

# DIOXIN LEVELS AND CONGENER PATTERNS IN WATER, SEDIMENT AND FISH FROM A COASTAL ESTUARY OF THE BALTIC SEA

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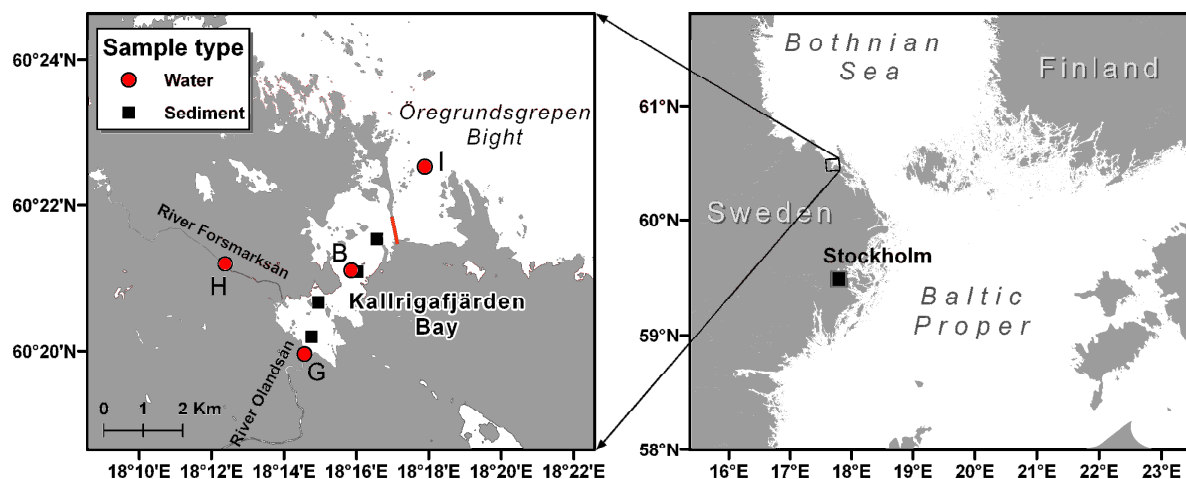
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## Abstract

An ecosystem approach was taken in order to study the turnover of PCDD/Fs in Kallrigafjärden Bay, a coastal estuary in the Baltic Sea. Samples from water within and flowing into the system, sediments and fish were collected, analysed on their content of 17 PCDD/Fs congeners and compared with each other in order to increase the understanding of present background levels of dioxins in Baltic Sea coastal ecosystems. In the water phase, PCDD/Fs were measured both as total levels using a specially designed high-volume filtration system and as the freely dissolved fraction using passive equilibrium samplers. Our results indicate that the PCDD/F contamination of the studied area was relatively low, which was anticipated since there are no known point sources in the vicinity of the area. There was congruence when PCDD/F levels from water, sediments and fish were compared with each other although the congener profiles varied considerably between the studied matrices. The congener profile for fish showed similarities with the equivalent profile for the freely dissolved water concentration. The temporal variability within the studied matrices, keeping in mind that the measured levels were low, was relatively high, which highlights the importance of not basing environmental assessments of dioxin contamination on too small datasets.

## Introduction

Dioxin levels in fatty fish from the Baltic Sea frequently exceed the limits for marketing the fish within the European Union<sup>1</sup>. The situation is pronounced in the southern Bothnian Sea<sup>2,3</sup>, where the field site of this study is situated (Fig. 1). Intense research has been initiated to clarify why PCDD/Fs levels in biota from the Baltic Sea no longer decrease, unlike other classical organic pollutants (see e.g. <sup>4,5,6</sup>). In this study, we measured PCDD/F levels in water, sediment and stationary fish and calculated the fluxes of PCDD/Fs to, from and within a semi-enclosed coastal area, Kallrigafjärden Bay. The aim of this work is to present background levels, variability and congener profiles for PCDD/Fs in the studied coastal ecosystem.



