ACCUMULATION OF POLYCHLORINATED NAPHTHALENES (PCNs) IN BALTIC SEA SAMPLES

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Introduction

Polychlorinated naphthalenes (PCNs) comprise a group of compounds consisting of 75 congeners with 1-8 chlorine atoms attached to the naphthalene molecule skeleton. PCNs have been produced, as technical mixtures for industrial purposes analogous to those of PCBs. Halowaxes are the most known technical mixtures produced in the USA. The production of the PCN technical mixtures has ceased world around, but PCNs are still found in for example electrical equipment[1]. In addition, PCNs are formed and released into the environment via different processes such as *incineration*[2] and *chloro-alkali production*[3].

The physicochemical properties of PCNs favour their accumulation in biota and persistence in the environment. Consequently, PCNs have been detected in a wide variety of environmental matrices including marine mammals[4,5], fish[6], urban air[7] and sediments[3]. Although PCNs are ubiquitous pollutants, reports on levels of PCNs in the environment are scarce compared to PCBs.

PCNs have structures similar to toxic polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs). The few studies on the toxicity of PCNs have shown that for example higher chlorinated PCN congeners elicit toxic effects similar to 2,3,7,8-tetrachlorodibenso-*p*-dioxin including induction of hepatic drug-metabolizing enzymes such as aryl hydrocarbon hydroxylase (AHH) and 7-ethoxyresorufin-*O*-deethylase (EROD)[8,9]. The fact that PCNs are found in the environment at levels comparable or higher to the non-*ortho* PCBs calls for a need to include this group of compounds in environmental monitoring studies.

In this paper the concentrations of tetra- to heptaCNs are presented for a benthic food chain from a coastal station in the Baltic proper. Furthermore, congener profiles are shown for the different samples.

Methods and Materials

Samples

Surface bottom sediment, settling particulate matter (SPM), isopod (*Saduria entomon)*, amphipod (*Monoporeia affinis)* and fourhorned sculpin (*Oncocottus quadricornis)* samples were collected from a coastal station in the Baltic proper (Stockholm archipelago). The isopod (n=5), amphipod (n=3) and surface sediments (n=2) samples were collected in the autumn of 1991 while the fourhorned sculpin (n=2) samples were collected in the autumn of 1993. Furthermore, the SPM (n=1) sample was collected during a period of 12 months.

The biological material was initially homogenized and pooled and subsampled into replicates. The subsamples were stored at –20 °C until analysis.

Extraction

All samples were placed in preextracted cellulose thimbles and Soxhlet extracted wet first with toluene for 24 h and then with acetone/hexane (59:41) for another 24 h. The Soxhlet was

equipped with a Dean-Stark trap to remove the water present in the samples. The lipid weight was determined gravimetrically in each sample after solvent reduction.

Before extraction a ^{13}C-labelled non-*ortho* PeCB (IUPAC#126) was added as an internal standard.

Clean-up

The clean-up was carried out by means of dialysis with semi-permeable membranes to reduce the bulk of the lipids[10] and the solvent used was cyclopentane. The dialysis fraction was split into two parts of which 90% was used for this study. This fraction was further cleaned-up by elution on a silica column with *n*-hexane and fractionated on an HPLC aminopropylsilica column (Waters, μBondapak, 300 x 7.8 mm, 10 μm). Three fractions were collected from the amino column; 1) aliphatic/monocyclic aromatic compounds 2) dicyclic aromatic compounds (PCBs, PCNs, and PCDD/Fs) and 3) polycyclic aromatic compounds[11].

The fraction containing dicyclic aromatic compounds was introduced to an HPLC activated carbon column (PX-21 on Lichrosphere RP-18, 150 x 4.6 mm, 15-25 μm) to achieve a final separation of the planar PCNs, non-*ortho* PCBs and PCDD/Fs from for example multi-*ortho* substituted PCBs by gradient elution with a mixture of methylene chloride (1%) in *n*-hexane and toluene (0-10%)[12]. The flow rate was 4 mL/min and the total separation time was 40 min. PCNs, non-*ortho* PCBs and PCDD/Fs were backflushed from the column with 80 mL toluene.

GC-MS analysis

The samples were injected in a splitless mode on a Hewlett Packard 5890 GC coupled to a VG Analytical 11-250J mass spectrometer. A 60 m x 0.32 mm i.d. Rtx-5 GC column was used. The initial oven temperature was 180 °C (2 min), raised to 200 °C at 20 °C/min and raised to the final temperature of 300 °C (15 min) at 4 °C/min. Electron impact was used at 70 eV and the detection was carried out in SIM mode. The MS resolution was 8000. The two most abundant isotopic ions from each chlorination degree (tetra through hepta for PCNs and tetra through hexa for non-*ortho* PCBs) were monitored. The identification of PCNs was based on literature data[13] and on a Halowax 1014 mixture.

Results and Discussion

Homologue distribution

Figure 1 shows the different homologue concentrations in the food chain studied. In the surface bottom sediment samples as well as in the SPM sample tetra- and pentaCNs were the dominating congeners although their relative contribution in the two samples differed. 65 and 27% in the sediment and 45 and 35% in the SPM sample, respectively. The difference in homologue profiles of the two samples could be due to that the SPM sample reflects air deposited PCNs to a greater extent than does the sediment samples.

Amphipods and isopods are sediment dwelling crustaceans. Amphipods feed on material from sediment as well as serve as a food source for isopods, which in their turn are carrion eaters. Fourhorned sculpins are bottom dwelling fish that feed on both isopods and amphipods.

