

PCDD/F MASS BALANCE IN A COASTAL ESTUARY OF THE BALTIC SEA: A FIELD STUDY

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Abstract

This paper presents mass balances for 17 congeners of PCDD/F in a coastal area in the southern Bothnian Sea, which is a sub basin of the Baltic Sea. The area is known to be one of the world's most contaminated areas in terms of toxic levels of dioxins and furans in fatty fish. The calculated mass balances were based on measured concentrations in tributary water and sea water combined with estimates of water fluxes in the tributaries and water exchange with the surrounding sea. Exchange with the atmosphere and with sediments was also indirectly quantified. We found that the mass balance was dominated by exchange with the surrounding sea with smaller contributions from tributary inflows and atmospheric deposition. The sediments appeared to function as sinks of PCDD/Fs. Apparently, all important fluxes into and out from the studied systems were quantified by our measurements and we did not need any additional sinks or sources to explain the results.

Introduction

Levels of PCDD/Fs in biota in the Baltic Sea frequently exceed established levels for human consumption, especially in the southern Bothnian Sea^{1,2}. The reason why this area has high levels is unclear³, and the data availability is limited especially concerning background concentrations in water⁴. In order to improve the knowledge about background concentrations, fluxes and dynamics of PCDD/Fs, a sampling program was implemented in a coastal area during one year and mass balances for 17 toxic congeners of dioxins and furans were established. The selected coastal area has no known point sources and the purpose of the study was to record the situation in a typical background location in the southern Bothnian Sea. The aim is for the results to be useful in further studies of areas contaminated by point sources.

Materials and Methods

The study area is located along the south-western coast of the Bothnian Sea in the county of Uppland, Sweden (Fig. 1). The surface area is 6.4 km² and the bay is relatively shallow (mean depth 2 m; maximum depth 10 m) and relatively enclosed towards the adjacent sea (Öregrundsgrepen). The bottom sediments consist of 52 % erosion sediments, 42 % transportation sediments and 6 % accumulation sediments⁵. Kallrigafjärden receives runoff from two streams – River Olandsån (mean discharge 6 m³ s⁻¹) and River Forsmarksån (mean discharge 3 m³ s⁻¹) – giving the area the characteristics of an estuary influenced by fresh water and a high biologic production. There are no known point sources of PCDD/Fs and the area may hence be regarded as a background location.

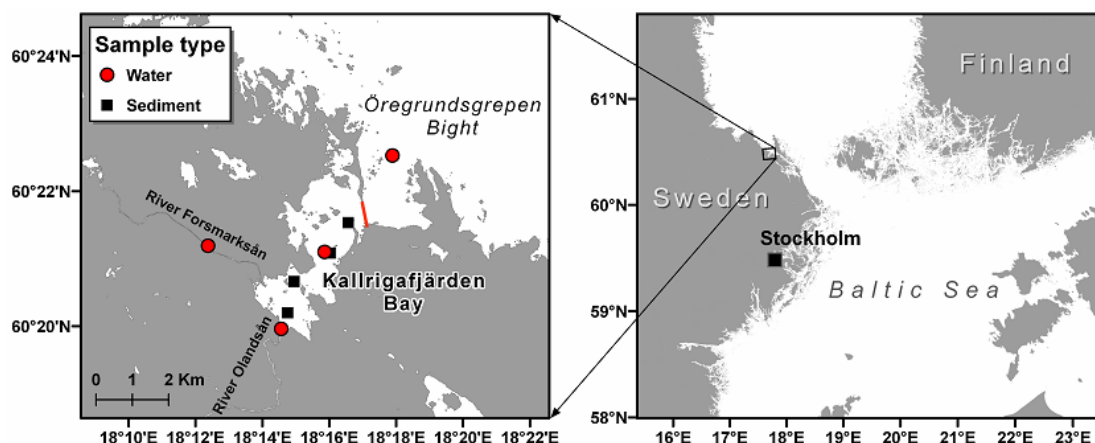


Figure 1 *Map of the study area including sampling stations. Red line demarks operational border between the Kallrigafjärden Bay and the adjacent sea.*

