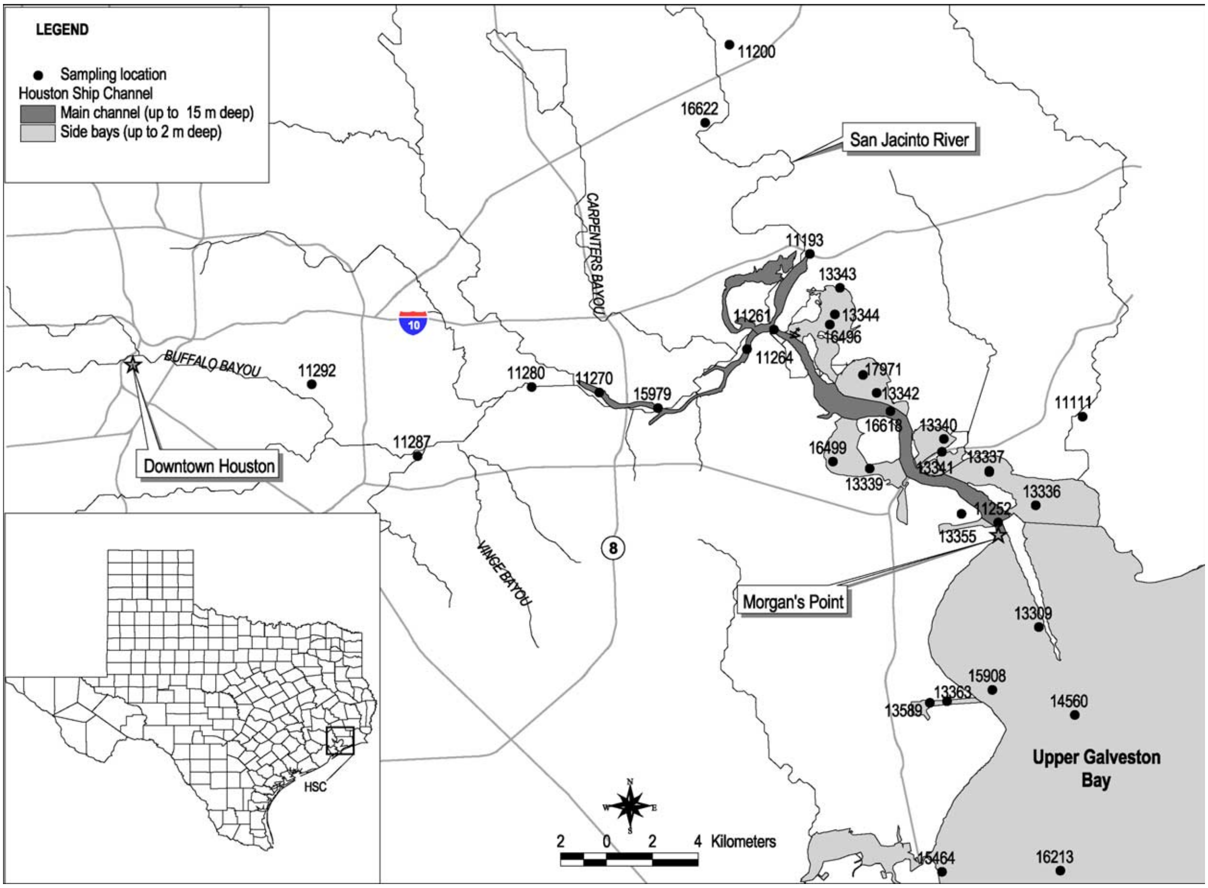


Fig. 1. Study area.

Channel is home to the largest petrochemical complex in the United States and the second largest worldwide.

The HSC receives significant municipal and industrial discharges as well as non-point source pollution. The water quality in the channel was severely impaired in the early 60s due to the high discharge loads but its water quality has significantly improved in recent years due to more stringent discharge permitting. PCDD/PCDF levels in waters of the HSC have not been measured prior to this study.

2.2. Sampling

Fig. 1 shows the HSC locations that were sampled to quantify PCDD/PCDFs in water and sediment. Three sampling events were undertaken: summer 2002 (July 25–September 11), fall 2002 (October 21–December 10), and spring 2003 (April 30–June 17). All locations were sampled during the summer 2002 and at least once during the remaining two events so that each station was sampled a minimum of 2 times. Sampling dates were selected to evaluate seasonal differences, if any, in the measured concentrations.

Since PCDD/PCDF concentrations in water are typically lower than the analytical detection limit, water sampling was conducted using the high-volume technique. For this research, a commercially available high-volume sampling system (Infiltrex 300, Axys Environmental Systems, Sydney, BC) was used. Using this technique allows concentrating PCDD/PCDFs from large volumes of water to obtain measurable quantities. The high-volume system uses a 4-in. 1 μm-glass fiber-filter (GFF) cartridge followed by a stainless steel column packed with hydrophobic polymeric resin beads (XAD-2) through which large volumes of water can be passed. Because PCDD/PCDFs are very hydrophobic, they rapidly sorb to the resin, making it possible to completely collect the dissolved PCDD/PCDFs from the sampled water. The PCDD/PCDFs can then be recovered from the GFF and resin by extraction with a non-polar organic solvent. Water was pumped at a rate of about 1.6 l/min and the volume of water processed varied between 300 and 750 l. This allowed for reporting limits ranging between 0.013 and 0.033 pg/l for 2378-TCDD. Additional grab water samples were collected and analyzed for total organic carbon (TOC), dissolved organic carbon (DOC), total suspended solids (TSS), and total dissolved solids (TDS). All water samples were preserved at 4 °C or less prior to analysis.

Sediment samples were collected with a previously decontaminated stainless steel Ponar dredge. Samples were collected and deposited into a stainless steel bowl. A minimum of three grab samples were composited using only the top 5 cm of sediment, mixed thoroughly with a clean stainless steel spoon, and deposited into a labeled, pre-cleaned amber glass jar with a Teflon® seal. Sediment samples were preserved at 4 °C or less prior to analysis.

2.3. Analytical methods

PCDDs and PCDFs in water and sediment samples were quantified by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) using EPA Method 1613B at a commercial laboratory. Sediment samples were homogenized, spiked with 15 $^{13}C_{12}$-labeled PCDD/PCDF internal standards and extracted using Soxhlet extraction apparatus. Resin and filters from water samples were homogenized, spiked with 15 $^{13}C_{12}$-labeled PCDD/PCDF internal standards, and mixed with sodium sulfate, allowing 12–24 h to dry. Subsequently, the samples were extracted for 18–24 h using methylene chloride: hexane (1:1) in a Soxhlet extractor and the extract was evaporated to dryness. The extracts (for both water and sediment samples) were then spiked with 2378-TCDD-$^{37}Cl_4$ enrichment efficiency standard and subjected to acid/base washes, multiplayer silica, alumina and carbon column cleanup procedures to remove interferences from the extracts. After cleanup, the extracts were concentrated to near dryness and spiked with recovery standards (1234-TCDD-$^{13}C_{12}$ and 123789- HxCDD-$^{13}C_{12}$) immediately prior to injection. Chromatographic separation was achieved with a DB-5, capillary chromatography column, (60 m, 0.25 mm i.d., 0.25 μm film thickness). A second column DB-225 (30 m, 0.25 mm i.d., 0.25 μm film thickness) was used for confirmation of TCDF identification.

