Extractability of dioxins from suspended substances in distributed water

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The extractability of dioxins from suspended substances (SS) in distributed water was evaluated. Dioxins adsorbed on the collected SS were extracted by pressurized liquid extraction with various solvents. High-polarity solvents (acetone, alcohols) extracted considerably higher amounts of some lower-chlorinated dibenzo-*p*-dioxins (LoCDDs) than did low-polarity solvents (dichloromethane, toluene), whereas the extracted amounts of higher-chlorinated dibenzo-*p*-dioxins (HiCDDs) were roughly the same, regardless of the solvent. The extractability of the LoCDDs depended on the isomer. Daily variations in quantities for PCDDs, organic matter (OM), and iron in the SS were examined, and the results suggested that in the SS, LoCDDs and HiCDDs were associated, respectively, with raw water-derived organic matter and microparticles sequestered in iron oxy(hydr)oxide floc. It was also suggested that the low extractability of certain congeners was not attributable to the enormously coexisting ferric compounds but was probably attributable to OM with which they strongly associate.

Keywords: Dioxins; Distributed water; Suspended substances; Extractability; Physical state

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (DL-PCBs) are highly toxic persistent organic compounds that have been detected in almost all kinds of environmental samples, such as soil, fly ash, sewage sludge, water, and so forth [1]. Many studies of their formation mechanisms, toxicity, intake into biota, and environmental behaviour have been published.

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The risks associated with human dietary intake of dioxins have been extensively investigated. Dietary intake is regarded as the most important route by which these compounds reach humans, contributing more than 90% of daily exposure [2].

Drinking water, which is indispensable for human life, also contributes to daily exposure. The USEPA has set the maximum allowable level for 2,3,7,8-TeCDD in drinking water at 0.13 pg/L for a human cancer risk of 10^{-5}, and at 0.0013 pg/L for a risk of 10^{-7} [3].

There have been many reports regarding the levels and behaviour of hazardous compounds such as pesticides [4, 5], polycyclic aromatic hydrocarbons [6, 7], heavy metals [8, 9], and trihalomethanes as disinfection by-products [10, 11] in treated water. However, only a few reports have been published on dioxins in treated water. Kim *et al*. found an increase in the level of 2,3,7,8-TeCDF as a by-product of chlorination during the water-treatment process [12].

Accurate estimation of dioxin levels in treated water is challenging because their concentrations are quite low. The conventional Japanese procedure for analysis of dioxins in raw and treated water [13] consists of percolation of a large amount of water (200 L for raw water and 2000 L for treated water) through a glass-fibre filter (GFF), to retain particle-bound dioxins, and polyurethane foam plugs (PUFs), to retain dissolved dioxins, followed by Soxhlet extraction of the filter and the plugs with a low-polarity organic solvent (dichloromethane or toluene).

In preliminary experiments, we found that the isomer profiles of some PCDD/F homologues in suspended substances (SS) in distributed water depended on the extraction solvent, which suggests differences in the extractability of the isomers from the SS. We suspected that the differences might have resulted from differences in the physical states of the isomers in the SS.

Almost all previous studies of dioxins in treated water have dealt with water sampled from water-treatment plants. However, some distinctive PCDF isomers in treated water (produced by chlorination, e.g. 2,3,7,8-TeCDF) [14] are reported to be produced mainly in water-distribution pipes [15]. Therefore, with regard to estimating human-intake levels through drinking water, accurately determining dioxin levels in distributed water is more important than determining levels in just-treated water. If dioxins are to be accurately determined, their physical state in distributed water should be investigated, and suitable extraction procedures should be adopted on the basis of their physical state. However, little information about the physical state of dioxins in distributed water has been published.

In this study, we first determined the extractability of dioxin congeners from SS in distributed water, and then we drew conclusions about their physical state, which might dominate extractability of the congeners, in distributed water SS. The physical states of dioxins were concluded on the basis of the daily variations in quantities for dioxins and coexisting matrices, i.e. organic matter (OM) and ferric compounds in the SS.

2. Experimental

2.1 *Water samples*

Distributed water was obtained from four taps in Saitama Prefecture (Tap 1 and Tap 2, Tokorozawa City; Tap 3 and Tap 4, Iruma City). A raw water sample, originated from

the Arakawa River, was collected from inside the water-treatment plant in Saitama City (Saitama Prefecture), which supplies treated water to all the taps. The taps were located about 18 km (Tap 1 and Tap 2) or 23 km (Tap 3 and Tap 4) from the plant. The treatment plant uses conventional process trains: pre-chlorination, polyaluminium chloride coagulation, sedimentation, mid-chlorination, sand filtration, and post-chlorination.

2.2 *Apparatus*

Water was sampled with an automatic *in situ* pre-concentration system (DS690, GL Sciences, Tokyo). Prior to extraction, PUFs were dried in an oven (FS-405, Advantec Tokyo). Concentrated dioxins were subjected to pressurized liquid extraction (PLE; ASE-300, Dionex, Sunnyvale, CA) under the following conditions: cell volume, 66 mL (for SS) or 99 mL (for PUFs); cell temperature, 200°C (for SS) or 50°C (for PUFs); cell pressure, 10 MPa (1500 psi); static time, 7 min; solvent flush volume, 100% of cell volume; purge time, 100 s with N_2 gas; and number of cycles, 2. For extraction from GFF, two repetitions of the extraction process were carried out.

PCDD/Fs and DL-PCBs were analysed by high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS) with an HP-6890 Plus gas chromatograph (Agilent, Palo Alto, CA) coupled to a JMS-700 mass spectrometer (JEOL, Tokyo). The analytes were determined on BPX-DXN (SGE, Austin, TX) and RH-12ms (InventX, Torrance, CA) capillary columns.

The levels of total organic carbon (TOC) and metal elements in distributed water SS were determined with an SSM-5000A + TOC-V_{CPN} total organic carbon analyser (Shimadzu, Kyoto, Japan) and a JSX-3202M (JEOL) X-ray fluorescence spectrometer, respectively.

2.3 *Materials and reagents*

The GFF (300 mm diameter, 0.5 μm particle retention) and the PUFs (100 mm diameter, 50 mm thick) used to collect the particle-bound and dissolved dioxins in the water samples were obtained from GL Sciences.

All dioxin-analytical-grade solvents and adsorbents were purchased from either Wako Pure Chemical Industries (Osaka, Japan) or Kanto Chemicals (Tokyo). Analytical-grade hydrochloric acid, sodium hydroxide, $FeCl_3 \cdot 6H_2O$, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, *o*-phenanthroline hydrochloride, sodium acetate, acetic acid, and hydroxylammonium chloride were purchased from Kanto Chemicals. Hydrochloric acid and ammonia solution (25.0–27.9% as NH_3; poisonous-metal analytical grade) were also obtained from Kanto.

