FLUX ESTIMATES AND SEDIMENTATION OF POLYCHLORINATED NAPHTHALENES IN THE NORTHERN PART OF THE BALTIC SEA

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Introduction

Polychlorinated naphthalenes (PCNs) have been detected in many environmental samples such as marine mammals[1,2], fish[3], sediments[3,4], and air[5,6]. In spite of the fact that the production of PCN technical mixtures has been prohibited worldwide, PCNs are still found in the environment being released via for example incineration processes[7] and chlor-alkali production[8]. Quantifiable levels of PCNs have been found in sediments from different parts of the world. The detected background levels in surface bottom sediments were typically in the range of 0.5-7.6 ng/g dw in the Baltic Sea[3,9] and a sample from the Swedish west coast (Kattegat) contained 0.62 ng/g dw[9]. In Italy (Venice and Orbetello lagoons) the levels were 0.03-1.51 ng/g dw[10]. PCN concentrations and fluxes were recently measured in a sediment core from a semirural lake in Northwest England[11]. The top layer of the core dated 1995 contained 2.8 ng/g dw of PCNs. A calculated current ÓPCN flux in that geographic area was five times higher than the preindustrial background levels. The ÓPCN fluxes peaked in the late 1950s to mid-1960s and were during these years five times higher than the current flux. The PCN concentrations in the “background” sediments in the geographic areas above are of the same magnitude (~1 ng/g dw), indicating similar background fluxes of PCNs. Much higher levels of PCNs have been found in sediment samples near a former chlor-alkali plant[12].

Methods and Materials

Samples

Surface bottom sediment samples were grab sampled at Harufjärden (HF) and Simpnäs (SN) in the northern part of the Baltic Sea (Fig. 1). The samples were taken from the second sediment accumulation bottom from the coastline at both locations in order to measure background levels. Sediment traps were placed near the bottom at coastal locations (SN, and HF) and offshore locations (SR5, and F9) collecting settling particulate matter (SPM) over a period of approximately 12 months. The following number of samples was taken: surface bottom sediments from HF (n = 3) and SN (n = 2); SPM from HF (n = 2), F9 (n = 1), SN (n = 1), and SR5 (n = 1). The total sampling period began in spring 1991 and ended in autumn 1993. Sampling data of the sediment trap sampling are presented in Table 1.

Extraction and clean-up

The samples were placed in pre-extracted cellulose thimbles and extracted wet in a Soxhlet apparatus (Dean Stark) with toluene for 24 h followed by acetone/hexane (59:41) for another 24 h. The lipid content was determined gravimetrically in each sample after solvent reduction. Prior to extraction, three ^{13}C-labelled non-*ortho* PCBs (PCB 77, 126, 169) were added as internal standards. The total carbon content (TC) was determined in a subsample using an element analyser (Carlo Erba EA 1108) according to standard procedures. The clean-up was carried out by means of dialysis with semi-

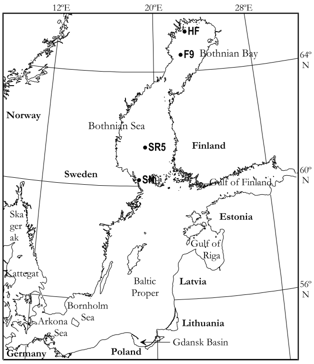

Figure 1. Sampling locations in the Baltic Sea.

Table 1. Sampling data for sediment traps.

Location	HF Bothnian Bay	F9 Bothnian Bay	SN Bothnian Sea	SR5 Bothnian Sea
Latitude (N)	65º34´72´´ 61º05´03´´	65º34´86´´	64º42´50´´	59º54´90´´
Longitude (E)	22º45´70´´ 19º32´94´´	22º45´95´´	22º04´32´´	19º10´92´´
No. of samples	2	1	1	1
Out (date)	Aug 17, 1991	May 13, 1991	Jun 16, 1992	Jan 17, 1991
In (date)	Aug 26, 1993	Nov 18, 1991	Jun 12, 1993	Mar 7, 1992
Trap out (days)	740	189	361	415
Water depth (m)	24 and 26.5	116	41	115
Placement of trap from bottom (m)	10	15	10	15

permeable membranes (SPMDs) to reduce the bulk of the lipids using cyclopentane[13]. The dialysis extract was further cleaned-up by elution on a silica column with n-hexane and fractionated on an HPLC aminopropylsilica column[14]. A fraction from the column containing dicyclic aromatic compounds was introduced onto an HPLC column containing PX-21 activated carbon to achieve a final separation of planar PCNs from *ortho*-substituted PCBs and other interfering compounds by gradient elution with a mixture of dichloromethane in n-hexane and toluene. PCNs were back-flushed from the column with 80 mL toluene[15].

HRGC-HRMS analysis

The samples (3 µl) were injected in splitless mode on a Hewlett Packard 5890 GC coupled to a VG Analytical 70-250S mass spectrometer. PCN separation was performed on an Rtx-5 capillary column (60 m, 0.32 mm i.d., 0.25 mm film thickness) using the following temperature program: 180 ºC (2 min), 20 ºC/min, 200º C, 4 ºC/min, 300 ºC (15 min). Electron impact was used at 35 eV and the HRMS operated at a mass resolution of 8000. The detection of PCN ions was carried out in SIM mode and the two most abundant isotopic ions in the molecular ion chlorine distribution cluster for each PCN homologue (tetra- through hepta-CNs) were monitored. The identification of PCNs was based on literature data[16] and the use of a Halowax 1014 mixture.