Physical properties of water and sediment were analyzed at a commercial laboratory using standard methods (US Environmental Protection Agency, 1983) as follows: TDS EPA 160.1, TSS EPA 160.2, TOC EPA 415.2, DOC EPA 415.2, organic content of sediments (TOC) Lloyd Kahn, and total solids content EPA 160.3. Standard field parameters (temperature, pH, salinity, and conductivity) were measured using a YSI multiparameter probe (model 6920 or 600XLM).

2.4. Quality control

Field duplicates and blanks were collected at a frequency of 5% or higher with each set of samples and processed in an identical manner to samples. In addition, laboratory duplicates and blanks were run at a frequency of 5%. Overall, when detected, both field and laboratory blanks showed levels below 5% of the levels in the samples. Results obtained from the duplicate samples were consistent and in agreement with the method requirements for the different congeners. Recoveries for 2,3,7,8-substituted congeners ranged from 72% to 92% with an average of 81%. Non-detects were assumed to be equal to half of the detection limit for total equivalence quotient (TEQ) calculations and summary statistics. World Health Organization equivalence factors (TEFs) (Van den Berg et al., 1998) were used to calculate total equivalent concentrations (TEQs).

3. Results and discussion

3.1. Water concentrations

Average PCDD/PCDF concentrations in water for all stations sampled for each event are presented in Table 1. PCDD/PCDF concentrations in water for summer 2002 varied between 0.10 and 0.82 pg TEQ/l with an average value of 0.32 pg TEQ/l. Samples for the fall 2002 sampling varied between 0.12 and 2.73 pg TEQ/l with an average value of 0.63 pg TEQ/l. PCDD/PCDF concentrations in water collected during spring 2003 varied between 0.11 and 3.16 pg TEQ/l with an average of 0.45 pg TEQ/l. It is noted that 100% of the samples exceeded the EPA water quality criterion of 0.014 pg/l (US Environmental Protection Agency, 2002). The observed PCDD/PCDF concentration ranges in the HSC are higher than those measured in other industrialized areas with the exception of those in the River Elbe, and are also significantly higher than those observed in pristine areas such as the Baltic Sea (Table 2). A comparison of dissolved and suspended concentrations for the locations measured during the three events using the ANOVA test shows that neither the congeners nor the TEQ exhibit statistically significant variation with season ($\alpha = 0.05$, p-values between 0.11 and 0.97) with the exception of OCDD in the dissolved phase that presents higher concentrations in the fall than the other two sampling events (p-value = 0.003).

The highest average TEQ concentrations for the three events were measured at locations 15979 and 11193. The first location is within the heavily industrialized confined section of the channel, whereas the second station is on the San Jacinto River, home to paper and pulp mills, heavy shipping traffic, and pipeline crossings.

Fig. 2 shows the concentration distribution for the 17 2378-substituted congeners and TEQ in dissolved and suspended phases for the three sampling events. The dissolved concentrations for the individual PCDD/PCDFs