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

## Materials and Methods

Kallrigafjärden Bay is situated along the Swedish coast of southern Bothnian Sea, a sub basin of the Baltic Sea (Fig. 1) and it is one of relatively few enclosed bays in the region. Due to the last glaciation, the land in the area still rises with around 6 mm yr<sup>-1</sup><sup>7</sup>. As the coast is flat, shoreline changes related to land uplift are marked. The large-scale circulation pattern in the Baltic Sea creates a south bound net current along the Swedish coast<sup>7</sup>, and

hence there is a transport of water, suspended and dissolved matter with origin in the Bothnian Sea into the study area. The water and bottom dynamic conditions in the Kallrigafjärden Bay are well documented<sup>8</sup>. The population density around Kallrigafjärden Bay is low. There are no known point sources of PCDD/Fs in the vicinity of the bay. Two streams discharge in the bay: River Forsmarksån and River Olandsån. River Forsmarksån drains a 375 km<sup>2</sup> large catchment area dominated by forested land. The average discharge is 3 m<sup>3</sup> s<sup>-1</sup>, and the runoff is rich in humic matter, strongly coloured, has a pH-value close to neutral and relatively low nutrient concentrations. River Olandsån, on the other hand, transports a nutrient and particle rich water with an average discharge of 6 m<sup>3</sup> s<sup>-1</sup>. The catchment area, 886 km<sup>2</sup>, is dominated by forested land, but the proportion of farm land is relatively high (27 %). The municipality Gimo, with 3000 inhabitants, discharges its effluent water into the river approximately 30 km upstream of the river mouth.

Water sampling was conducted in the tributaries, the Kallrigafjärden Bay and the adjacent Öregrundsgrepen Bight, using a specially designed high-volume filtration system described in Broman et al.<sup>9</sup>. Approximately 800 L per sampling occasion was pumped through a prefilter, a glass fibre filter (pore size 0.7 µm) and finally a polyurethane foam (PUF) plug, which enabled separation between the particulate and the apparently dissolved fraction of PCDD/Fs. Furthermore, we used equilibrium passive samplers, consisting of polyoxymethylene (POM) strips<sup>10</sup> to measure the freely dissolved fractions of PCDD/Fs in surface water and sediment pore-water. In Kallrigafjärden Bay, we also measured the PCDD/F levels in the soft bottom sediments and in pooled muscle homogenates from 10 individuals (15-20 cm length) of a relatively stationary and lean fish species, *Perca fluviatilis*.

