

PCNs, PCDD/Fs, and Non-ortho PCBs, in Water and Bottom Sediments from the Industrialized Norwegian Grenlandsfjords

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EXPERIMENTAL

Sampling in the Study Region. The Grenlandsfjords are five jointed fjords in the south of Norway (59° 5' N, 9° 38' E, Figure 1). The innermost fjord, the Frierfjord, has since the 1950s been substantially polluted by PCDD/F discharges from a magnesium production plant, Heroya (Figure 1) operating from 1951 until 2002.

The locations for the water samples were chosen to map two expected major spatial trends in concentrations. First a horizontal decline with increasing distance to Heroya, and second, a vertical trend in the water column. Since water in silled Norwegian fjords often has a restricted renewal, we hypothesized that different vertical water layers may have different contaminant concentrations. The samples were taken during two excursions on 29 June–1 July 1999 (“W2”-samples), and 2–5 May 2000 (“W3”-samples) (Figure 1 and Table S1). In addition, two reference water samples were collected in 1999 far from the discharge location; one upstream in river Farelva (W2-5) and one upstream in the coastal currents of Skagerrak Sea (W2-1). Sample W3-9 (from 2000) was like W2-5 collected upstream in River Farelva.

Samples in vertical profiles were collected in two different locations in the Frierfjord; closest to Heroya, (two samples, W2-7 and W2-9 taken in 1999 and W3-7 and W3-8 taken in 2000) and the other west of Heroya at W3-2 and W3-3 (Table S1).

The locations for the sediment samples were chosen to map both spatial and time trends in concentrations. Sediment samples were taken in October 1989 and May 2000 to map the expected PCDD/F, PCN and non-ortho PCB contamination in the Grenlandsfjords. Sample S12 was taken in Brevikfjord in 1997 (Figure 1).

Sample Collection and Handling. Water samples were taken at various locations in the Grenlandsfjords and the river Farelva during two excursions on 29 June–1 July 1999 (“W2”-

samples), and 2–5 May 2000 (“W3”-samples) (Figure 1 and Table S1). Collection of particulate and dissolved fractions from the water column was carried out primarily according to previously described methodology [1–3]. Briefly, 600–1400 L was pumped onboard through 12–112 m silicone-coated tubing (id ~3 cm) at >15 L/min, and split to a lower flow rate (~8 L/min) for each water sample. The sample was led through a 293 mm Whatman, Millipore, Millford, UK, GF/F filter (precombusted at 450°C) for collection of suspended particles. For one water sample 2 to 8 filters were used. The pump was stopped, filters changed, and pumping continued. The filtrate was passed through a precleaned polyurethane foam (PUF) sorbent cylinder of 7 cm diameter and 12 cm height to collect the dissolved and the filter-passing fraction. The PUF is considered to be a reliable sorbent giving sufficient/high sampling efficiency and low break-through for the studied compounds [1, 4].

Sediment samples from the fjords were collected with a Niemistö gravity corer [5] and with a gravity Kajak corer 2–4 May 2000 [1]. The cores were vertically sliced to 2-cm (year 1989) and 1-cm (year 2000) sections and the most surficial sections were placed in machine-washed (60°C) polyethylene boxes and sealed. Sample S7 (from 2000) was sliced further down to 29 cm in six sections to examine vertical congener patterns (Table S1).

Extraction of the Samples. Subsamples of surficial sediments were placed in precleaned (Soxhlet extracted in acetone, 24 h and toluene, 24 h) cellulose thimbles and extracted wet in a Soxhlet apparatus for 24 h using toluene (Burdick and Jackson, B & J, Fluka Chemie AG, Buchs, Switzerland). The Soxhlet was attached to a Dean Stark trap to isolate the water present in the sample. Other subsamples were taken at the same occasion for the determination of organic matter content and composition.

The GF/F filters (2–8 per sample) and PUFs were placed in separate Soxhlet extractors equipped with Dean-Stark traps and extracted wet in toluene (B & J) for 48 h.

Before extraction, ^{13}C -labelled standard mixtures (Cambridge Isotope Laboratories, CIL, Woburn, MA, USA) were added to the samples. The standards contained 2,3,7,8-TCDD, 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-TCDF, 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, OCDF, 3,3',4,4'-TeCB (IUPAC-77), 3,3',4,4',5-PeCB (IUPAC-126) and 3,3',4,4',5,5'-HxCB (IUPAC-169).