Table 1
Average (±standard deviation) concentrations by sampling event

Congener	Summer 2002				Fall 2002				Spring 2003			
	Dissolved [pg/l] $n = 37$	Suspended matter [ng/kg] $n = 37$	Total water [pg/l] $n = 37$	Sediment [ng/kg] $n = 39$	Dissolved [pg/l] $n = 20$	Suspended matter [ng/kg] $n = 37$	Total water [pg/l] $n = 20$	Sediment [ng/kg] $n = 17$	Dissolved [pg/l] $n = 22$	Suspended matter [ng/kg] $n = 37$	Total water [pg/l] $n = 22$	Sediment [ng/kg] $n = 27$
2378-TCDD	0.04 ± 0.05	4.8 ± 4.9	0.14 ± 0.11	20.3 ± 56.3	0.07 ± 0.09	9.3 ± 15.6	0.38 ± 0.47	12.4 ± 12.0	0.04 ± 0.04	10.2 ± 18.2	0.23 ± 0.44	10.1 ± 19.5
12378-PeCDD	0.01 ± 0.005	0.7 ± 0.3	0.02 ± 0.01	1.1 ± 1.7	0.01 ± 0.002	0.4 ± 0.2	0.02 ± 0.01	1.1 ± 1.1	0.01 ± 0.01	0.9 ± 0.4	0.02 ± 0.01	0.7 ± 0.7
123478-HxCDD	0.01 ± 0.008	1.6 ± 1.1	0.04 ± 0.02	2.0 ± 2.0	0.01 ± 0.01	0.9 ± 0.4	0.04 ± 0.02	2.9 ± 2.9	0.01 ± 0.01	2.0 ± 0.6	0.05 ± 0.02	1.6 ± 1.2
123678-HxCDD	0.02 ± 0.01	3.2 ± 1.9	0.08 ± 0.04	4.8 ± 4.9	0.02 ± 0.01	2.2 ± 1.4	0.08 ± 0.04	9.3 ± 16.5	0.02 ± 0.01	4.9 ± 1.6	0.11 ± 0.04	3.3 ± 2.6
123789-HxCDD	0.02 ± 0.02	5.7 ± 3.7	0.15 ± 0.09	3.9 ± 3.3	0.02 ± 0.01	3 ± 1.5	0.11 ± 0.05	5.8 ± 5.4	0.02 ± 0.01	7.4 ± 1.7	0.17 ± 0.07	3.1 ± 2.3
1234678-HpCDD	0.33 ± 0.30	137.2 ± 79.9	3.27 ± 1.52	117.6 ± 108.7	0.79 ± 0.44	103.6 ± 53.5	3.88 ± 1.79	269.7 ± 488.1	0.49 ± 0.31	183.9 ± 55.4	4.14 ± 1.78	104.1 ± 83.4
OCDD	5.62 ± 5.67	3321.3 ± 2079.4	77.94 ± 41.94	2712.7 ± 2217.6	26.44 ± 16.49	4257.3 ± 2374.7	156.74 ± 90.41	5840.5 ± 9379.4	11.27 ± 7.39	5150.9 ± 2493	113.54 ± 69.41	2435.9 ± 1876.7
2378-TCDF	0.16 ± 0.17	12.8 ± 12.6	0.42 ± 0.34	60.7 ± 178.3	0.23 ± 0.25	27.1 ± 50.7	1.11 ± 1.43	31.7 ± 38.5	0.14 ± 0.13	30.1 ± 63.1	0.71 ± 1.55	29.7 ± 75.8
12378-PeCDF	0.01 ± 0.01	1.4 ± 1.2	0.04 ± 0.02	2.1 ± 5.1	0.01 ± 0.01	1.1 ± 1.3	0.04 ± 0.04	2.8 ± 3.4	0.01 ± 0.01	1.8 ± 2.0	0.04 ± 0.04	0.9 ± 1.5
23478-PeCDF	0.01 ± 0.01	1.2 ± 0.9	0.04 ± 0.02	2.7 ± 4.5	0.01 ± 0.01	0.9 ± 0.8	0.04 ± 0.03	3.9 ± 5.7	0.02 ± 0.01	1.9 ± 1.5	0.05 ± 0.03	1.8 ± 2.1
123478-HxCDF	0.02 ± 0.04	2.8 ± 2.3	0.08 ± 0.05	4.2 ± 7.4	0.03 ± 0.02	3.2 ± 2.8	0.13 ± 0.08	6.2 ± 11.5	0.01 ± 0.01	4.6 ± 4.1	0.1 ± 0.08	2.6 ± 3
123678-HxCDF	0.01 ± 0.01	1.6 ± 1.1	0.04 ± 0.02	1.8 ± 4.6	0.01 ± 0.004	0.7 ± 0.7	0.03 ± 0.02	3.4 ± 5.8	0.01 ± 0.01	1.6 ± 1.1	0.03 ± 0.02	1.1 ± 1.0
234678-HxCDF	0.01 ± 0.02	1.6 ± 1.2	0.05 ± 0.02	1.5 ± 1.6	0.01 ± 0.004	0.7 ± 0.4	0.03 ± 0.01	2.3 ± 3.0	0.01 ± 0.01	1.1 ± 0.7	0.02 ± 0.01	0.9 ± 1.0
123789-HxCDF	0.01 ± 0.01	0.7 ± 0.6	0.02 ± 0.01	0.9 ± 1.1	0 ± 0.002	0.3 ± 0.4	0.01 ± 0.01	1.3 ± 2.2	0.01 ± 0.01	0.2 ± 0.2	0.01 ± 0.01	0.6 ± 0.6
1234678-HpCDF	0.07 ± 0.18	20.4 ± 18.9	0.47 ± 0.30	20.4 ± 26.6	0.04 ± 0.02	9.1 ± 4.5	0.34 ± 0.23	50.4 ± 108.8	0.04 ± 0.05	23.1 ± 15.8	0.47 ± 0.30	15.2 ± 15.6
1234789-HpCDF	0.01 ± 0.01	1.6 ± 1.2	0.04 ± 0.02	2.3 ± 3.5	0.01 ± 0.004	0.9 ± 0.7	0.03 ± 0.02	3.8 ± 6.8	0.01 ± 0.01	1.7 ± 1.2	0.04 ± 0.02	1.6 ± 1.8
OCDF	0.25 ± 0.38	136.9 ± 157.1	3.02 ± 2.99	360.1 ± 1065.6	0.29 ± 0.26	86.6 ± 86.4	3.5 ± 5.71	254.8 ± 332.7	0.29 ± 0.21	201.7 ± 260.3	3.48 ± 3.11	123.9 ± 163.5
$SWHO_{98}$-TEQ	0.09 ± 0.08	11.1 ± 8.4	0.32 ± 0.17	32.6 ± 80.8	0.13 ± 0.13	15.6 ± 21.6	0.63 ± 0.66	25.7 ± 25.8	0.08 ± 0.05	20.1 ± 25.8	0.45 ± 0.62	17.5 ± 28.8

(*continued on next page*)

Table 1 (*continued*)

Congener	Summer 2002				Fall 2002				Spring 2003			
	Dissolved [pg/l] *n* = 37	Suspended matter [ng/kg] *n* = 37	Total water [pg/l] *n* = 37	Sediment [ng/kg] *n* = 39	Dissolved [pg/l] *n* = 20	Suspended matter [ng/kg] *n* = 37	Total water [pg/l] *n* = 20	Sediment [ng/kg] *n* = 17	Dissolved [pg/l] *n* = 22	Suspended matter [ng/kg] *n* = 37	Total water [pg/l] *n* = 22	Sediment [ng/kg] *n* = 27
Total TCDDs	0.28 ± 0.33	19.7 ± 14.0	0.70 ± 0.42	33.9 ± 65.5	0.29 ± 0.25	14 ± 16.4	0.76 ± 0.62	27.8 ± 19.6	0.22 ± 0.11	28.5 ± 23.2	0.74 ± 0.50	20 ± 24.6
Total PeCDDs	0.10 ± 0.17	9.5 ± 8.6	0.32 ± 0.30	11.9 ± 15.4	0.06 ± 0.03	3.5 ± 1.8	0.17 ± 0.09	15.1 ± 15.2	0.06 ± 0.05	13.9 ± 6.6	0.34 ± 0.18	8.0 ± 8.7
Total HxCDDs	0.28 ± 0.37	84.1 ± 62.4	2.20 ± 1.67	101.3 ± 95.7	0.41 ± 0.25	43.4 ± 25.1	1.73 ± 0.88	179.8 ± 214.9	0.36 ± 0.22	127.9 ± 36.6	2.98 ± 1.45	73.9 ± 55.4
Total HpCDDs	1.05 ± 1.04	437.7 ± 262.6	10.53 ± 5.57	369.8 ± 334.1	2.16 ± 1.16	287.2 ± 168.6	10.88 ± 5.36	940.9 ± 1834.7	1.48 ± 0.85	583.8 ± 147.1	13.15 ± 5.47	330.5 ± 250.8
Total TCDFs	0.44 ± 0.47	31.8 ± 27.7	1.08 ± 0.78	121.1 ± 340.6	0.49 ± 0.48	46.9 ± 86.8	2.03 ± 2.52	82.6 ± 90.1	0.36 ± 0.3	64.0 ± 114.3	1.56 ± 2.81	65.5 ± 155.2
Total PeCDFs	0.15 ± 0.21	14.2 ± 11.1	0.43 ± 0.27	19.4 ± 32.2	0.12 ± 0.08	7.7 ± 5.4	0.37 ± 0.25	38.5 ± 67.9	0.10 ± 0.12	17.7 ± 14.6	0.41 ± 0.27	12.5 ± 13.9
Total HxCDFs	0.12 ± 0.28	19.8 ± 14.8	0.53 ± 0.34	24.8 ± 34.4	0.07 ± 0.05	11.5 ± 7.3	0.43 ± 0.25	64.5 ± 141.1	0.07 ± 0.06	27.4 ± 17.2	0.57 ± 0.31	18.9 ± 20.8
Total HpCDFs	0.17 ± 0.37	46.7 ± 36.9	1.12 ± 0.63	54.7 ± 77.4	0.13 ± 0.12	32.6 ± 24.7	1.15 ± 0.73	136.1 ± 354.1	0.08 ± 0.06	51.4 ± 36.9	1.04 ± 0.71	36 ± 40.3
Temperature (°C)			29.99 ± 1.39	30.12 ± 1.49[a]			20.03 ± 2.17	21.19 ± 1.59[a]			28.98 ± 1.38	25.81 ± 1,10[a]
pH (pH units)			7.70 ± 0.54	7.75 ± 0.68[a]			7.22 ± 0.46	7.82 ± 0.60[a]			7.44 ± 0.78	7.33 ± 0.55[a]
Salinity (‰)			7.40 ± 5.26	5.16 ± 3.83[a]			2.70 ± 3.23	5.59 ± 5.17[a]			10.40 ± 4.70	8.81 ± 3.72[a]
TSS (mg/l)			25.45 ± 13.92	N/A			34.70 ± 21.05	N/A			21.00 ± 8.94	N/A
TOC (mg/l or %)[b]			30.63 ± 8.49	1.20 ± 0.64			22.54 ± 12.78	1.00 ± 0.64			26.92 ± 6.58	1.60 ± 1.12
DOC (mg/l)			27.96 ± 8.60	N/A			18.62 ± 7.64	N/A			23.03 ± 4.28	N/A
Total solid content (%)			N/A	53.3 ± 17.5			N/A	49.3 ± 16.5			N/A	53.5 ± 14.8