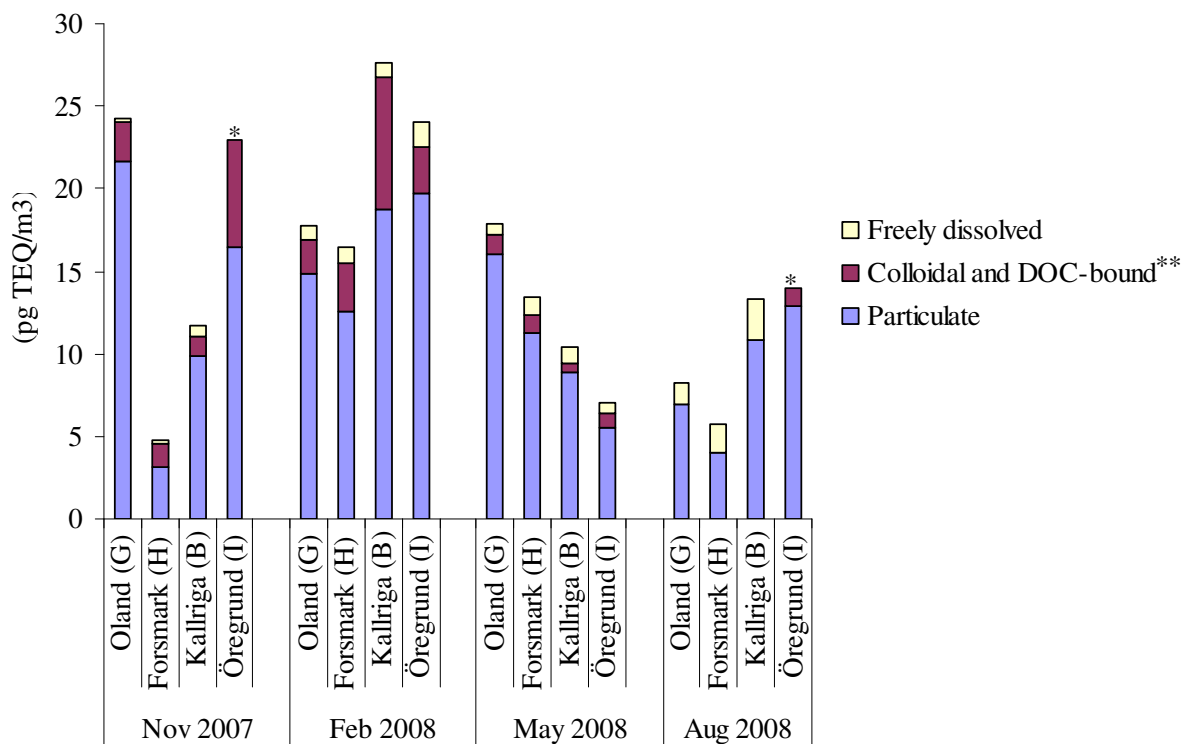
All samples were prepared and analyzed according to a validated method based on Swedish standard SS-EN 1948:1-3. Before use, PUFs and POMs were solvent cleaned using Soxhlet extraction and sonication, respectively, while filters were cleaned by heating to 450°C. PUFs, filters and POMs were stored cold (-20°C) until use. After use, PUFs and filters were extracted for 24 hours or until all water had been removed using Soxhlet-Dean-Stark with toluene as solvent. POMs were extracted by shaking with *n*-hexane for 48 h. Before extraction, isotope-labelled PCDD/Fs were added as internal standards. After extraction, samples were cleaned on columns with acid (H<sub>2</sub>SO<sub>4</sub>) and basic (KOH) impregnated silica, followed by fractionation on columns containing activated carbon. Additional isotope-labelled standards were added as recovery standards, and the samples were reduced to a volume of 40 µL of tetradecane using a rotary evaporator. Final analysis was carried out by GC-HRMS using an Agilent 6890N GC and a Micromass AutoSpec-Ultima HRMS.

The freely dissolved concentrations of PCDD/Fs in water were determined from the concentrations in the POM-samplers, using partition coefficients (K<sub>POM</sub>) established by Cornelissen et al.<sup>11</sup>. Since the POMs were placed along a salinity gradient – from the tributaries to the Bothnian Sea – the partition coefficients were corrected using the Setschenow equation.

## Results and Discussion

Concentrations of PCDD/F in all water samples are shown in Figure 2. The total concentrations varied between 5 and 28 pg TEQ m<sup>-3</sup>. The largest amounts were found on filters, as the particulate fraction, representing on average 82 % of the total concentration. The PCDD/F concentrations varied considerably both over time and between the sampling sites. The average concentrations in Kallrigafjärden Bay and Öregrundsgrepen Bight were 12 and 14 pg TEQ m<sup>-3</sup>, respectively. In the rivers, the PCDD/F concentrations averaged 8 pg TEQ m<sup>-3</sup> (Forsmarksån) and 15 pg TEQ m<sup>-3</sup> (Olandsån). There are no other recent measurements of total PCDD/F concentrations of Bothnian Sea water. However, the PCDD/Fs levels recorded in the estuary were found to be of the same magnitude as levels measured in the open Bothnian Sea in the early 1990s<sup>9</sup>.