PCDD/F and DL-PCB standards, including ^{13}C-labelled homologues, were purchased from Wellington Laboratories (Ontario, Canada) or Cambridge Isotope Laboratories Inc. (Andover, MD). The abbreviations for the number of chlorine atoms are as follows: tetra (Te), penta (Pe), hexa (Hx), hepta (Hp), and octa (O). All DL-PCBs are referred to by their International Union of Pure and Applied Chemistry (IUPAC) numbers.

A surrogates solution (SuS) was prepared in toluene. This solution contained 17 ^{13}C-labelled 2,3,7,8-substituted CDD/F congeners (2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF,

1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, and OCDF) and 12 ^{13}C-labelled DL-PCBs (IUPAC Nos 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189), each at a concentration of 20 µg/L, with the exception of ^{13}C-OCDD/F at 40 µg/L.

A recovery standards solution (RS) in nonane was prepared containing ^{13}C-labelled 1,2,7,8-TeCDF, 1,2,3,4,7-PeCDD, 1,2,3,4,6,9-HxCDF, 1,2,3,4,6,8,9-HpCDF, 2,3′,4′,5-TeCB (No. 70), 2,2′,3,4,4′-PeCB (No. 85), 2,2′,3,4,4′,5′-HxCB (No. 138) and 2,2′,3,3′,5,5′,6-HpCB (No. 178), each at a concentration of 10 µg/L.

A sampling standard solution (SaS) in toluene was prepared containing ^{13}C-labelled 1,2,3,4-TeCDD at a concentration of 20 µg/L.

A reference material comprising fly ash was provided by the National Institute for Environmental Studies, Japan.

2.4 *Sampling, extraction, clean-up, and HRGC–HRMS analysis*

A flow chart of the sample treatment procedure is shown in figure 1. Prior to the application of the water sample, the top PUF was spiked with 10 µL of the SaS. The water samples (raw water, 200 L; distributed water, 2000 L) were passed through the glass-fibre filter and the four PUFs at the rate of 1.4 L/min. The sampling time was about 2.4 h for raw water and 24 h for distributed water. PLE extracts from the GFF and the PUFs were spiked with the SuS and subjected to clean-up procedures. For the analysis of raw water, the extracts from the GFF and PUFs were combined, spiked with SuS, and then analysed.

Aliquots (1 µL or 2 µL) of the solutions obtained after clean-up and concentration were injected onto a GC equipped with a BPX-DXN column for analysis of PCDD/Fs (60 m × 0.25 mm i.d.) and an RH-12ms column for analysis of DL-PCBs (60 m × 0.25 mm i.d.), in splitless mode. Acquisition parameters for selected ion monitoring (SIM) mode and other GC/MS conditions are described elsewhere [16]. Toxicity equivalency (TEQ) values for all 2,3,7,8-chlorinated congeners were calculated using 2,3,7,8-TeCDD toxicity equivalency factors (TEF) reported by the World Health Organization [17].

2.5 *Estimation of extractability of dioxins from distributed water SS*

After percolation of distributed water according to the procedure described above, the GFF was evenly divided into two or four pieces, and each piece was extracted with a variety of solvents (dichloromethane, toluene, methanol, ethanol, or acetone). The extracted amounts of dioxins were quantified according to the procedure in figure 1.

2.6 *Daily variation of dioxin concentrations in distributed water*

Distributed water was sampled daily for 5 days running (sampling period; 21–29 October 2004 and 8–16 March 2005). The GFF and PUFs were changed every 24 h. We also measured the temperature and residual chlorine concentration of the tap water and observed no significant daily variation in these parameters. Dioxins retained on the GFF and on the PUFs were separately determined according to the procedure in figure 1. A portion (one-quarter) of the GFF was used for the determination of iron and total organic carbon (TOC) levels. The GFF containing the SS was cut into two

Raw water (200 L) or distributed water (2000 L)

← SaS 10 μL (spiked on the top PUF)

Drawn through a GFF and four PUFs

Flow rate: 1.4 L min^{-1}

GFF (SS)   PUFs

Air-dried   Dried in an oven (35°C)

Pressurized liquid extraction

GFF: acetone or other solvents

PUFs: acetone

← SuS 10 μL   ← SuS 10 μL

Redissolved in *n*-hexane   Evaporated to ca. 5 mL

                                       ← *n*-Hexane 100 mL

                                       Washed with water

                                          (30 mL, 3 times)

                                       Dehydrated with Na$_2$SO$_4$

Multilayer silica gel chromatography

10% AgNO$_3$ / silica (2 g) - 22% H$_2$SO$_4$ / silica (4 g)

- 44% H$_2$SO$_4$ / silica (4 g)- 2% KOH / silica (1 g)

eluted with 120 ml *n*-hexane

Active-carbon-dispersed silica gel reversible
column chromatography (1 g)

washed with 50 ml *n*-hexane

eluted with 25 ml 25%-toluene /*n*-hexane (v/v)

eluted with 40 ml toluene (by reverse flow)