N/A = not applicable.

[a] Parameter measured at the bottom of the water column at the time of sediment sampling.

[b] mg/l for water and % for sediment samples.

Table 2
Dioxin concentrations in water from various studies

Location	Area description	Dissolved	Suspended	Total	Diss/susp ratio	Reference
Japanese coastal area	*Non-polluted*	*0.10*[b]	*1.17–2.87*[b]	*1.27–2.87*[b]	*0.085*	Hashimoto et al. (1995)
Baltic Sea	*Offshore and pristine areas*	*0.036–0.257*[a]	*0.167–0.388*[a]	*0.239–0.552*[a]	*0.13–1.54*	Broman et al. (1991)
River Elbe, Germany		0.211–0.275[a]	86.13–276.49[a]	86.40–276.70[a]	0.0007–0.003	Gotz et al. (1994)
Lower Fraser River, BC, Canada urbanized				0.427–0.658[a]		Rantalainen et al. (1998)
Rantin Bay, NY	Highly industrialized and urbanized	2.94[a]	14.85[a]	17.79[a]	0.19	Lohmann et al. (2000)
Hudson River, NY	Highly industrialized and urbanized	2.35[a]	36.2[a]	38.55[a]	0.065	Lohmann et al. (2000)
The Grenlandsfjords, Norway	Near discharges from magnesium plant	0.09–2.74[a]	0.26–60.80[a]	0.35–63.43[3]	0.01–0.36	Persson et al. (2002)
Bayou Meto, AR	Near a herbicide manufacturer			4[c]		Lebo et al. (1995)
Houston Ship Channel, TX	Highly industrialized and urbanized	0.99–69.13[a,d]	11.28–392.74[a,d]	26.73–461.87[a,d]	0.01–0.44	This study

Studies in non-polluted areas are in italics.
[a] Total PCDD/PCDF concentrations in pg/l.
[b] Total PCDD concentrations in pg/l (PCDFs were not detected).
[c] TCDD + TCDF concentration in pg/l.
[d] Range for all three sampling events.

ranged from 0.001 to 63.37 pg/l, while the suspended concentrations varied between 0.001 and 356.44 pg/l. Overall, congener concentrations in water samples (dissolved plus suspended) exhibited the sequence OCDD > 123478-HpCDD > 1234789-HpCDF > OCDF > TCDF > TCDD. Most of the total 2378-substituted PCDD/PCDF concentration can be attributed to OCDD with an average contribution of 91%. However, 2378-TCDD was the major contributor to the total TEQ (41% on average) followed by OCDD (36% on average).

As expected for hydrophobic compounds, the dissolved concentrations were typically lower than their respective suspended concentrations, with average dissolved/suspended ratios between 0.11 and 0.59 for individual congeners. The dissolved/suspended ratios for total PCDD/PCDF, between 0.01 and 0.44, were higher than those observed in other studies except those in Broman et al. (1991) (Table 2). Overall, the dissolved fraction decreases with increased chlorination (data not shown). For example, average dissolved fractions for 2378-TCDD, 123678-HxCDD, and OCDD are 27%, 19%, and 11%, respectively. The average dissolved and suspended fractions did not show statistically significant ($\alpha = 0.05$) changes with season.