Results and Discussion

Fluxes and sedimentation of PCNs

Sample data, levels of PCNs, sedimentation rates and ΣPCN fluxes are presented in Table 2.

The load of PCNs in the surface sediment samples from SN (1.95 ng/g dw, Bothnian Sea) was six times higher compared to samples from HF (0.33 ng/g dw, Bothnian Bay). These background sediment levels are in agreement with other studies[9].

The sedimentation rates of SPM (g m-^{2} y-^{1}) as well as the ΣPCN fluxes (µg m-^{2} y-^{1}) in the offshore and coastal locations in the Bothnian Sea were approximately twice as high compared to the locations in the Bothnian Bay, i.e. elevated values in the south. The deposition of sediment material was three to five times higher in the coastal locations (SN and HF) as compared to the offshore locations (SR5 and F9). The higher deposition of SPM at the coastal locations reflects the extra input of materials from river outlets, air, surface streams etc.

Table 2. PCN levels, sediment trap fluxes of ΣPCNs, and sedimentation rates.

Type of sample	Sediment	SPM				
Location	HF	SN	HF	F9	SN	SR5
Level of PCNs (ng/g dw)	0.33	1.95	0.34	1.38	0.30	1.00
Carbon content (%)	3.1	3.1	4.5	14	4.5	5.6
Lipid content (%)	2.5	2.5	0.83	4.9	1.4	5.2
Level of PCNs (ng/g C)	10.6	62.9	7.6	9.9	6.7	17.9
Sedimentation rate (g m-^{2} y-^{1})	-	-	1700	350	3100	860
ΣPCN Fluxes (µg m-^{2} y-^{1})	-	-	0.58	0.49	0.93	0.86

The estimated ΣPCN fluxes in Northwest England[11] (2.7 µg m-^{2} y-^{1}) were higher than the fluxes (0.49-0.93 µg m-^{2} y-^{1}) obtained in this study showing the impact of the closeness to industrial activities. The obtained ΣPCN flux values were similar to the preindustrial levels determined in England[11].

The total annual sedimentation of PCNs in the Bothnian Bay (Area = 36 800 km^{2}) and Bothnian Sea (Area = 66 000 km^{2}) using the values obtained in this study were approximately 20 kg y-^{1} and 60 kg y-^{1} during this period of time.

An estimation of the annual sedimentation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans, ΣPCDD/Fs[17], in the same region (Bothnian Bay and Bothnian Sea, i.e. Gulf of Bothnia) was 120 kg y-^{1}. The investigations above have shown that the annual sedimentations of ΣPCNs and ΣPCDD/Fs were of equal magnitude in the Gulf of Bothnia around 1990.

PCN homologue profiles and congener patterns

PCN homologue profiles and congener patterns from samples collected in the Bothnian Bay are shown in Figures 2 and 3. A PCN profile of an air sample[5], sampled in the northern part of Sweden, is also shown. The PCN composition in the offshore SPM sample (SPM, F9) and the background air sample are alike, dominated by the TCNs. The PCN homologue profiles in the sediment and SPM samples of the coastal location HF are similar. These findings are confirmed by the PCN congener patterns shown in Figure 3.

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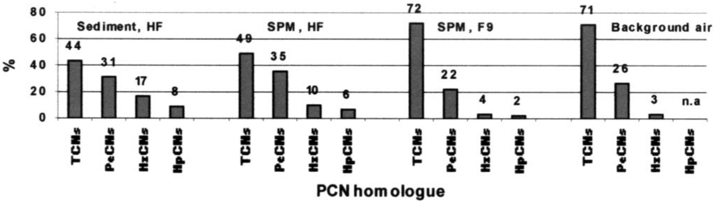

Figure 2. PCN homologue profiles in sediment and SPM samples collected in the Bothnian Bay together with a background air sample[5] collected in the north of Sweden.

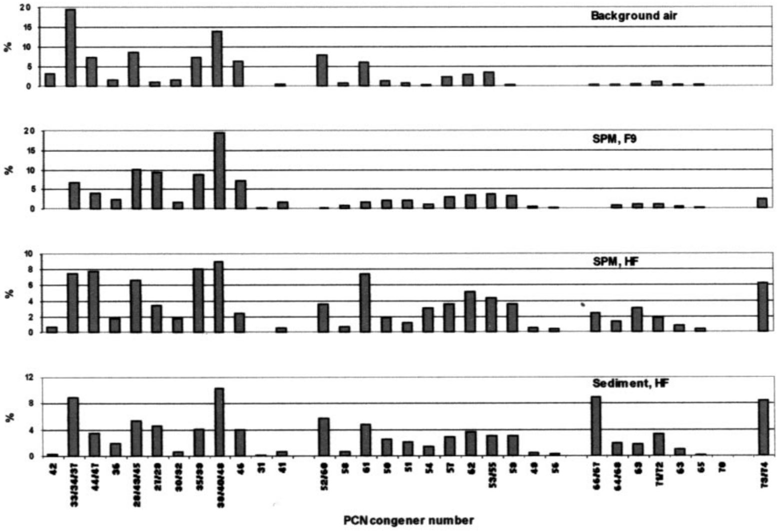

Figure 3. Composition (%) of PCNs in sediment and SPM samples collected in the Bothnian Bay together with a background air sample[5] collected in the north of Sweden.

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