← RS 10μL →

Concentration to 10 μL

1 μL GC-MS inj.   2 μL GC-MS inj.
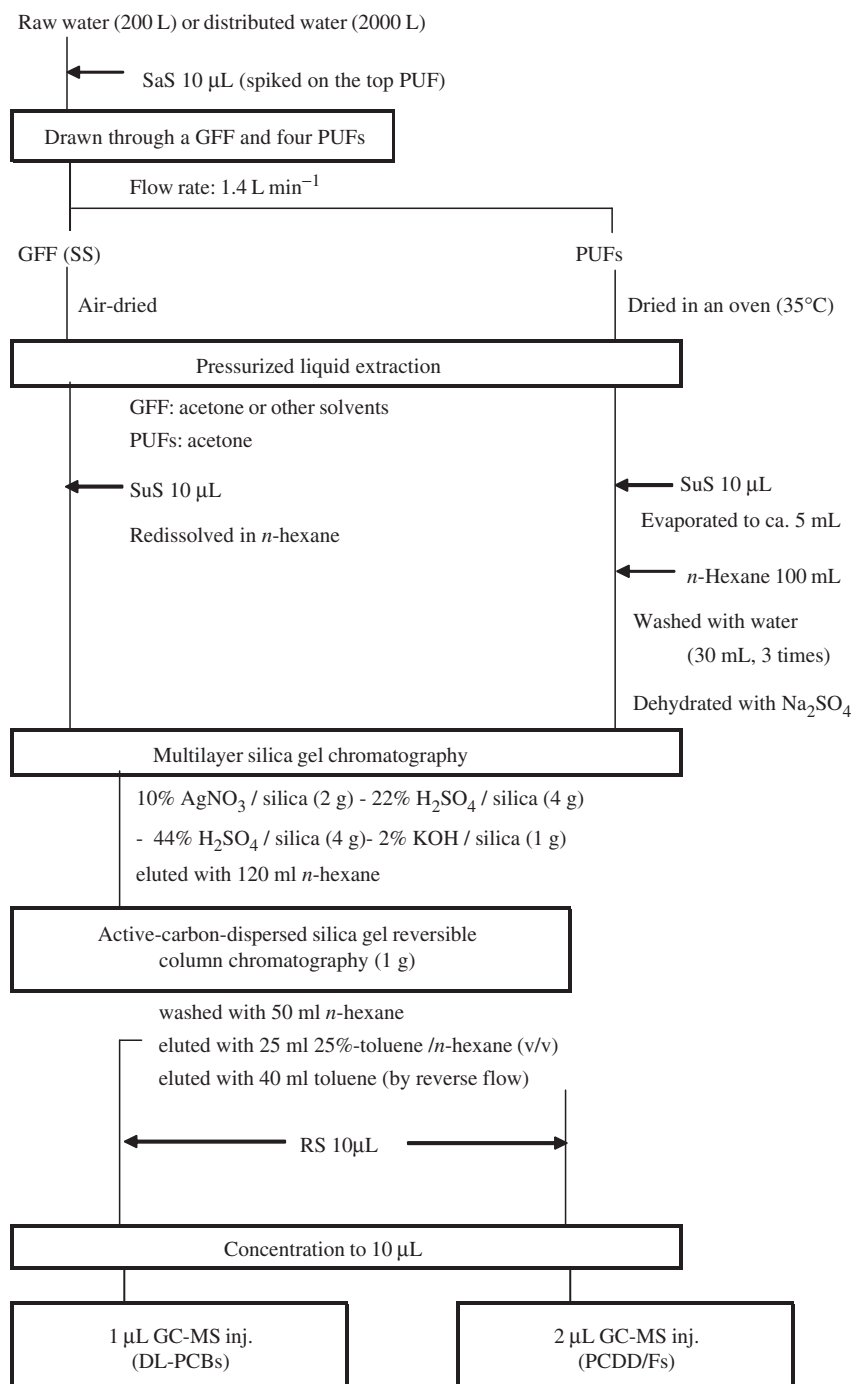(DL-PCBs)   (PCDD/Fs)

Figure 1.   Analytical protocol for determination of PCDD/Fs and DL-PCBs in raw and distributed water.

sample circles (42 mm diameter). One sample circle was used for TOC analysis, and another circle was used for colorimetric iron determination using *o*-phenanthroline [18] after thermal digestion of organic matter (by heating at 500°C for 12 h).

2.7 *Accuracy control*

Glassware was rinsed with acetone and *n*-hexane, and the GFF was heated at 450°C (for 4 h) prior to use in order to remove analyte residues. PUFs were also prewashed by refluxing them in a Soxhlet apparatus with dichloromethane (for 24 h).

An instrumental blank of clean *n*-nonane was measured prior to every GC–MS run to confirm the absence of analytes. A method blank was analysed in each sample batch to demonstrate the absence of contaminants.

All samples were spiked with the SaS and SuS (including the blank tests), and the recoveries of the standards were confirmed before data processing. In this study, the recoveries from all the samples were sufficient (88–98% for the SaS and 72–120% for the SuS), which proved the validity of the analytical method.

Assay accuracy was confirmed by determining dioxins in a certified reference material (fly ash) and comparing the quantitative results with the certified values. As shown in table 1, the quantitative results of each 2,3,7,8-substituted isomer and homologue showed good agreement with the certified values, proving that the assay was reliable.

3. Results and discussion

3.1 *Extractability of dioxin congeners from distributed water SS*

The conventional procedure in Japan for the analysis of dioxins in treated water [13] calls for extraction of particle-bound dioxins (from GFFs) and dissolved dioxins (from PUFs) with dichloromethane, which is a low-polarity solvent. However, we suspected that extracting the SS with a high-polarity solvent such as acetone might be preferable, because the matrices carrying the dioxins are probably hydrophilic. Therefore, we investigated the extraction efficiency of various solvents in extracting dioxins from SS in distributed water.

The amounts of PCDDs extracted from the divided GFF pieces with a variety of solvents are shown in table 2; only the data for PCDDs are displayed because the extracted amounts of PCDFs and DL-PCBs were insignificant. We found that all the dioxin congeners adsorbed on the PUFs could be extracted quantitatively with both high-polarity and low-polarity solvents (dichloromethane, toluene, and acetone; data not shown), which indicates that the dioxins retained on the PUFs existed in an easily extractable form. However, the extractability of some PCDD homologues from the SS varied with the type of extracting solvent.

For samples from Tap 1 and Tap 2, the amounts of lower-chlorinated dibenzo-*p*-dioxins (LoCDDs; tetra- to hexa-chloro) obtained by extraction of the SS with high-polarity solvents were considerably higher than the amounts obtained with low-polarity solvents. Samples from Tap 3 and Tap 4 showed a similar trend, although the extracted amounts were lower than those for Tap 1 and Tap 2.

Table 1. Quantitative results of dioxins in the certified reference material (fly ash) (units in ng/g).