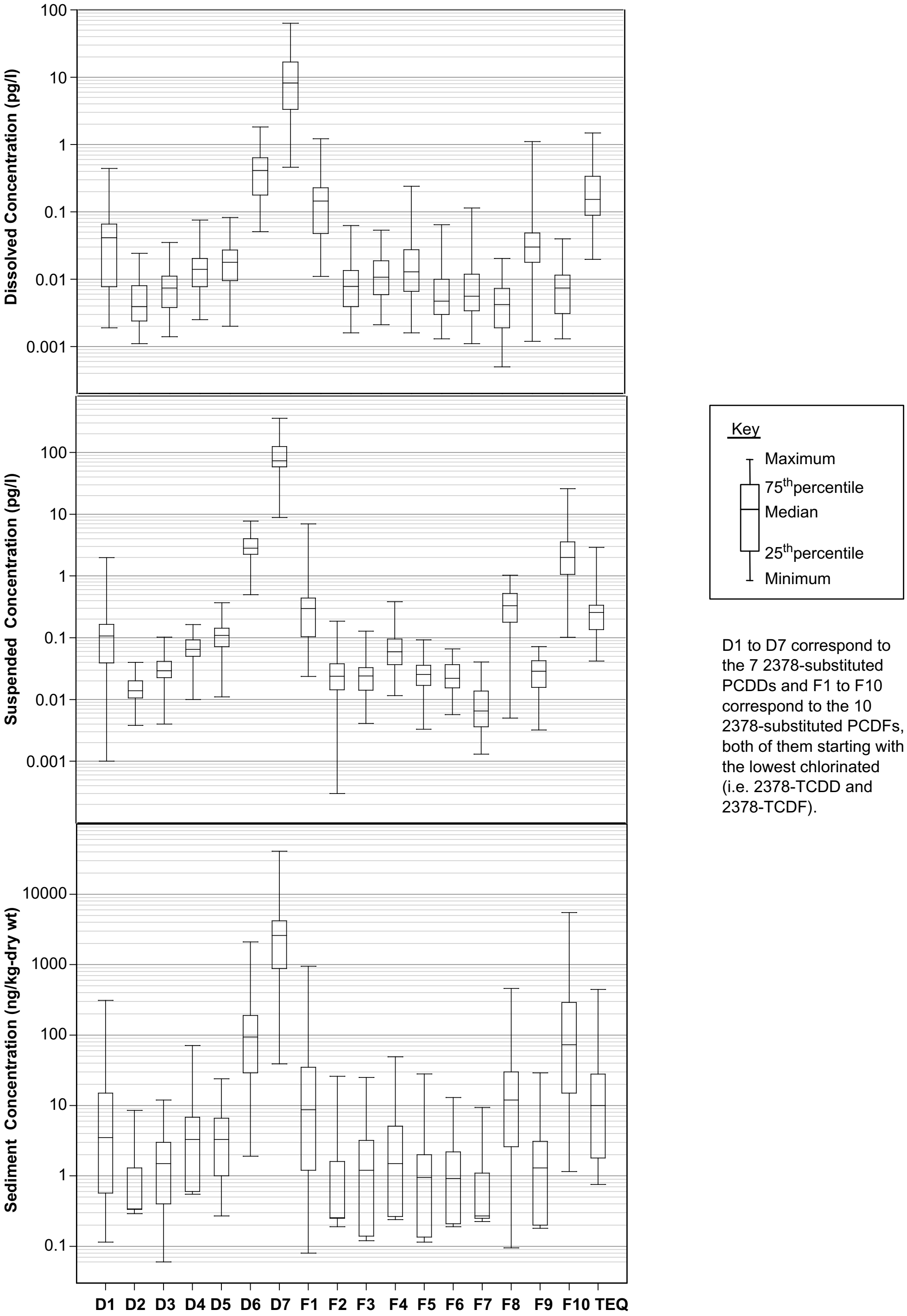
3.2. Sediment concentrations

The average levels of 2378-substituted PCDD/PCDFs in sediment samples are presented in Table 1. PCDD/PCDF concentrations in sediment varied within the ranges 0.7–443.8 ng TEQ/kg dry wt, 0.8–99.9 ng TEQ/kg dry wt, 0.9–139.8 ng TEQ/kg dry wt, for summer 2002, fall 2002 and spring 2003, respectively. Average sediment TEQ concentrations were 32.6, 25.7, and 17.5 ng/kg dry wt, for the three events respectively.

Fig. 2 shows the concentration distribution for the 17 PCDD/PCDF-like congeners and TEQ in sediment. The concentrations for the individual congeners ranged from 0.1 to 41 000 ng/kg dry wt. In general, sediment samples exhibited congener concentrations that followed the sequence OCDD > HpCDD > OCDF > HpCDF > TCDF > TCDD. As with water samples, most of the total concentration of 2378-substituted PCDD/PCDFs can be attributed to OCDD with an average contribution of 89%, while 2378-TCDD is the major contributor to the total TEQ (41% on average).

3.3. Spatial trends

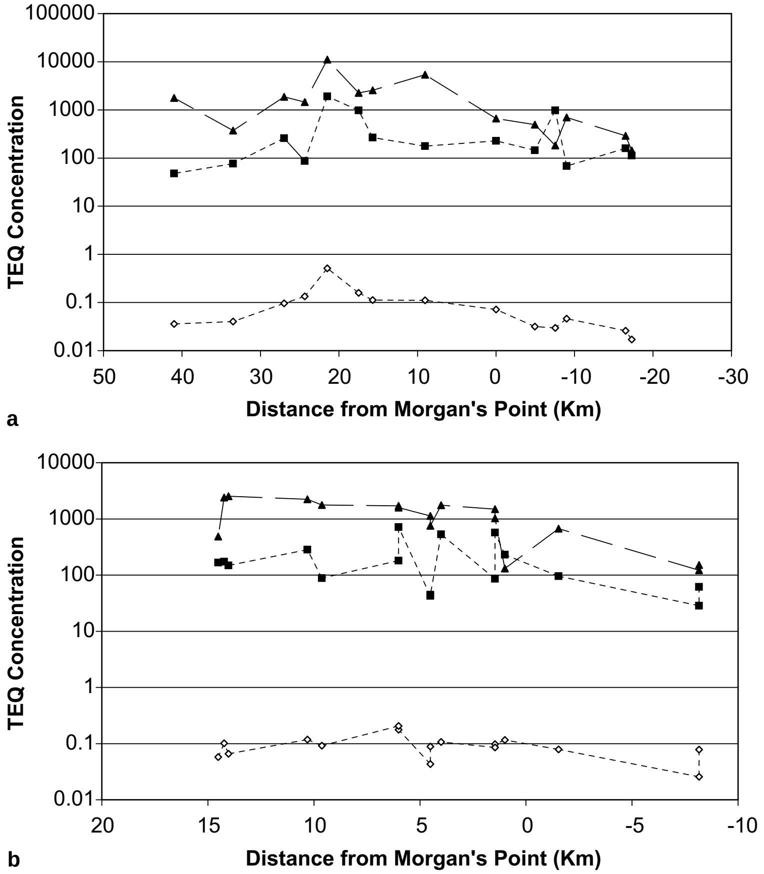
Average TEQ concentrations for dissolved, suspended sediment and bottom sediment samples were plotted at each location in Fig. 3a and b to evaluate data correlations among the different media. Data in Fig. 3a show that, in the main channel, PCDD/PCDF levels are consistent among the different media. A sudden increase in TEQ concentration in bottom sediment at a given station is accompanied by increases in the TEQ levels for the other two media, with the exception of one sample



D1 to D7 correspond to the 7 2378-substituted PCDDs and F1 to F10 correspond to the 10 2378-substituted PCDFs, both of them starting with the lowest chlorinated (i.e. 2378-TCDD and 2378-TCDF).