The amphipod samples show no major deviation in homologue distribution from the sediments they live in. This can be due to a limited capacity of these organisms to metabolize the compounds. However, when moving upwards in the food chain the homologue distribution becomes more rich in the higher chlorinated homologues. This is observed for the isopods where pentaCNs comprise 53% of the total PCNs. In addition, this trend is especially obvious in the sculpins where the hexaCNs comprise 42% of the total PCNs analyzed. This might indicate higher metabolic activity/diffusive clearance in the sculpins of the lower chlorinated congeners compared to the other organisms in the food chain studied.

Congener profiles

The sediment and SPM samples correlate well with each other through the whole congener range being almost identical in congener composition (Fig. 2). When comparing amphipods with sediment samples, similarities are observed for the lower chlorinated congeners. However, differences in the composition of hexaCNs are observed. Congeners #66/67 and #71/72 contribute more to the total hexaCNs in the amphipods compared to those in the sediments.

Interestingly, in the isopod samples the pentaCN congener #61 is larger than #52/60. Furthermore, the contribution of hexaCN congeners #66/67 in isopods dominate being nearly 80% of the total hexaCNs. In the sculpin samples the pentaCN #52/60 are the major congeners contributing to almost 70% of the total pentaCNs. In addition, the contribution of hexaCNs #66/67 is the largest followed by #69 which becomes more significant in the sculpins compared to the other species.

Furthermore, it has been shown that PCN congeners that lack two unsubstituted carbon atoms adjacent to each other (either on a single or both aromatic rings) bioaccumulate to a greater extent than other congeners[5,14]. Congeners #52, 60, 61, 66 and 67 fulfil this structure criterion.

Acknowledgements

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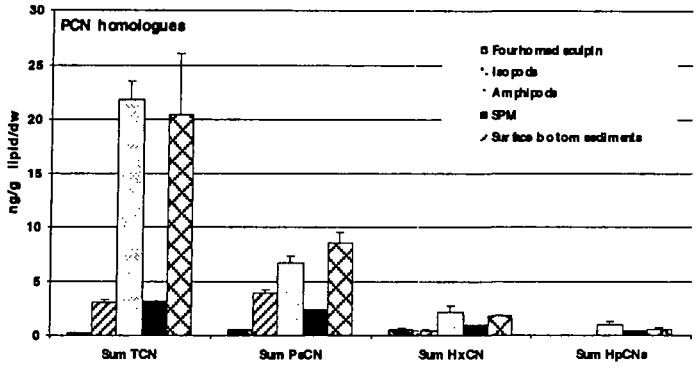

Figure 1. Mean concentrations (lipid and dry weight normalized for biotic and sediment samples, respectively) and standard errors of PCN homologue groups in samples from a benthic food chain from a coastal station in the Baltic proper.

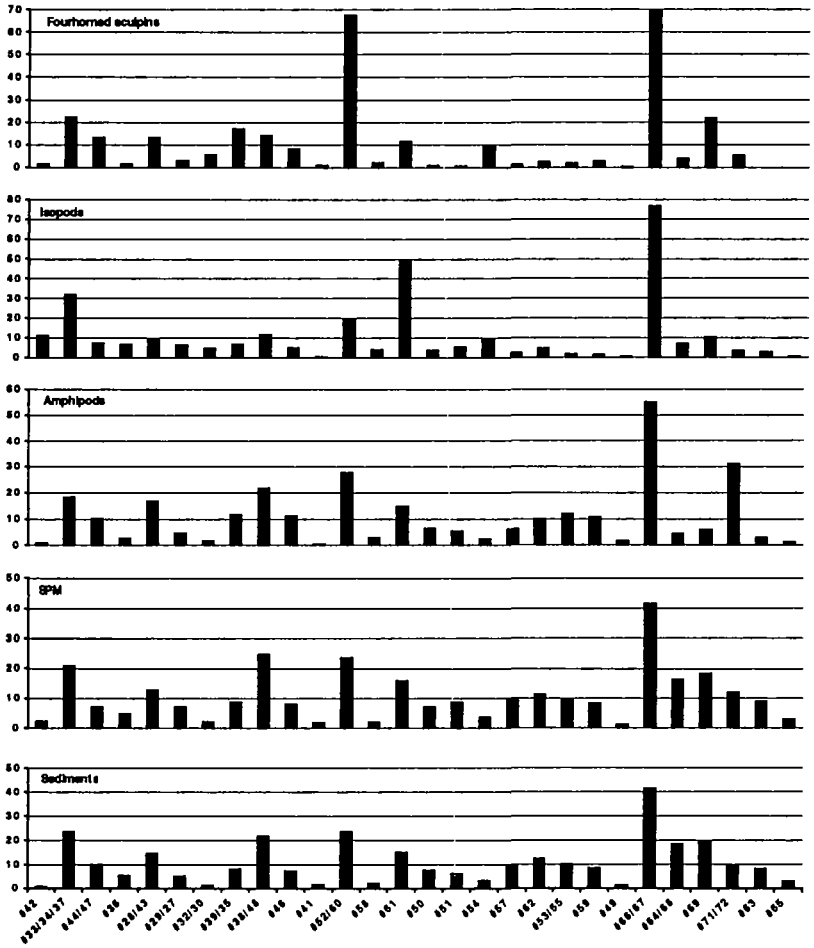

Figure 2. Comparison of tetra- to hexaCN congeners (% of total PCNs) between different samples in a benthic food chain from a coastal station in the Baltic proper. The congener numbering is according to Weidmann and Ballschmiter (1993)[15].