Procedural blanks were extracted and analyzed in the same manner as the samples with every set of (6) sample to control the quality of analysis and account for interferences.

Clean-up and Fractionation of the Extracts. The water sample extracts (filter and PUF fractions) were first cleaned up on a silica-gel in 100×10 mm glass columns (63–200 μm silica, Merck, Darmstadt, Germany, impregnated with 10% water, w/w). Samples were eluted with 50 mL of toluene (B & J). The eluate was cleaned up on another column (same dimensions as above) with three layers of modified silica gel (equally high layers of silica impregnated with 10% water, 33% KOH, and 40% H_2SO_4). This column was eluted with 50 mL of *n*-hexane [6].

The sediment samples were cleaned up on an identical multilayer column as mentioned above. Subsequently, copper powder was added to the eluate. The mixture was ultrasonicated for 15 minutes and left in the dark overnight for complete sulfur reduction after which the copper particles were removed.

The extracts were fractionated on HPLC first according to aromaticity using an aminopropylsilica column ($\mu\text{Bondapak } 300 \times 7.8$ mm, 10 μm particles, Waters, MA, USA). By

elution with n-hexane (Lichrosolv, flowrate 3 mL/min) a fraction containing dicyclic aromatic compounds (e.g. PCBs, PCNs and PCDD/Fs), was collected. This fraction was further fractionated according to planarity by utilizing a 2-(1-pyrenyl)ethyldimethylsilylated silica (Cosmosil PYE, 150 × 4.6 mm, 5 µm particles, Nacalai Tesque, Japan) column. This fractionation was carried out to separate target compounds (PCNs, PCDD/Fs and non-ortho PCBs, i.e. coplanar compounds) from non-planar compounds. Non-planar compounds were eluted in the forward direction with n-hexane (LiChrosolv, flow rate 0.7 mL/min at 0°C) while target compounds were back flushed from the column with dichloromethane (LiChrosolv, flow rate 1.5 mL/min at 25°C) [7]. The planar fraction was further cleaned up on a small disposable open silica gel column (10% H₂O, w/w) prior to the final GC/MS analysis.

GC/MS analysis. Analysis of non-ortho PCBs and PCNs was achieved by injection on a nonpolar capillary column (PTE 5, 30 m × 0.25 mm i.d. with 0.25 µm film, Supelco, Bellefonte, PA, USA). The column was temperature programmed as follows; 100°C (2 min), 25°C/min to 200°C, 3°C/min to 250°C and 20°C/min to 300°C (5 min). Analysis of PCDD/Fs was achieved by injection on a polar capillary column (SP 2331, 30 m × 0.25 mm i.d. with 0.25 µm film, Supelco) which was programmed as follows; 100°C (1 min), 15°C/min to 200°C, 3°C/min to 265°C (5 min). The injections were made on-column using a 2 m deactivated fused silica as a retention gap after adding ¹³C-labelled 1,2,3,4,7-PeCDD and 2,3,3',4,4'-PeCB (IUPAC-105) as recovery standards. Helium was used as a carrier gas (flow rate 1 mL/min). An HP 6890 plus Series high-resolution gas chromatograph, HRGC (Hewlett Packard, Avondale, PA, USA) with an HP 6890 Series auto sampler coupled to an Autospec Ultima magnetic sector mass spectrometer, HRMS (Micromass, Ultricham, UK). Electron impact (EI) was used at 34 eV and the detection was carried out in selected ion monitoring (SIM) mode. The transfer line and ion source temperatures

were 200°C and 250°C, respectively. The HRMS was tuned using Perfluorokerosene (PFK) at the resolution of 10 000. An external standard mixture containing 1,3,5,7-TeCN (-42), 1,2,3,5,7-PeCN (-52), 1,2,3,4,6,7-/1,2,3,5,6,7-HxCN (-66/67, 1:1 mixture), 1,2,4,5,6,8-/1,2,4,5,7,8-HxCN (-71/72, 1:1 mixture), 1,2,3,4,5,6,7-HpCN (-73) (congener numbering of 1,3,5,7-TeCN according to Wiedmann and Ballschmiter, 1993) [8] and ¹³C-labelled -77, -126 and -169 was run on the HRGC/HRMS to establish response factors. The two most abundant isotopic ions from each homologue group (tetra to hexa for non-ortho PCBs and their corresponding ¹³C-labelled standards and tetra to octa for PCNs) were monitored in different time windows. The identification of PCNs was based on literature data [9] using Halowax 1014 and ¹³C-labelled non-ortho PCBs mixture. For PCDD/F quantification, calibration standards containing ¹³C-labelled and native standards were made (at 4 concentration levels). Identification of 2,3,7,8-tetra- to octa-CDD/F congeners was done using the external calibration standard. Procedural blanks were analyzed for all target compounds to control the quality of the analyses and to trace any interfering peaks. Interfering peaks of target compounds detected were subtracted from each sample, i.e. all concentrations were blank subtracted.