Fig. 2. Distribution of individual congeners in the dissolved, suspended and bottom sediment phases.

in Galveston Bay (river km—7.5) for which the suspended concentration exhibited a peak that was not observed in the other two media. In addition, data in Fig. 3a suggest the presence of a major contributor to PCDD/PCDF contamination somewhere along river km 15–30, where a sudden increase in concentration for all three media is observed. This peak may also be the result of sediment transport dynamics, redistribution



Notes: lines are shown to facilitate visualization only and do not imply continuity.
suspended and bottom sediment concentrations are normalized by the organic content of the sample
dissolved concentrations in pg/L, suspended and bottom sediment concentrations in ng/kg-oc

Fig. 3. Comparison of total I-TEQ levels in (a) the main channel and (b) side bays for dissolved (◇), suspended (■), and sediment (▲).

of historic sediments by tidal currents, erosion in previously depositional environments, and dredging/disposal practices. Similarly, in side bays (Fig. 3b), levels of PCDD/PCDFs are generally consistent among the three media.

In order to investigate possible changes in patterns due to differences in depth and hydraulics, plots for the main channel (top) were compared to those for side bays (bottom), but no obvious differences could be implied from visual inspection. However, results of a non-parametric correlation test among TEQs in the three sampled media for individual sets of samples indicate that dissolved PCDD/PCDF concentrations in the main channel are positively correlated to their organic carbon (oc)-normalized counterparts in suspended and bottom sediment samples (p-value < 0.05), while oc-normalized suspended and bottom sediment concentrations are not statistically correlated. For side bay samples, on the other hand, the dissolved TEQ concentrations showed a statistically significant correlation with oc-normalized suspended sediment concentrations, and the oc-normalized suspended and bottom sediment concentrations are statistically correlated (p-value = 0.01). This may indicate that the sources and processes contributing to the PCDD/PCDF concentrations may differ between the main channel and the side bays.

3.4. Suspended–dissolved partitioning in the water column

Partitioning between the suspended and dissolved phases can be quantitatively characterized by the linear partitioning coefficient (K_P) or by an organic carbon-normalized partitioning coefficient (K_{oc}), that describes the ratio of a chemical's concentration in suspended sediment to that in the dissolved phase at steady-state equilibrium conditions (Karickhoff, 1981):

$$K_P = f_{oc}K_{oc} = \frac{C_s}{C_{w,e}} \tag{1}$$

where C_s is the concentration of a specific PCDD/PCDF congener in the particulate phase in ng/kg dry wt, f_{oc} is the mass fraction organic carbon in the particulate phase, and $C_{w,e}$ is the concentration of the same compound in the truly dissolved phase at equilibrium.

In this research, observed partitioning coefficients (K_P^{obs} and K_{oc}^{obs}) for the HSC were calculated using the measured PCDD/F concentrations in the filter and XAD-2 resin samples, using the following equation:

$$K_P^{obs} = \frac{C_s}{C_w} \quad \text{or} \quad K_{oc}^{obs} = \frac{C_{oc}}{C_w} \tag{2}$$

where C_{oc} is the organic carbon-normalized concentration of a congener in the particulate phase in ng/kg-oc, and C_w is the concentration of the same compound in the truly dissolved phase. Concentrations measured in the XAD-resin were not corrected for the particle-concentration effect (PCE), since most of the colloidal portion passes through the XAD-2 resin as observed by Morehead et al. (1986) and Burgess et al. (1996) and, thus, PCDD/Fs sorbed to colloidal organic constituents are not included in the estimated concentrations. Only concentrations above the detection limits were included for calculating partitioning coefficients.

The $\log K_P^{obs}$ for the 17 congeners ranges from 3.29 to 6.67 l/kg dry wt, with average values varying from 4.93 ± 0.28 (mean ± standard deviation) to 5.71 ± 0.40 l/kg dry wt. Overall, $\log K_P^{obs}$ values increase with increased level of chlorination. $\log K_P^{obs}$ values showed a statistically significant (p-value < 0.01) but weak ($r^2 = 0.145$) inverse correlation with the amount of suspended matter (TSS) confirming similar observations reported by Bergen et al. (1993) and Eadie et al. (1992) for other HOCs. Given that solubility is affected by temperature, the relationship between $\log K_P^{obs}$ and temperature was also examined, but no statistically significant correlation was observed. Finally, the observed $\log K_P$ data were correlated to $\log K_{ow}$ values for the different PCDD/PCDF congeners given by Govers and Krop (1998). This analysis indicated that $\log K_{ow}$ alone only accounted for 21.7% of the observed variability in $\log K_P$.

In order to obtain organic-carbon-normalized PCDD/PCDF concentrations in suspended sediments (C_{oc}), the particulate organic carbon concentration (POC) was calculated as the difference between total organic carbon (TOC) and dissolved organic carbon (DOC) measured in grab water samples. The POC concentration in units of mass per volume was then converted to a percentage using the total suspended solid concentration (TSS) measured from the same sample. $\log K_{oc}^{obs}$ varied between 4.92 and 8.59 l/kg-oc,with average values ranging from 5.99 ± 0.59 to 6.78 ± 0.72 l/kg-oc (Fig. 4). Observed $\log K_{oc}$ values for locations measured during the three events were analyzed using a paired t-test to determine seasonal variation. Partitioning coefficients for most congeners showed no significant differences among seasons. The only exceptions were 1234678-HpCDD and OCDD for which the partitioning coefficients measured in the summer were significantly higher than those measured in the fall and in the spring.

The observed values of $\log K_{oc}$ were compared with equilibrium $\log K_{oc}$ values calculated using a linear model with 95% confidence limits developed by Seth et al. (1999):

$$\log K_{oc} = 1.03 \log K_{ow} - 0.61 \tag{3}$$

Because the K_{oc}–K_{ow} regressions were determined at 25 °C, observed K_{oc} values were corrected for temperature using the van't Hoff equation as proposed in the literature (Sobek et al., 2004):

$$\log K_{ow}(T) = \log K_{ow}(298.12\ \text{K}) + \frac{\Delta H_{ow}}{2.303R}\left(\frac{1}{298.15\ \text{K}} - \frac{1}{T}\right) \tag{4}$$