Compound	Sample 1[a]	Sample 2[a]	Sample 3[a]	Average	SD[b]	CV%[c]	Certified conc.[d]	Difference[e] (%)
2,3,7,8-TeCDD	4.12	4.42	4.06	4.20	0.19	4.5	3.94	6.6
1,2,3,7,8-PeCDD	24.7	28.5	24.7	26.0	2.2	8.4	27.6	5.8
1,2,3,4,7,8-HxCDD	38.7	41.0	40.5	40.0	1.2	3.0	38.3	4.5
1,2,3,6,7,8-HxCDD	35.2	37.2	34.9	35.8	1.3	3.6	37.7	5.1
1,2,3,7,8,9-HxCDD	48.5	52.9	51.6	51.0	2.3	4.5	47.3	7.8
1,2,3,4,6,7,8-HpCDD	213	217	222	217	4.6	2.1	240	9.4
OCDD	282	298	290	290	8	2.8	267	8.6
2,3,7,8-TeCDF	6.68	6.99	7.21	6.96	0.27	3.9	6.66	4.5
1,2,3,7,8-PeCDF	23.2	25.2	24.1	24.2	1.0	4.1	21.8	10.9
2,3,4,7,8-PeCDF	23.5	24.6	23.5	23.8	0.64	2.7	22.7	5.0
1,2,3,4,7,8-HxCDF	44.2	44.0	42.5	43.6	0.93	2.1	43.4	0.4
1,2,3,6,7,8-HxCDF	44.0	46.6	46.4	45.7	1.5	3.2	43.8	4.2
1,2,3,7,8,9-HxCDF	3.45	3.96	2.98	3.46	0.49	14	3.18	8.8
2,3,4,6,7,8-HxCDF	38.5	38.9	39.7	39.1	0.6	1.5	37.3	4.7
1,2,3,4,6,7,8-HpCDF	143	134	150	142	8.3	5.8	157	9.4
1,2,3,4,7,8,9-HpCDF	16.1	18.6	17.3	17.3	1.2	7.2	17.5	1.0
OCDF	64.0	72.0	70.3	68.8	4.2	6.1	59.6	15.4
TeCDDs	57.1	60.6	57.4	58.4	1.9	3.3	53.9	8.3
PeCDDs	153	166	152	157	8.2	5.2	175	10.3
HxCDDs	378	400	390	389	10.6	2.7	384	1.4
HpCDDs	349	362	360	357	6.8	1.9	398	10.4
TeCDFs	197	213	208	206	8.1	3.9	208	1.1
PeCDFs	319	334	322	325	8.3	2.5	319	1.9
HxCDFs	416	419	408	414	5.6	1.4	399	3.9
HpCDFs	233	233	244	237	6.1	2.6	253	6.4
#77-TeCB	3.20	3.40	3.23	3.28	0.11	3.2	3.29	0.4
#81-TeCB	0.451	0.440	0.477	0.456	0.019	4.2	0.433	5.3
#126-PeCB	3.85	4.09	3.96	3.96	0.12	3.1	4.15	4.5
#169-HxCB	1.87	2.00	1.85	1.91	0.08	4.4	2.01	5.1
#105-PeCB	2.49	2.77	2.07	2.44	0.35	14	2.35	3.9
#114-PeCB	0.134	0.178	0.168	0.160	0.023	14	0.161	0.6
#118-PeCB	1.33	1.33	1.56	1.41	0.14	9.6	1.66	15.3
#123-PeCB	0.397	0.344	0.467	0.403	0.062	15	0.443	9.1
#156-HxCB	1.70	1.58	1.71	1.66	0.07	4.5	1.88	11.5
#157-HxCB	1.22	1.31	1.31	1.28	0.05	4.2	1.37	6.5
#167-HxCB	1.03	1.07	1.10	1.07	0.04	3.6	1.13	5.6
#189-HpCB	1.74	2.01	1.97	1.90	0.15	7.7	1.92	0.9

[a]Results of triplicate experiments. [b]Standard deviation. [c]Coefficient of variation. [d]Averaged value of the intercalibration exercise. [e]Difference between the averaged quantitative result and the certified amount.

In contrast, the amounts of higher-chlorinated dibenzo-*p*-dioxins (HiCDDs; hepta- and octa-chloro DDs) extracted from the SS were almost equal for all of the solvents. We also determined the extractability of the various dioxin congeners at higher temperatures: we extracted the SS with acetone at 50°C (three times) and then at 200°C (three times), and then measured the amounts of the congeners extracted into each fraction. For some homologues, the isomer profile obtained at 50°C differed from that at 200°C, as a result of differences in the extractabilities of the various isomers. The congeners that showed extractabilities that changed substantially with temperature were 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, 2,4,6,8-TeCDF, 1,2,4,6,8-PeCDF, 2,3,4,6,8-PeCDF, and 1,2,3,4,6,8-HxCDD (figure 2). These congeners were predominantly extracted at 200°C, which indicates that their extractability was lower than that of the other isomers. However, these do not have a TEF value, and therefore the TEQ concentration from SS did not vary with extracting solvents.

Table 2. Amounts of PCDDs extracted from distributed water SS with various solvents.

	Extracted amount (pg)[a]					
	Blank[b]	DCM[c]	Toluene	Methanol	Ethanol	Acetone
Tap 1, 1st trial						
TeCDDs	< 0.4	6.1	5.9	100	—[d]	170
PeCDDs	< 0.4	2.4	2.0	3.3	–	3.4
HxCDDs	< 0.4	3.4	2.9	10	–	8.7
HpCDDs	< 0.4	7.3	7.4	9.1	–	8.3
OCDD	< 2	30	32	35	–	33
Tap 1, 2nd trial						
TeCDDs	< 0.4	8.7	–	–	–	2000
PeCDDs	< 0.4	1.7	–	–	–	38
HxCDDs	< 0.4	2.9	–	–	–	26
HpCDDs	< 0.4	9.2	–	–	–	13
OCDD	6.1	41	–	–	–	49
Tap 2, 1st trial						
TeCDDs	< 0.4	12	–	470	430	370
PeCDDs	< 0.4	5.5	–	8.6	5.1	5.8
HxCDDs	< 0.4	6.6	–	20	19	18
HpCDDs	< 0.4	5.1	–	6.1	5.9	5.7
OCDD	4.1	20	–	24	23	24
Tap 2, 2nd trial						
TeCDDs	< 0.4	7.1	6.8	92	–	220
PeCDDs	< 0.4	2.7	2.4	4.0	–	5.3
HxCDDs	< 0.4	4.2	3.9	13	–	12
HpCDDs	< 0.4	9.4	9.2	11	–	11
OCDD	2.8	41	42	48	–	44
Tap 3						
TeCDDs	1.7	4.0	4.2	9.1	–	22
PeCDDs	< 0.4	< 0.4	< 0.4	< 0.4	–	< 0.4
HxCDDs	< 0.4	1.6	1.6	2.0	–	4.1
HpCDDs	< 0.4	4.2	3.5	5.1	–	5.8
OCDD	< 2	22	20	23	–	24
Tap 4						
TeCDDs	2.4	4.7	–	7.3	–	21
PeCDDs	< 0.4	< 0.4	–	< 0.4	–	< 0.4
HxCDDs	< 0.4	1.8	–	1.8	–	2.0
HpCDDs	< 0.4	2.4	–	2.8	–	2.7
OCDD	< 2	10	–	12	–	11

[a]Amount extracted from a divided filter after percolation. [b]Amount extracted from a blank filter with acetone. [c]Dichloromethane. [d]Not tested.