The water concentrations as found by PUF measurements are plotted in Figure 2 as the measured value subtracted with the corresponding measured value in the POMs, hence representing the sum of the colloidal fraction (particles with diameter <0.7 µm) and the dissolved organic carbon (DOC) bound fraction. However, it should be noticed that these concentrations are not directly comparable since the PUF concentration is an instantaneous value, while the POM measurement represents the equilibrium concentration for the last three months. The freely dissolved concentration as measured by the passive samplers was on average 1.2 pg TEQ m<sup>-3</sup>, which averaged 40 % of the apparently dissolved fraction measured on the PUFs. The freely dissolved concentrations of PCDD/Fs in the open Baltic Sea was studied by Cornelissen et al.<sup>10</sup>, who found a median value in the surface water twice as high or 2.4 pg TEQ m<sup>-3</sup>. A higher freely dissolved concentration in the open sea could possibly be explained by a, compared with coastal areas, lower particle and DOC-content in the water pushing the PCDD/F equilibrium towards the dissolved phase. This could be the case, for example, if a large proportion of the PCDD/Fs emanate from gaseous deposition.



\* No measurement on POM, \*\* Measured value in PUF reduced with fraction measured on POM.

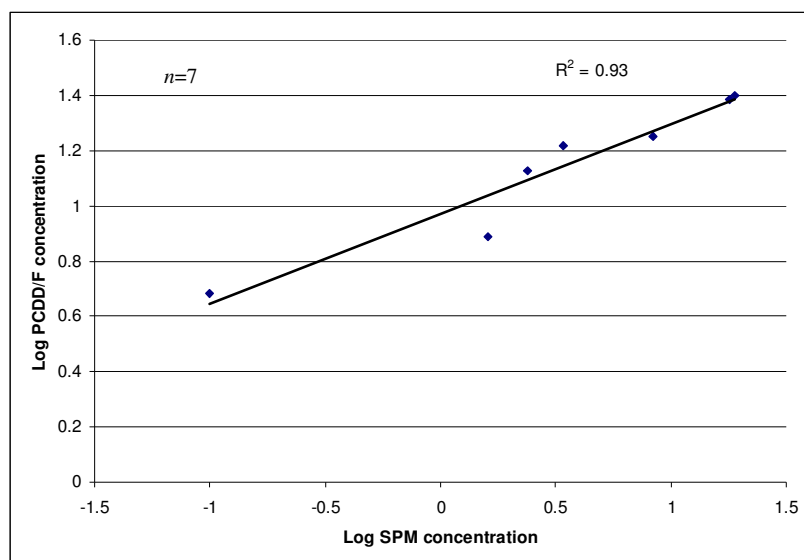
**Figure 2.** Results from four water sampling campaigns of PCDD/Fs (pg TEQ m<sup>-3</sup>) in Kallrigafjärden Bay, the tributaries and the adjacent sea.

The PF-value, defined as the ratio between particulate and total concentration of a substance in aquatic ecosystems, is often recognized as the “entry gate” towards aquatic ecosystem modelling, because it defines how much of the substance that can potentially settle on the sea bed due to gravity<sup>12</sup>. In Table 1, the measured PF values for different PCDD/F congeners are presented. The PF-values varied between 0.60 and 0.95. There was a trend towards higher PF-values as the degree of chlorination increased, which is in agreement with differences in the octanol-water partitioning coefficients ( $K_{ow}$ ) among the congeners, and also in line with other field studies<sup>9, 13</sup>.

**Table 1.** The proportion of total PCDD/Fs detected as particulate phase in the water (PF-value).

PCDD-congener	12378-PeCDD	123478-HxCDD	123678-HxCDD	123789-HxCDD	1234678-HpCDD	OCDD			
PF-value	0.75	0.60	0.86	0.83	0.94	0.94			
PCDF-congener	2378-TCDF	12378-PeCDF	23478-PeCDF	123478-HxCDF	123678-HxCDF	234678-HxCDF	1234678-HpCDF	1234789-HpCDF	OCDF
PF-value	0.69	0.74	0.80	0.89	0.84	0.83	0.95	0.69	0.94

Figure 3 shows the correlation between the logarithmic values on suspended particulate matter (SPM) and total PCDD/Fs concentration (TEQ) in the river samples. The  $r^2$ -value was 0.93 indicating that the SPM content in river runoff appears to be an important factor governing the PCDD/F transport from catchments. The PCDD/Fs concentrations in the rivers were of the same magnitude as values recorded in other Swedish rivers using the same sampling technique<sup>14</sup>.