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Figure 1. The Grenlandsfjords, the study area.

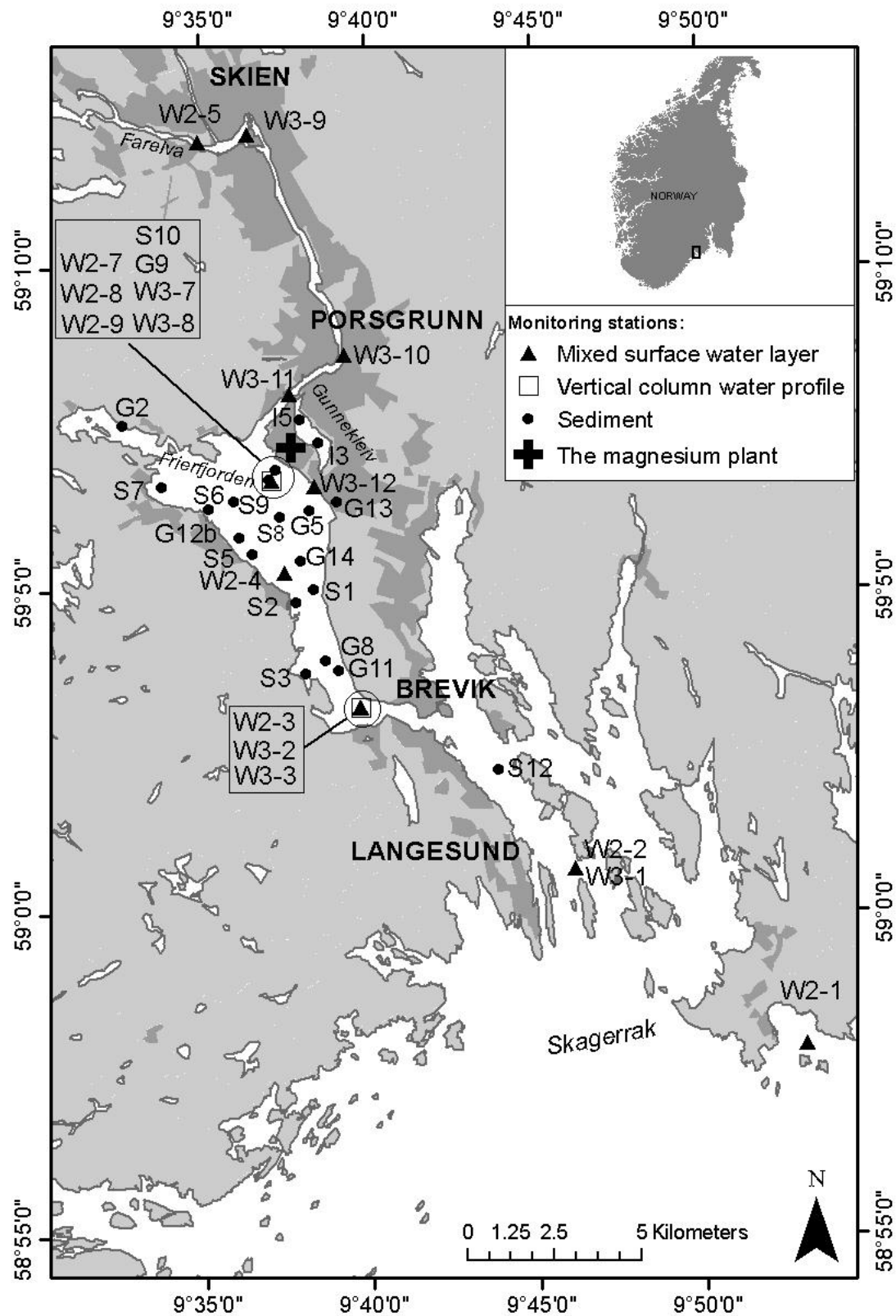


Figure 2. Concentration (ng/m³) and filter/PUF distribution of PCDFs, PCDDs and PCNs in water samples.