In this study, field measurements were performed from September 2007 to August 2008. Water concentrations of PCDD/Fs were measured at four stations, including the two tributaries, Öregrundsgrepen and Kallrigafjärden (Fig. 1), using active sampling. Methodology and measured concentrations are presented elsewhere (Karlsson et al., this issue). Passive samplers of polyoxymethylene (POM) were also used, mainly for purposes beyond the scope of this paper, but the results from the passive sampling were utilized to compare concentrations between the water mass and sediment pore water. In addition, water chemistry and profiles of temperature and salinity were measured. Surface sediment samples were collected at four different locations within the Kallrigafjärden Bay, including three samples from accumulation areas (at water depths of 4, 7 and 10 meters, respectively).

Flow measurements in the tributary streams were supplied by the Swedish Meteorological and Hydrological Institute (SMHI). Water exchange between Kallrigafjärden and Öregrundsgrepen were calculated from measured salinity differences and compared to site specific estimates from different methods found in the literature (see below). Literature values of atmospheric deposition fluxes were used.

Results and Discussion

Measured concentrations and congener distributions are presented in more detail in Karlsson et al. (this issue). In Figure 2, the total concentrations (sum of 17 congeners) are shown as measured by active water sampling. In the majority of the samples, all 17 congeners were detected. However, in several samples – especially in the dissolved phase reflected on the polyurethane foam adsorbents (PUFs) – some congeners were missing.

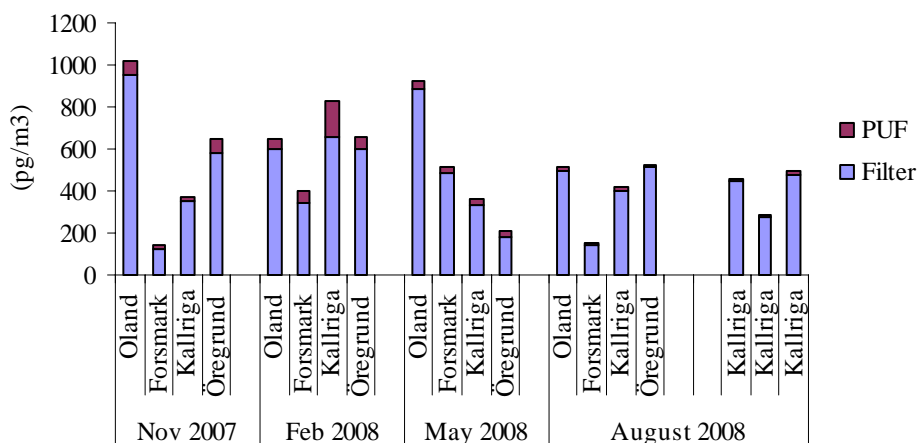


Figure 2 Total concentrations of 17 toxic congeners of PCDD/Fs at the four sampling stations at different sampling occasions. The concentrations include particulate material trapped on glass-fibre filters and operationally dissolved substances absorbed on polyurethane foam adsorbents (PUFs). The columns to the right show the variation between three individual samples from the same station in August.

To calculate the influx of PCDD/Fs to Kallrigafjärden from the streams and the sea, the water flows were multiplied with the concentrations of each congener in the different water bodies. Monthly values were used, and for missing data points, concentrations were interpolated linearly. Detailed information about the water exchange between Kallrigafjärden and Öregrundsgrepen was lacking, but based on salinity measurements, we estimated the water inflow from the sea to be on average five times larger than the freshwater inflow, about $20 \text{ m}^3 \text{ s}^{-1}$. The water retention time has been estimated to ~ 8 days in summer⁶, which gives $\sim 19 \text{ m}^3 \text{ s}^{-1}$ in water exchange (assuming minimum tributary inflow in summer). The salinity variations mostly reflected the variation in runoff from the tributaries. The water exchange between the coastal area and the sea is also affected by winds and currents and is hence subject to temporal variation. Based on available data, however, it was not possible to estimate this variation and a constant water exchange was assumed. The outflow from Kallrigafjärden was calculated as the sum of inflows from the tributaries and from the sea.