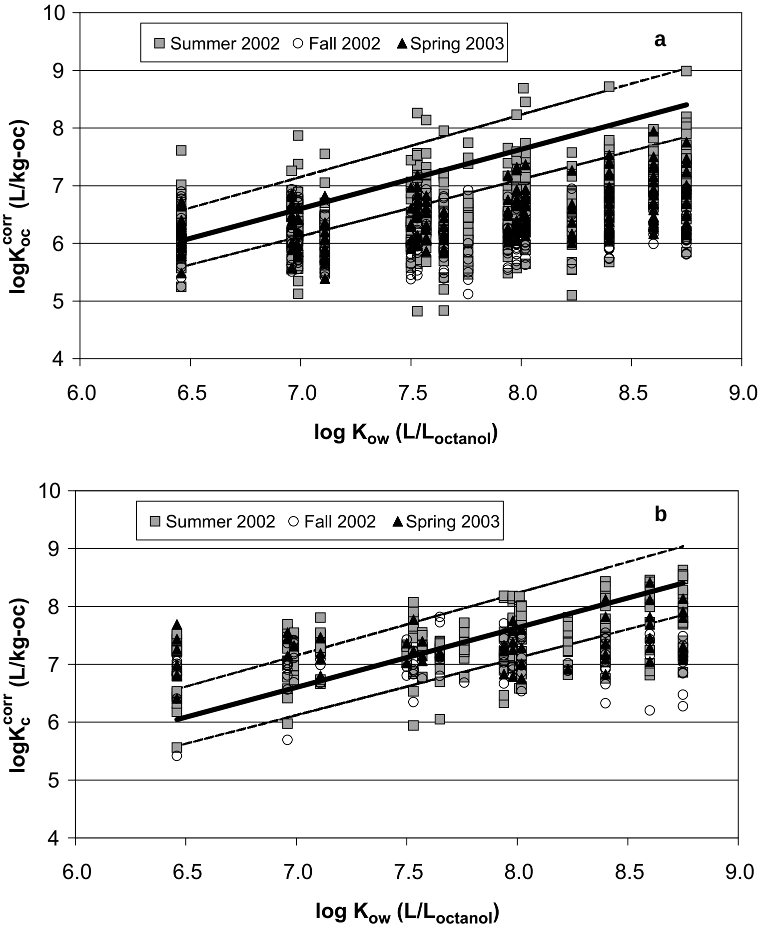
where ΔH_{ow} is the enthalpy of phase transfer (J/mol), R is the gas constant (J/mol/K), and T is the water temperature at sampling (K). Values of ΔH_{ow} were obtained from Shiu and Ma (2000), and assumed constant over the temperature interval of the samples. Correcting for temperature changed the observed $\log K_{oc}$ values between −2% and 2%.

Corrected $\log K_{oc}$ values agreed within a factor of 0.64–1.25 with equilibrium $\log K_{oc}$ predicted using Eq. (3). Data in Fig. 4a show that the compounds with the best agreement between equilibrium and corrected $\log K_{oc}$ values are the lower chlorinated PCDD/PCDFs (2378-TCDD, 2378-TCDF, and PeCDFs), with $\log K_{oc}^{corr}$ falling within the predicted range for equilibrium in more than 50% of the samples. For higher chlorinated PCDD/PCDFs, only 4% to 20% of the $\log K_{oc}^{corr}$ were within the predicted range. K_{oc}^{corr} values for hepta- and octa-PCDD/Fs were overpredicted in more than 90% of the samples by factors of 4–703 from those predicted by the equilibrium model.

Possible explanations for the differences between predicted and corrected partitioning coefficients include (i) error in POC concentrations, given that POC was not directly measured but calculated from TOC and DOC measurements; (ii) equilibrium K_{oc} values were calculated using a linear model that was obtained using data for various HOCs but not specifically for PCDD/PCDFs; site-specific K_{oc} measurements for the HSC are not available as of this writing; and (iii) the partitioning of PCDD/PCDF among the various media and the PCDD/PCDF loading from various sources constantly change over time and at the local scale, the system may not be at equilibrium.

3.5. Bottom sediment–water partitioning

Similar to suspended–dissolved partitioning, observed bottom sediment–dissolved partitioning coeffi-



Solid lines correspond to the equilibrium model as suggested by Seth et al. (1999).
Dashed lines correspond to the 95% confidence limits.

Fig. 4. Observed organic carbon-normalized partition coefficients for the HSC (a) suspended–dissolved and (b) bottom sediment–dissolved.

cients can be calculated using Eqs. (1) and (2). Because the referred to water column measurements were taken at depths between 1–2 feet and may not be at equilibrium with deeper bottom sediments if the channel exhibits stratification, partitioning coefficients were calculated only for the side bays (water depth < 6 ft). Observed $\log K_P$ values for the 17 congeners varied between 3.55 and 6.56 l/kg dry wt, with average values ranging from 4.91 ± 0.54 to 5.69 ± 0.58 l/kg-dry wt. These values compare very well with the observed $\log K_P$ values for suspended–dissolved partitioning. Correlations between different measured parameters and $\log K_P^{obs}$ values showed significant but weak correlations with sediment solids content (p-value < 0.01, $r^2 = 0.230$, inverse correlation) and sediment organic carbon content (TOC) (p-value < 0.01, $r^2 = 0.324$). Similar to the suspended–dissolved observed K_P values, a very weak correlation between sediment and water $\log K_P^{obs}$ and temperature (p-value = 0.04, $r^2 = 0.009$) suggested that the partitioning coefficients are not affected by seasonal variations in this system. A correlation between $\log K_P^{obs}$ and $\log K_{ow}$ showed that $\log K_{ow}$ only accounted for a very small percentage (4%) of the variability in $\log K_P^{obs}$.

Observed $\log K_{oc}$ values for sediment–water partitioning varied between 5.48 and 8.48 l/kg-oc, with average values between 6.86 ± 0.51 and 7.62 ± 0.56 l/kg-oc. The observed sediment–dissolved $\log K_{oc}$ values were generally higher than their suspended–dissolved counterparts, with differences of up to two logs. This might be due to higher degree of PCDD/PCDF contamination in the sediment. However, it is noted that unlike the suspended sediment and dissolved phase concentrations, that were measured simultaneously from the same sample, the bed sediment concentration and dissolved concentration measurements were taken up to a few days apart.

Corrected $\log K_{oc}$ values agreed within a factor of 0.76–1.26 with equilibrium $\log K_{oc}$ values (Fig. 4b). The congeners with the best agreement between equilibrium and corrected $\log K_{oc}$values were the penta- and hexa-PCDD/Fs; values being within the predicted range for equilibrium in 50–96% of the samples. Once again, the higher chlorinated PCDD/PCDFs show low agreement with the equilibrium model with more than 50% of the values outside the equilibrium range. It is noted that for the lower chlorinated congeners, $\log K_{oc}^{corr}$ is underpredicted by the equilibrium model for the majority of the samples, in contrast to what was observed for suspended–dissolved partitioning of the same congeners. K_{oc}^{corr} values for hepta- and octa-PCDD/Fs are overpredicted in more than 50% of the samples by factors of 5–95, while K_{oc}^{corr} values for 2378-TCDD and 2378-TCDF are underpredicted by the equilibrium model by factors up to 10 and 40, respectively.

Possible explanations for the differences between predicted and observed partitioning coefficients include: (i) uncertainty in the estimation of K_{oc} values as noted earlier, site-specific K_{oc} measurements are not available for the HSC; and (ii) disequilibrium between phases at the local scale.