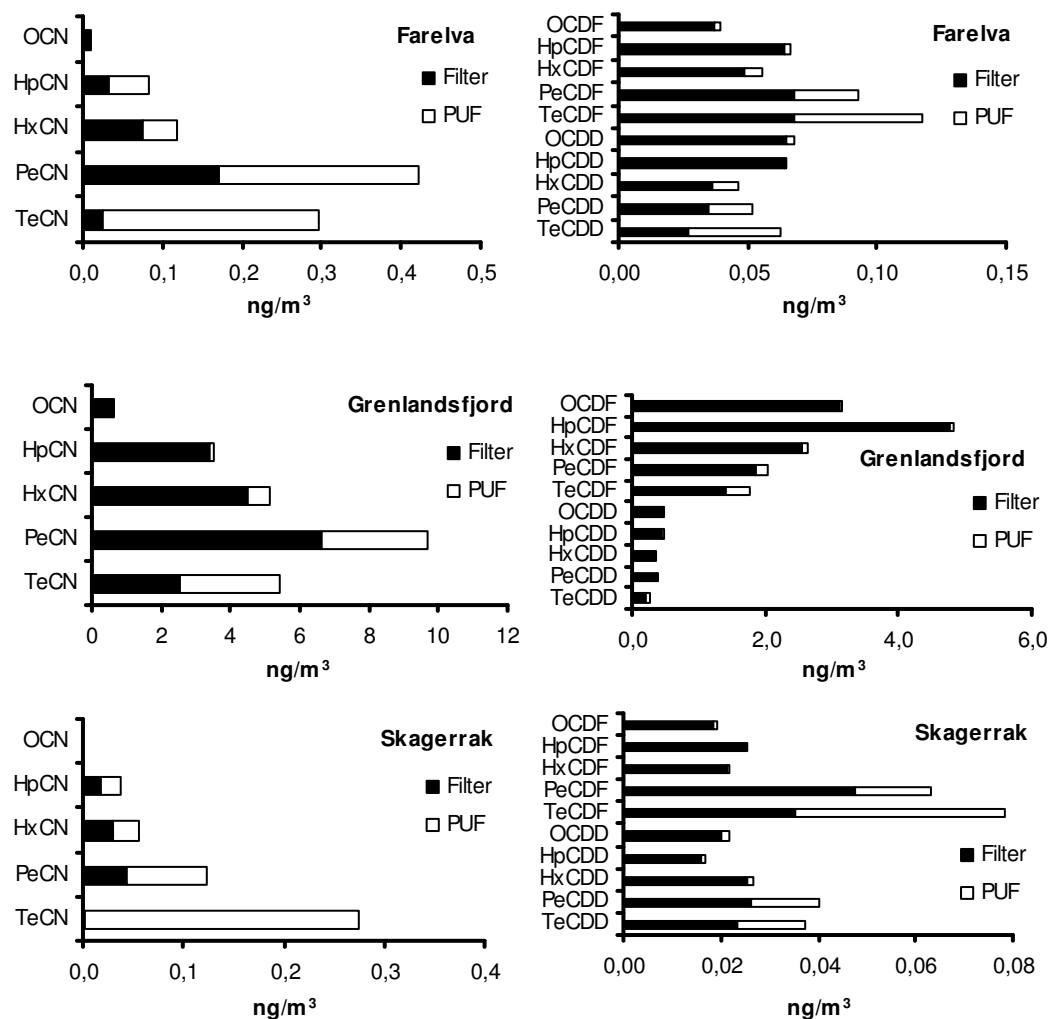


Figure 3. Homologue compositions of PCDFs, PCDDs and PCNs in water samples.