No measurements of atmospheric deposition were performed in this study. One study of atmospheric deposition of PCDD/Fs sampled at the Swedish west coast⁷ reports values between 0.5 and 1.3 pg WHO-TEQ $\text{m}^{-2} \text{ d}^{-1}$. Another study estimated the PCDD/F deposition over the Baltic Sea to 1.1 pg WHO-TEQ $\text{m}^{-2} \text{ d}^{-1}$ during the winter months⁸. The latter study also presented model estimates of annual deposition in the Bothnian Sea corresponding to 0.7 pg WHO-TEQ $\text{m}^{-2} \text{ d}^{-1}$, including wet, dry and gaseous deposition. We hence assume that the atmospheric deposition of PCDD/Fs in our study area was 0.7 pg WHO-TEQ $\text{m}^{-1} \text{ d}^{-1}$. Based on a general ambient air pattern from a compilation of 26 worldwide air measurements⁹, individual contributions of 17 congeners to the atmospheric deposition were estimated.

In Table 1, annual mass balances (sums of 12 months) for the 17 measured congeners in Kallrigafjärden are presented. Theoretically, the observed residual, i.e. inflows minus outflow, should reflect the mass of each substance leaving the system either to the sediments or to the atmosphere, assuming that these substances are conservative. Comparison of concentrations in the water mass measured with passive samplers applied for three months (four samples during the year) with pore water concentrations measured by employing passive samplers (POM) in a batch shaking test revealed that pore water concentrations were generally similar to or below water concentrations implying that the diffusive flux from the sediments should be minor. Neglecting volatilization, the observed residual may be interpreted as a net sedimentation of PCDD/Fs, which should mainly take place in accumulation areas. In erosion and transportation areas, the net sedimentation is less or absent due to the

occurrence of resuspension. The mass balance is illustrated in Figure 3 for the total sum of 17 toxic congeners and for toxic equivalents (WHO-TEQ).

Table 1 Annual mass balances for 17 congeners including inflows (from River Forsmarksån, River Olandsån, the surrounding sea and atmospheric deposition) and outflow to the surrounding sea. Unit: mg yr⁻¹.

	Inflows				Outflow To sea	Residual In – Out
	River F.	River O.	From sea	Atm. dep.		
2378-TeCDD	0.01	0.10	0.45	0.12	0.42	0.26
12378-PeCDD	0.14	0.40	1.8	0.33	2.3	0.33
123478-HxCDD	0.21	0.54	1.7	0.41	3.3	-0.46
123678-HxCDD	0.34	0.99	6.6	0.65	8.0	0.62
123789-HxCDD	0.40	1.0	4.7	0.65	6.7	0.14
1234678-HpCDD	2.8	10	28	8	43	7
OCDD	9.6	54	100	25	160	26
2378-TeCDF	1.0	2.9	19	1.3	19	5.2
12378-PeCDF	0.40	1.1	6.2	1.0	9.5	-0.8
23478-PeCDF	0.46	1.3	8.4	0.9	8.9	2.2
123478-HxCDF	1.1	2.5	8.9	1.3	13	1.1
123678-HxCDF	0.47	1.1	3.7	1.1	5.7	0.7
234678-HxCDF	0.49	1.2	4.6	0.9	6.2	1.0
123789-HxCDF*	-	0.09	-	0.33	0.77	-0.35
1234678-HpCDF	2.2	5.7	48	4.9	50	11
1234789-HpCDF	0.30	0.72	2.2	1.6	3.7	1.2
OCDF	2.2	6.9	76	8	72	20

* This congener was not detected in River Forsmarksån and in Öregrundsgrepen and rarely detected elsewhere, making the mass balance of little use.