3.2 *Variation of dioxins quantities and coexisting organic matter and iron in SS*

The extractability of dioxin congeners from the SS might be dependent on their physical states in the SS. To obtain a high extraction efficiency of dioxins from the SS, appropriate extraction conditions must be chosen on the basis of the form in which the dioxins occur in the SS. If dioxins are associated with some matrices, there will be a correlation between dioxins and the matrices quantities in the SS. Therefore, in order to obtain information on the physical state of dioxins in the SS, we examined the daily variation in the amounts of dioxins extracted and coexisting matrices in the SS. As part of this investigation, we measured OM content (expressed as TOC) in the SS. Dissolved humic substances (DHS), a major component of dissolved OM in treated water [19], can associate with lipophilic organic compounds such as dioxins and raise their solubility in water containing DHS [20].
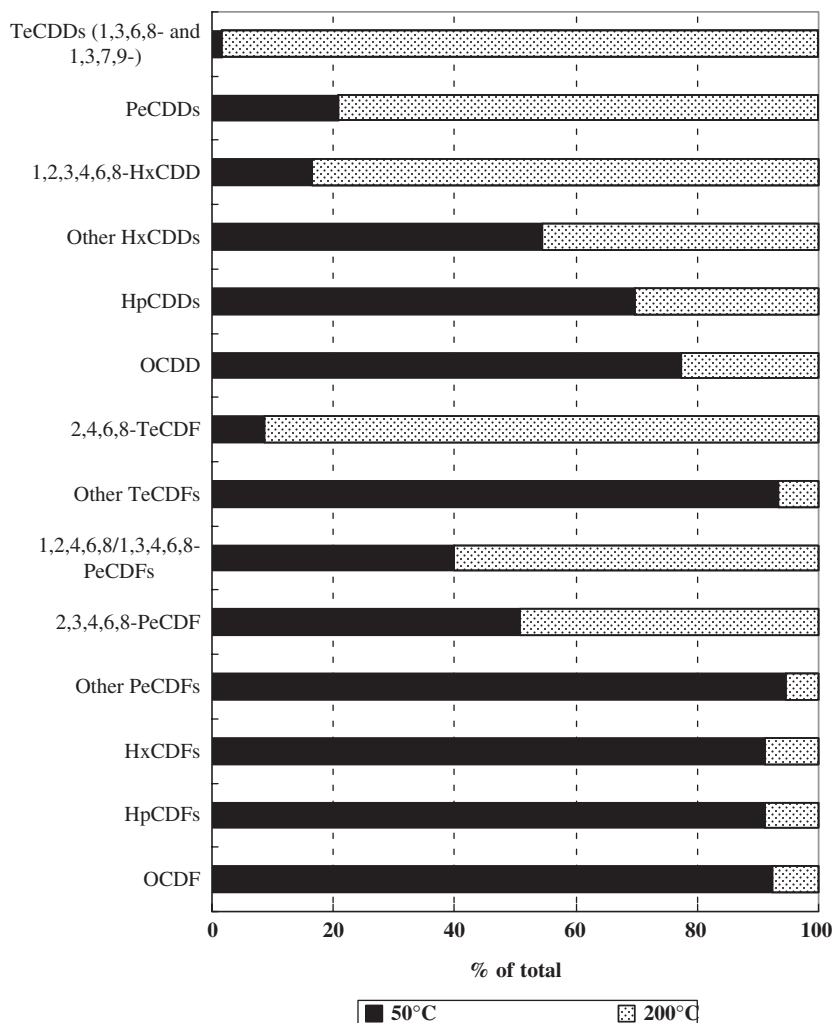
Figure 2. Proportions of PCDD/Fs extracted at 50°C and 200°C from SS in distributed water.

Therefore, we suspected that the dioxins may have been associated with DHS in the treated water we tested.

We also measured the iron content in the SS. Figure 3 shows the X-ray fluorescence spectra of the SS on the GFF, which show significant amounts of Fe, Cu, and Pb compared with the amounts in a blank filter. In particular, Fe compounds (ferric oxide or ferric hydroxide) were the largest component of the SS. Thus, not only TOC but Fe variation may give a clue to elucidate the physical states of dioxins in the SS.

The quantities for dioxins, iron, and TOC in each sampling period are listed in tables 3 and 4, and the daily variation in the PCDD concentrations is plotted in figure 4.

The variation in the amounts of PCDD/Fs in the SS (GFF) was higher (higher coefficients of variation) than the variation in the amounts in the dissolved
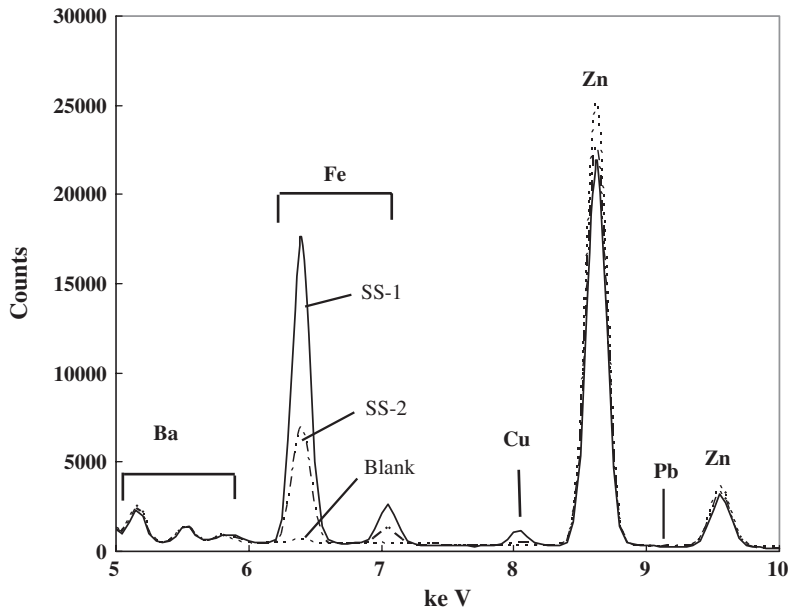
Figure 3. Magnified X-ray fluorescence spectra of a blank GFF and SS collected on a GFF. SS-1 was collected on 25–26 October; SS-2 was collected on 26–27 October.

phase (PUFs). The PCDD values were correlated with both iron and TOC values (figure 4). However, the degree of correlation varied with the homologues.

Figure 5 shows the correlation between the PCDD values and the iron and TOC values for SS from Tap 2 water. The amounts of all the PCDD homologues were strongly correlated (correlation coefficients, 0.76–0.96) with iron content. However, the correlation of PCDD values with TOC values decreased as the number of chlorine substituents increased (correlation coefficients, 0.18–0.80).

With respect to TEQ values, as shown in table 3, the values from SS seemed to be correlated with iron and TOC quantities. However, total TEQ values (summed TEQ values obtained from SS and PUFs) exhibited no variation because most part of dioxin congeners contributing to TEQ values (2,3,7,8-LoCDFs) were detected from PUFs.