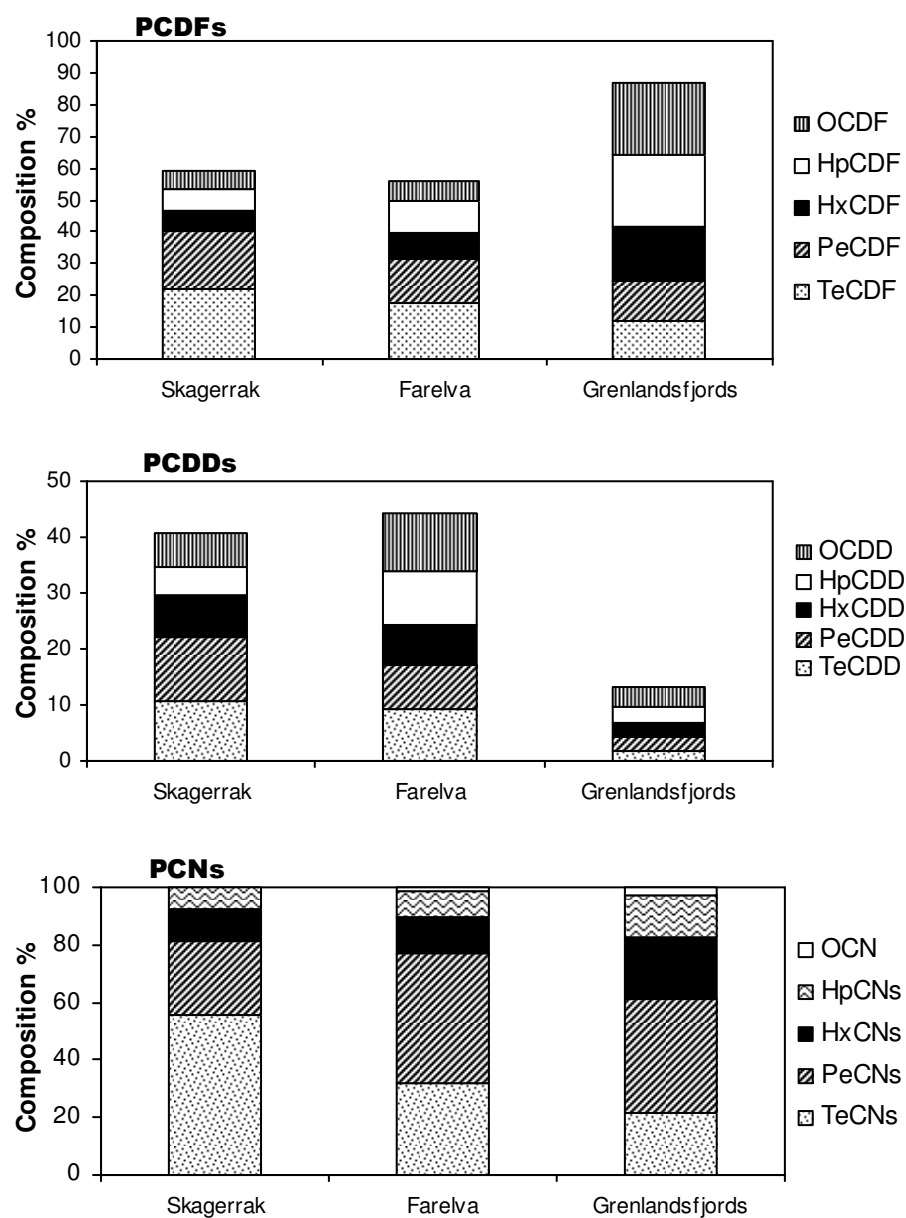


Figure 4. Homologue compositions of PCDFs & PCDDs in sediment samples.