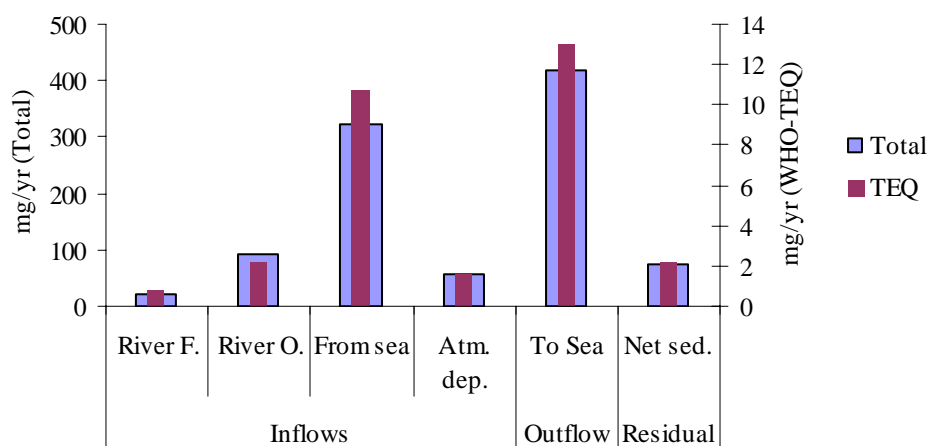


Figure 3 Annual fluxes of PCDD/Fs in and out of Kallrigafjärden illustrated as total sum of 17 toxic congeners (left y-axis) and toxic equivalents (WHO-TEQ; right y-axis).

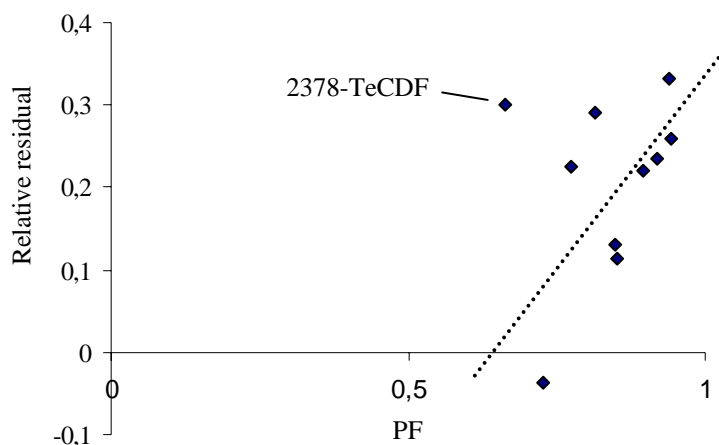


Figure 4 *Relative residual (residual/outflow) versus PF. Since concentrations (especially the dissolved phase) were sometimes below detection limits only ten congeners are included.*

Dividing residuals (net sedimentation flux) by sediment concentrations for each congener, the net sedimentation of solids may be estimated. Assuming net sedimentation only on accumulation bottoms (averaging PCDD/F concentrations from the three accumulation area samples) we obtained an average value for net sedimentation of $750 \text{ g m}^{-2} \text{ yr}^{-1}$ (standard deviation $740 \text{ g m}^{-2} \text{ yr}^{-1}$), which is a reasonable estimate in this area¹⁰. In theory, the settling amount should be related to the particulate fraction (amount on particle filter/total amount; PF) of each congener. In Figure 4, the relative residuals (residual/outflow) are plotted against PF. Since concentrations (especially the dissolved phase) were sometimes below detection limits only ten congeners are included in the plot. We excluded one outlier (2378-TeCDF) to get a reasonably good positive relation ($r^2=0.44$).

We conclude that the estimated fluxes in the mass balance appear to be reasonable for most congeners and that the PCDD/F budget residuals are well in the expected order of exchange with the sediments. In general, the sediments appear to be sinks of PCDD/Fs. Hence we argue that all important fluxes into and out from the studied system are quantified by our measurements and we do not need any additional sinks or sources to explain our results. The mass balance is dominated by exchange with the surrounding sea but some of the seasonal dynamics may be explained by tributary inflow. We find this mass balance useful in describing the background situation in coastal areas in the southern Bothnian Sea. Future investigations may utilize these results in exploring the situation in other areas, e.g. contaminated by point sources. Ultimately a mass balance approach may help to explain the dynamics of a complicated system where concentrations of PCDD/Fs radically exceed background concentrations in the Baltic region.

Acknowledgements

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