**Figure 3.** The observed correlation between SPM and PCDD/Fs in river water.

The PCDD/Fs concentrations in surface sediments varied between 3 and 7 pg TEQ g<sup>-1</sup> dw, which can be recognised as a background level of the same magnitude as found in offshore parts of the Bothnian Sea<sup>6,15</sup>. Significantly higher levels have been recorded at contaminated sites along the Swedish and Finnish coasts of the Baltic Sea<sup>6,15</sup>. In the sediment pore-water, the freely dissolved PCDD/F concentration varied between 0.4 and 0.8 pg TEQ m<sup>-3</sup>, which is approximately half of the concentrations in the surface water (Fig. 2). This indicates that diffusion from sediment to water is not a particularly important transport process for PCDD/Fs in Kallrigafjärden Bay. Also in comparison with equivalent measurements in offshore sediments from the Baltic Sea<sup>10</sup> the pore-water concentrations were low in our study area.

In the collected fish muscle homogenates, relatively low levels of PCDD/Fs compared to other studies on *Perca fluviatilis* (perch) in Scandinavian waters were found<sup>4</sup>. The concentrations in the 15-20 cm long perches caught in Kallrigafjärden Bay were 0.07 pg TEQ g<sup>-1</sup> ww and 0.11 pg TEQ g<sup>-1</sup> ww in spring and autumn seasons, respectively. Perch from a reference coastal area, without riverine inflow, approximately 30 km north of Kallrigafjärden showed similar PCDD/Fs levels, supporting the idea that the river borne PCDD/F transport is not particularly important for the PCDD/F turnover in Kallrigafjärden Bay, c.f. Malmaeus et al.<sup>16</sup>

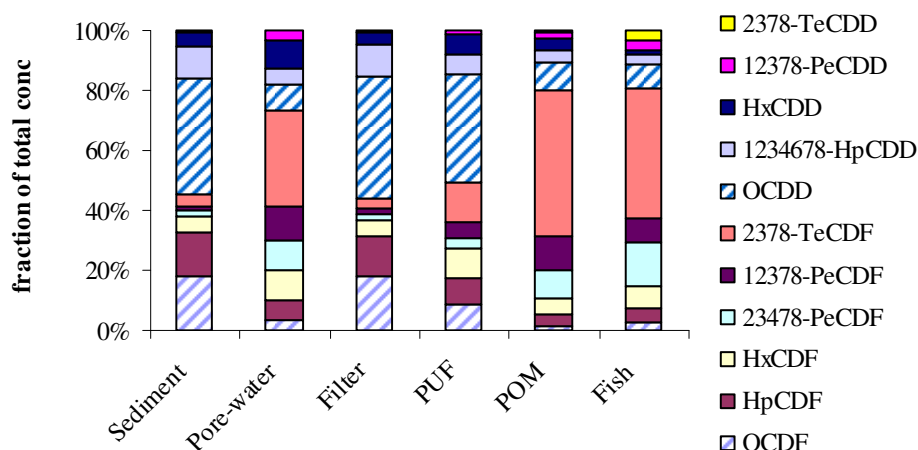
In Table 2, the coefficients of variance (CV) for PCDD/Fs concentrations in the studied matrices in Kallrigafjärden Bay are presented. We also indicate the number of samples required to establish a mean value that with 95 % certainty has an error within 20 % according to Håkanson<sup>17</sup>. The results presented in Table 2 indicate that the PCDD/Fs concentrations in water have a higher variability compared to concentrations in sediments and fish, which is in agreement with observations of other chemical variables in aquatic ecosystems<sup>18</sup>. The results furthermore indicate that approximately 15 samples are required for establishing a representative yearly mean value of total PCDD/F concentration in water within 20 % error margin.