3.3 *Physical state of dioxins in distributed water SS*

Inoue *et al.* reported that ferric compounds in distributed water SS originate from distribution pipes [21]. That is, Fe^{2+} produced by corrosion of iron pipes is oxidized in the presence of dissolved oxygen to produce Fe^{3+}. Thereafter, Fe^{3+} reacts with hydroxide ions to produce insoluble $Fe(OH)_3$. The strong correlation between PCDD values and iron contents in the SS in our tests suggests that there was an interaction (adsorption) between the two. However, such an interaction is unlikely because in preliminary experiments, we found that dioxins had little adsorbability on $Fe(OH)_3$ floc and that the lower extractability of certain congeners was not improved, even by removal of

Table 3. Quantities of dioxins (in SS-bound and dissolved phases), iron, and TOC in distributed water collected from Tap 1.

Quantities (pg/kL)		21–22 October	25–26 October	26–27 October	27–28 October	28–29 October	Average	SD[a]	CV (%)[b]
TeCDDs	SS-bound	370	870	250	220	310	400	270	68
	Dissolved	540	470	420	400	360	440	69	16
PeCDDs	SS-bound	5.7	12	5.8	4.8	5.7	6.9	3.1	45
	Dissolved	69	72	62	61	59	65	5.8	9.0
HxCDDs	SS-bound	20	44	18	17	17	23	12	50
	Dissolved	28	29	29	27	27	28	0.74	2.6
HpCDDs	SS-bound	7.3	14	5.4	5.3	6.7	7.7	3.6	47
	Dissolved	23	24	24	23	24	24	0.55	2.3
OCDD	SS-bound	30	50	21	22	27	30	12	40
	Dissolved	34	31	32	33	33	32	1.1	3.3
TeCDFs	SS-bound	5.5	5.2	4.0	2.8	4.5	4.4	1.1	25
	Dissolved	490	470	430	420	410	440	34	7.8
PeCDFs	SS-bound	2.3	2.2	2.5	1.9	3.0	2.4	0.41	17
	Dissolved	65	63	57	55	57	59	4.4	7.4
HxCDFs	SS-bound	1.5	1.9	1.4	0.84	1.4	1.4	0.39	28
	Dissolved	17	16	16	15	16	16	0.53	3.3
HpCDFs	SS-bound	0.94	1.7	0.66	0.80	1.1	1.0	0.42	40
	Dissolved	5.5	4.9	5.3	4.9	5.3	5.2	0.26	5.1
OCDF	SS-bound	0.45	0.85	0.65	0.62	0.61	0.6	0.14	22
	Dissolved	1.1	1.0	0.82	1.0	1.1	1.0	0.12	12
Non-ortho DL-PCBs	SS-bound	<2	<2	<2	<2	<2	–	–	–
	Dissolved	220	160	130	130	130	150	39	26
Mono-ortho DL-PCBs	SS-bound	40	54	46	45	46	46	5.0	11
	Dissolved	1900	2200	2000	1900	2000	2000	120	6.0
Total TEQ (pg TEQ/kL)	SS-bound	0.21	0.99	0.37	0.16	0.61	0.47	0.34	73
	Dissolved	28	28	26	25	25	26	1.5	5.7
	Total	28	29	26	25	26	27	1.7	6.2
TOC in SS (mg in a sample circle)		0.13	0.18	0.053	0.045	0.065	0.095	0.058	62
Iron in SS (mg in a sample circle)		0.58	1.0	0.38	0.46	0.46	0.58	0.25	43

[a]Standard deviation. [b]Coefficient of variation.

Table 4. Quantities of dioxins (in SS-bound and dissolved phases), iron, and TOC in distributed water collected from Tap 2.

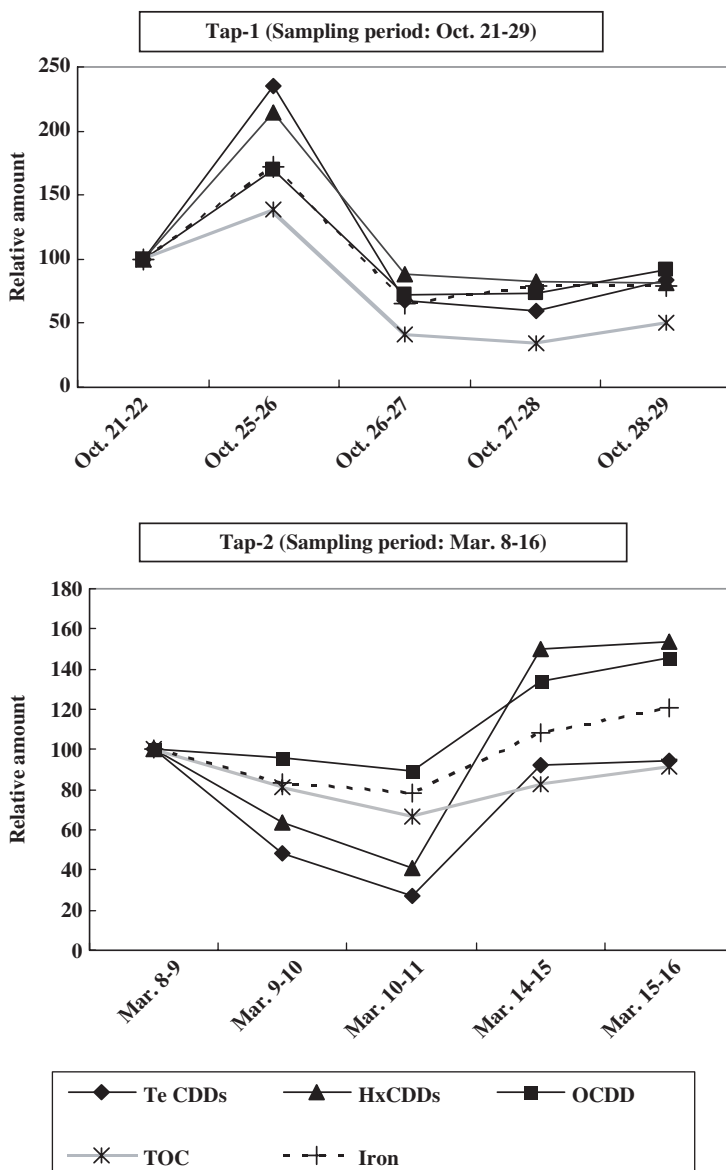| Quantities (pg/kL)		8–9 March	9–10 March	10–11 March	14–15 March	15–16 March	Average	SD	CV (%)
TeCDDs	SS-bound	520	250	140	480	490	380	170	45
	Dissolved	380	390	410	400	400	400	11	2.8
PeCDDs	SS-bound	9.4	6.5	4.9	10	11	8.4	2.6	31
	Dissolved	36	43	44	44	46	42	3.7	8.6
HxCDDs	SS-bound	38	25	16	58	59	39	19	50
	Dissolved	15	16	16	16	17	16	0.87	5.4
HpCDDs	SS-bound	10	9.2	8.6	13	13	11	2.1	19
	Dissolved	10	10	11	10	10	10	0.43	4.3
OCDD	SS-bound	42	40	38	57	62	48	11	22
	Dissolved	10	11	12	11	11	11	0.4	3.8
TeCDFs	SS-bound	13	6.5	7.0	7.7	9.7	8.7	2.5	29
	Dissolved	310	340	360	320	350	340	21	4.7
PeCDFs	SS-bound	4.1	3.1	3.3	3.8	4.4	3.7	0.56	15
	Dissolved	37	38	41	38	39	39	1.2	3.1
HxCDFs	SS-bound	2.3	1.9	2.1	2.8	3.0	2.4	0.48	20
	Dissolved	8.2	8.2	8.6	8.5	8.4	8	0.19	2.3
HpCDFs	SS-bound	1.7	1.6	1.7	2.3	2.6	2.0	0.44	22
	Dissolved	2.2	2.2	2.3	2.3	2.4	2.3	0.06	2.8
OCDF	SS-bound	1.2	1.1	0.92	1.5	1.7	1.3	0.32	25
	Dissolved	0.37	0.42	0.43	0.40	0.44	0.4	0.03	7.2
Non-ortho DL-PCBs	SS-bound	4.7	3.0	2.7	3.2	4.0	3.5	0.81	23
	Dissolved	150	150	160	150	160	150	5.6	3.7
Mono-ortho DL-PCBs	SS-bound	70	51	52	53	62	58	8.0	14
	Dissolved	1100	1200	1200	1000	1100	1100	84	7.6
Total TEQ (pg TEQ/kL)	SS-bound	0.96	0.79	0.60	1.7	1.1	1.0	0.42	41
	Dissolved	18	19	20	18	19	19	0.84	4.5
	Total	19	20	21	20	20	20	0.60	3.0
TOC in SS (mg in a sample circle)		0.44	0.36	0.29	0.36	0.40	0.37	0.055	15
Iron in SS (mg in a sample circle)		1.5	1.3	1.2	1.6	1.8	1.5	0.26	18