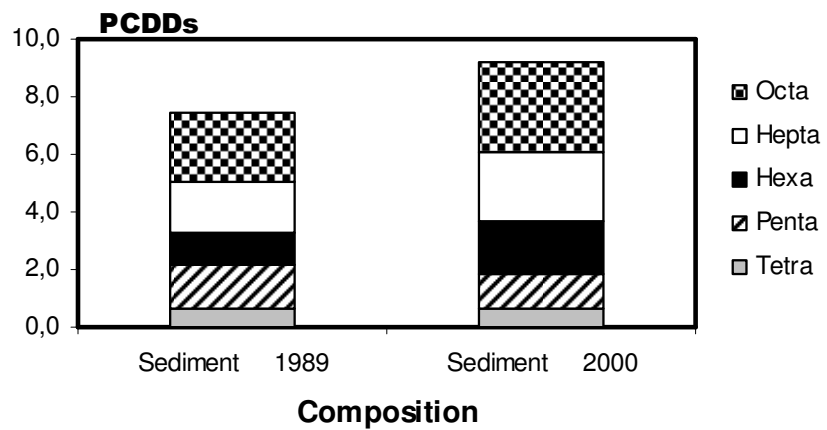
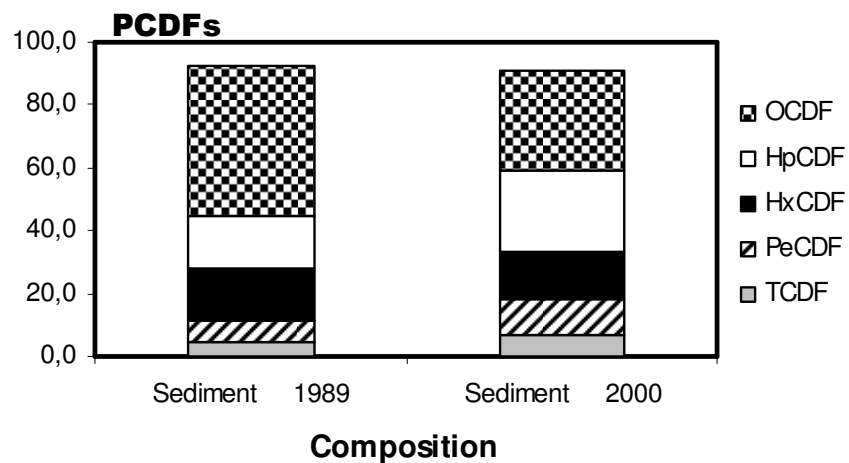


Figure 5. Congener profiles of PCNs in water samples.

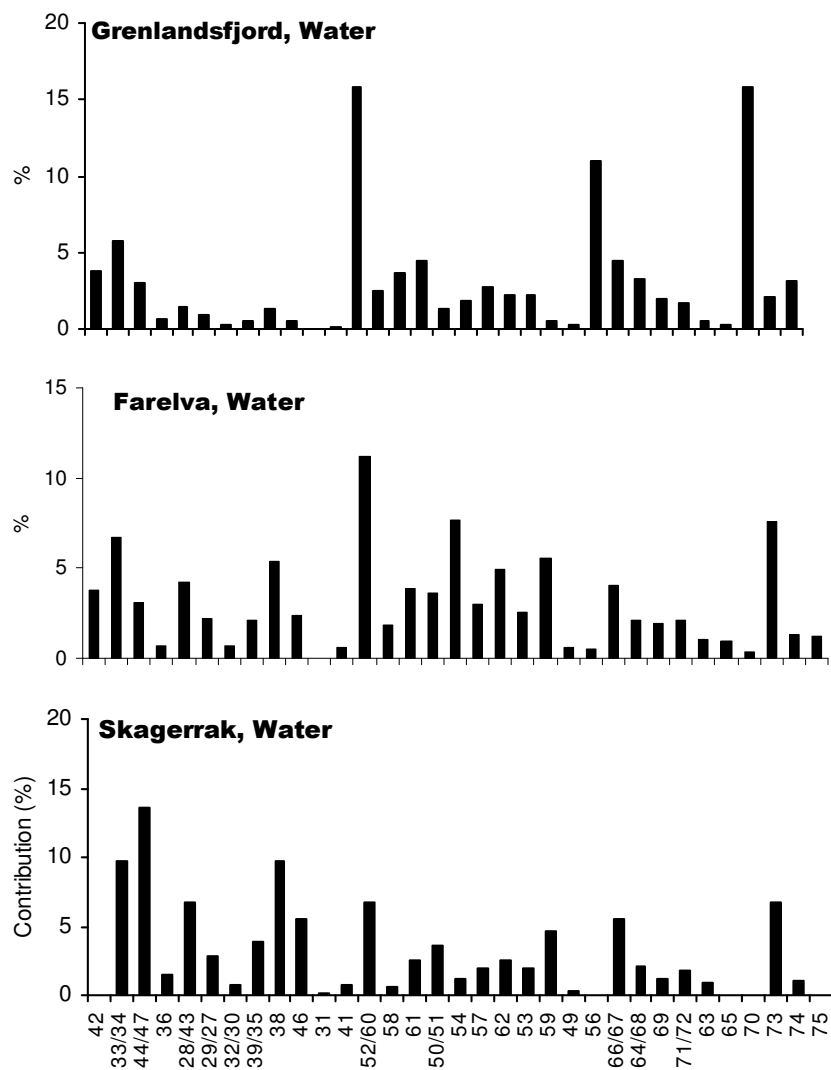


Figure 6. Congener profiles of PCDD/Fs in sediment and water samples.