**Table 2.** CV-values for PCDD/Fs in different matrices from Kallrigafjärden Bay and the calculated number of samples (*n*) required to achieve a representative mean value.

PCDD/F variable	Total concentration water	Freely dissolved fraction water (POM)	Sediment	Sediment pore-water	Fish muscle*
CV	0.37	0.70	0.36	0.28	0.3
<i>n</i>	14	48	14	8	10

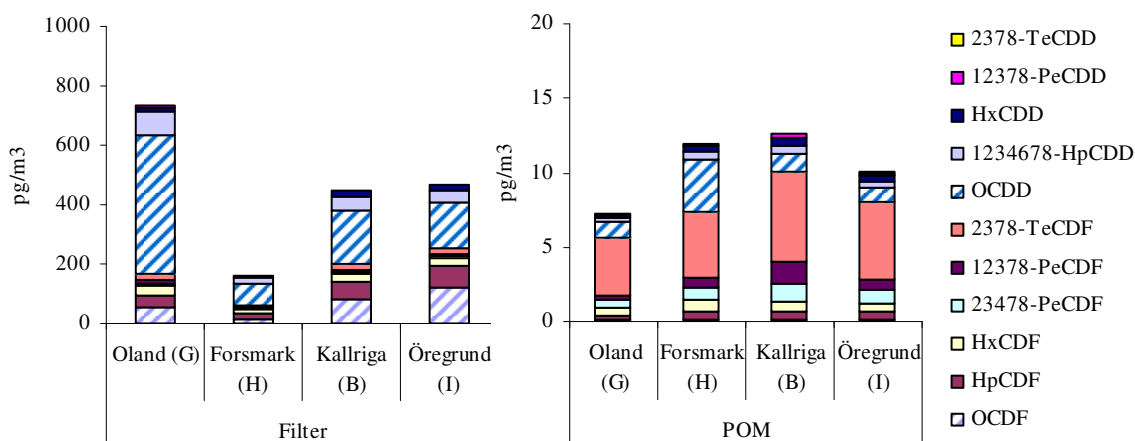
\* Estimated value based on two samples

Figure 4 shows average congener patterns in Kallrigafjärden Bay for the different matrices (different congeners of HxCDD, HxCDF and HpCDF are lumped together in the figure). The profile of the freely dissolved fraction measured with POM in surface water and sediment pore-water show similarities with the profile in fish muscle. Interestingly, the fractions of TeCDD, PeCDD och 23478-PeCDF increased from POM to fish. These congeners have also been identified as biomagnifying<sup>19</sup> in contrast to other toxic congeners of PCDD/F. Moreover, there were also striking similarities between the congener profiles for sediment and particle bound PCDD/Fs in water.



**Figure 4.** Average congener patterns in Kallrigafjärden Bay for different matrices included in this study.

Finally, the average congener patterns in the particulate fraction and the freely dissolved fraction, from all water sampling stations are shown in Figure 5. From the filters, one can note that the variability in total concentration between the stations to a large extent is explained by the OCDD concentration, which in turn likely is related to the SPM-concentration. OCDD is the most hydrophobic congener and has therefore the highest affinity to particles<sup>9,12</sup>. The freely dissolved congener profiles recorded on the POMs do not vary particularly between the sampling sites.



**Figure 5.** Average congener patterns at the different water sampling stations.

To conclude, this study has brought new information on the possibilities to sample, analyse and interpret PCDD/F concentrations in the water within a coastal estuary. The overall picture when comparing data for water, sediment and biota is that they point in the same direction and are congruent. However, our data shows a large temporal variability, which is important to keep in mind when addressing PCDD/F contamination at more polluted sites. Since the costs for analyzing PCDD/Fs are high, judgements on PCDD/F contamination are often based on limited datasets. This study shows that such an approach may lead to questionable conclusions.

#### Acknowledgements

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