Figure 4.   Daily variation in the quantities of PCDDs, iron, and TOC in the SS. The quantities are relative to the concentration on the first day, which was set at 100%.

ferric compounds by HCl pretreatment (data not shown). Therefore, we considered the possibility that a complex between PCDDs and some type of matrix was associated with the iron floc in the SS.

We assumed that the dioxin-containing iron floc was made up of three dioxin-carrying matrices: DHS, micro-organisms, and microparticles. In raw water that contains humic materials (surface water), LoCDD/Fs in aqueous phase can exist in both a DHS-bound form and a freely dissolved form. Micro-organisms (algae or bacteria)

can be expected to incorporate and accumulate freely dissolved LoCDD/Fs, as has been reported for some hydrophobic pesticides [22, 23]. Utsugi *et al.* [24] have found that SS in raw water carry predominantly HiCDDs (especially OCDD). Even well-managed water treatment plants allow some part of these matrices (i.e. DHS, micro-organisms, and microparticles) to pass through. All of them have a negative surface charge [25, 26], and therefore as they travel through distribution pipes, they can be adsorbed onto positively charged iron floc surfaces or serve as nucleation sites for the formation of floc [27–29]. The dioxin-carrying iron floc can form adhesive deposits and sediments in water distribution pipes or on tank surfaces, and these deposits can be resuspended by hydraulic variation [30].

Unlike the homologue values for the SS (GFF), none of the homologue values for the PUFs exhibited a significant daily variation (table 3). Therefore, it is likely that the variation in the quantities for the SS was caused by intermittent resuspension of deposited floc, and not by variations in the dioxin contamination levels in raw water or by variations in the removal efficiency of dioxins in the water-treatment plant.

The strong correlation between iron content and PCDD homologues values (figure 5) suggests that the dioxin-carrying matrices listed above were involved in the formation of iron floc in the distributed water, as proposed above.

In contrast, the differences in the correlation coefficients for the PCDD homologue values and OC content likely reflected differences in the OC contents of the matrices with which each homologue was associated. General organic carbon contents in aquatic humic substances and soil particles are 50–60% [31] and 2–7% [32], respectively. In SS in distributed water, TeCDDs that showed a strong correlation with OC content (correlation coefficient, 0.80) can be expected to be associated with (or surrounded by) OC-rich OM, whereas HiCDDs that showed a weak correlation (correlation coefficient, 0.18–0.31) might have been adsorbed on OC-poor microparticles.

The apparent differences in extractability between the congeners can probably be attributed to differences in their physical states in the distributed water SS. HiCDDs adsorbed on microparticles would be in an easily extractable form, as has been reported in the literature [33], and thus would be sufficiently extracted regardless of the type of extracting solvent. In contrast, the extractability of specific LoCDD/F congeners listed in section 3.1 (i.e. 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, 1,2,3,4,6,8-HxCDD, etc.) is presumably lowered by OM, that is, by strong association with humic substances [33] or sequestration in hydrophilic components of micro-organisms. Note that the LoCDD/F congeners, which exhibited a lower extractability than other isomers, are known to be impurities in 1,3,5-trichloro-2-(4-nitrophenoxy)benzene (CNP), an agrochemical that was widely used in large quantities in paddy fields in the 1970s and 1980s [34]. Although, in 1994, the use of CNP was prohibited, the dioxin congeners contained therein as impurities can still be detected in various environmental media in Japan [35].