An important observation from Fig. 4a and b is the flatness of the relationship between $\log K_{oc}^{corr}$ and the "hydrophobicity" of the chemical, as indicated by $\log K_{ow}$. This effect is frequently observed (see for example, Baker et al., 1991; Axelman et al., 1997) and commonly attributed to disequilibrium caused by kinetic factors.

If the difference between equilibrium and corrected $\log K_{oc}$ values discussed is interpreted as a lack of equilibrium at the local scale of PCDD/PCDFs among different phases in the HSC, contaminant fluxes between the phases can be expected. Values of $\log K_{oc}^{corr}$ that are higher than their respective equilibrium $\log K_{oc}$ indicate a tendency for a specific congener to partition in the particulate phase, while $\log K_{oc}^{corr}$ values that are lower than their respective equilibrium $\log K_{oc}$ indicate a tendency for a specific congener to partition in the dissolved phase. Data in Fig. 4 also suggest that on average a compound has a lower tendency to move from the particulate phase to the dissolved phase with increasing K_{ow}, indicating that lower chlorinated compounds (lower K_{ow}) are magnified in the suspended sediments to a greater degree than the higher chlorinated compounds. This suggests that organisms feeding on sediment may experience more exposure to lower K_{ow} chemicals (tetra- and penta-PCDD/Fs) via the diet than equilibrium bioaccumulation relationships would predict.

In summary, the equilibrium model best fits the HSC lower chlorinated data, whereas it overpredicts the higher chlorinated partitioning coefficients. Data suggest fluxes of PCDD/PCDFs across interfaces. Ongoing work to further explore these findings includes analysis of fingerprints to find relationships between possible sources and observed contamination.

Acknowledgments

This research was funded by the Texas Commission on Environmental Quality (TCEQ) and the Texas Advanced Technology Program (ATP). Their funding is gratefully acknowledged.

References

Axelman, J., Broman, D., Naf, C., 1997. Field measurements of PCB partitioning between water and planktonic organisms: influence of growth, particle size, and solute–solvent interactions. Environ. Sci. Technol. 31, 665–669.

Baker, J.E., Eisenreich, S.J., Eadie, B.J., 1991. Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorobiphenyl congeners in Lake Superior. Environ. Sci. Technol. 25, 500–509.

Bergen, B.J., Nelson, W.G., Pruell, R.J., 1993. Partitioning of polychlorinated biphenyl congeners in the seawater of New Bedford Harbor, Massachusetts. Environ. Sci. Technol. 27, 938–942.

Broman, D., Naf, C., Rolff, C., Zebuhr, Y., 1991. Occurrence and dynamics of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons in mixed surface layer of remote coastal and offshore waters of the Baltic. Environ. Sci. Technol. 25, 1850–1864.

Burgess, R.M., McKinney, R.A., Brown, W.A., Quinn, J.G., 1996. Isolation of marine sediment colloids and associated polychlorinated biphenyls: an evaluation of ultrafiltration and reverse-phase chromatography. Environ. Sci. Technol. 30, 1923–1932.

Eadie, B.J., Morehead, N.R., Klump, J.V., Landrum, P.F., 1992. Distribution of hydrophobic organic compounds between dissolved and particulate organic matter in Green Bay waters. J. Great Lakes Res. 18, 91–97.

Gotz, R., Enge, P., Friesel, P., Roch, K., Kjeller, L.-O., Kulp, S.E., Rappe, C., 1994. Sampling and analysis of water and suspended particulate matter of the River Elbe for polychlorinated dibenzo-*p*-dioxins (pcdds) and dibenzofurans (PCDFs). Chemosphere 28, 63–74.

Govers, H.A.J., Krop, H.B., 1998. Partition constants of chlorinated dibenzofurans and dibenzo-*p*-dioxins. Chemosphere 37, 2139–2152.

Hashimoto, S., Matsuda, M., Wakimoto, T., Tatsukawa, R., 1995. Simple sampling and analysis of PCDDs and PCDFs in Japanese coastal seawater. Chemosphere 30, 1979–1986.

Karickhoff, S.W., 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere 10, 833–846.

Lebo, J.A., Gale, R.W., Petty, J.D., Tillitt, D.E., Huckins, J.N., Meadows, J.C., Orazio, C.E., Echols, K.R., Schroeder, D.J., 1995. Use of the semipermeable membrane device as an in situ sampler of waterborne bioavailable PCDD and PCDF residues at sub-parts-per-quadrillion concentrations. Environ. Sci. Technol. 29, 2886–2892.

Lohmann, R., Nelson, E., Eisenreich, S.J., Jones, K.C., 2000. Evidence of dynamic airwater exchange of PCCC/Fs: a study in the Raritan Bay/Hudson River Estuary. Environ. Sci. Technol. 34, 3086–3093.

Morehead, N.R., Eadie, B.J., Lake, B., Landrum, P.F., Berner, D., 1986. The sorption of PAH onto dissolved organic matter in Lake Michigan waters. Chemosphere 15, 403–412.

Persson, N.J., Gustafsson, O., Bucheli, T.D., Ishaq, R., Naes, K., Broman, D., 2002. Sootcarbon influenced distribution of PCDD/Fs in the marine environment of the Grelandsfjords, Norway. Environ. Sci. Technol. 36, 4968–4974.

Rantalainen, A.-L., Ikonomou, M.G., Rogers, I.H., 1998. Lipid-containing semipermeable membrane devices (SPMDs) as concentrators of toxic chemicals in the Lower Fraser River, Vancouver, British Columbia. Chemosphere 37, 1119–1138.

Seth, R., Mackay, D., Muncke, J., 1999. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. Environ. Sci. Technol. 33, 2390–2394.

Shiu, W.Y., Ma, K.C., 2000. Temperature dependence of physical–chemical properties of selected chemicals of environmental interest. II. Chlorobenzenes, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, and dibenzofurans. J. Phys. Chem. Ref. Data 29, 387–462.

Sobek, A., Gustafsson, Ö, Hajdu, S., Larsson, U., 2004. Particle–water partitioning of PCBs in the photic zone: a 25-month study in the open Baltic Sea. Environ. Sci. Technol. 38, 1375–1382.

US Environmental Protection Agency, 1983. Methods for chemical analysis of water and wastes. Office of Research and Development, Washington, DC. EPA/600/4-79/020.

US Environmental Protection Agency, 2002. National recommended water quality criteria. USEPA, Office of Water, Washington, DC.

Van den Berg, M., Birnbaum, L., Bosveld, A., Bjorn, B., Cook, P., Feeley, M., Giesi, J., Hanberg, A., Hasegawa, R., Kennedy, S., Kubiak, T., Larsen, J., Van Leeuwen, R., Liem, A., Nolt, C., Peterson, R., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Younes, M., Waem, F., Zacharewski, T., 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ. Health Perspect. 106, 775–792.