Figure 6 shows TeCDD/Fs chromatograms of raw water originated from the Arakawa River. The predominance of 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, and 2,4,6,8-TeCDF indicates the contribution of CNP impurities to the raw water (1,2,3,8-TeCDD was also an impurity in early CNP products) [34]. It would be reasonable to expect that these congeners originated from paddy fields located upstream from the water-treatment plant and thus may have been strongly associated with paddy humus flowing into the adjacent river. They may also have been associated with river
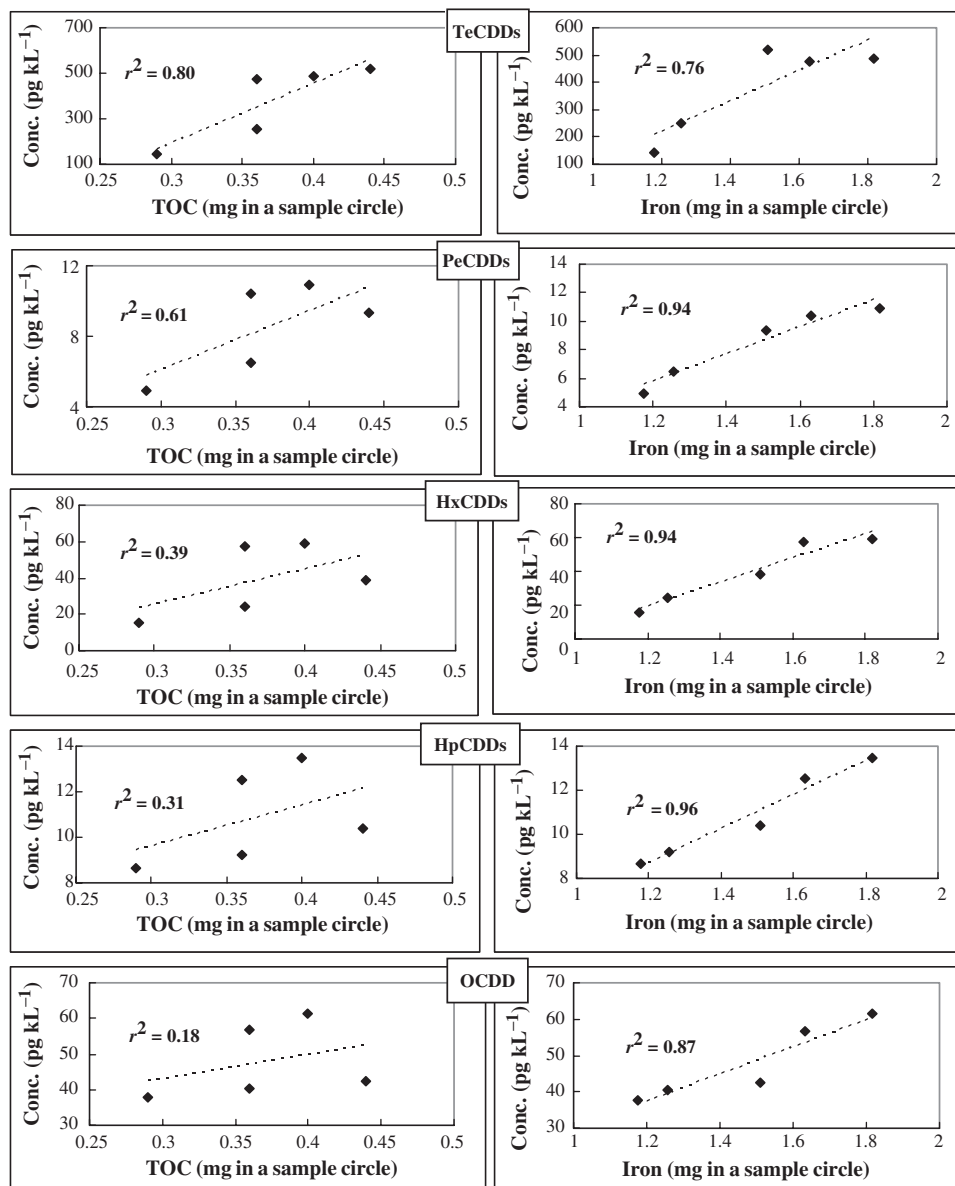
Figure 5.   Correlation between PCDD concentrations and TOC or iron quantities in SS from Tap 2.

DHS or have accumulated into micro-organisms during their long journey downstream to the water-treatment plant.

In conclusion, we found that certain dioxin congeners in distributed water SS could not be extracted by conventional dichloromethane extraction. The amounts of PCDD/Fs in SS showed a significant daily variation, and the variation was correlated with the content of ferric compounds and OM in the SS. In distributed water SS, certain PCDD congeners may have been associated with OM or microparticles sequestered
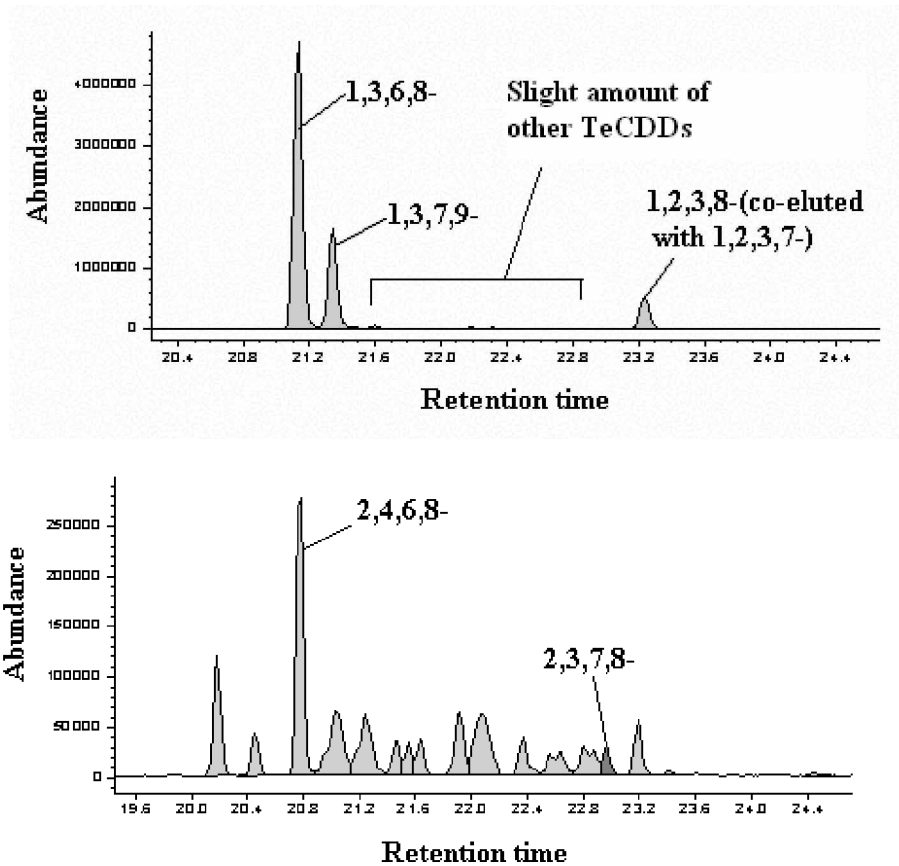
Figure 6.   GC–MS chromatograms of TeCDDs (upper) and TeCDFs (lower) in raw water.

in hydrophilic iron floc, and the low extractability of the congeners would be attributable to OM with which they have been strongly associated. As both OM and iron floc are hydrophilic, high-polarity extraction solvents such as acetone should be used to ensure sufficient extraction of the analytes. As stated in section 3.2, congeners detected in the SS contributed little to total TEQ values: most of the contributing PCDF congeners were extracted from the PUFs. However, when the behaviour of dioxins during water treatment and distribution is investigated or when a detailed assessment of levels of human exposure to dioxins is necessary, accurate isomer-specific determination of all dioxin congeners is required. Our results provide useful information about the physical state of dioxins in distributed water, which is essential for the optimization of analytical procedures.

Acknowledgement

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