

## POLYCHLORINATED NAPHTHALENE LEVELS AND CONGENER PROFILES IN A BENTHIC FOOD CHAIN IN THE BALTIC SEA

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### Introduction

Polychlorinated naphthalenes (PCNs) are ubiquitous environmental contaminants that have their origin, like polychlorinated biphenyls (PCBs), from technical mixtures used for different industrial applications. The PCN molecule consists of two fused aromatic rings with 1-8 chlorine atoms substituted to the naphthalene molecule skeleton and resulting in 75 theoretically possible congeners. As for the PCBs, the physicochemical properties of PCNs makes them not only bioaccumulate in the environment but also persistent to degradation. PCNs have been detected in many environmental samples such as sediments<sup>1</sup>, marine mammals<sup>2,3</sup>, fish<sup>4</sup> and urban air<sup>5</sup>.

Because of the planarity of PCNs and their structure resemblance to polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), they are expected to be toxic. A few toxicity studies done on a number of PCN congeners have shown that for example higher chlorinated PCN congeners are potent inducers of hepatic drug-metabolising enzymes such as aryl hydrocarbon hydroxylase (AHH) and 7-ethoxyresorufin-*O*-deethylase (EROD)<sup>6,7</sup>.

In spite of the fact that the production of PCN technical mixtures has been prohibited world wide, PCNs are still found in the environment being released via for example incineration processes<sup>8</sup> and chloro-alkali production<sup>9</sup>.

### Methods and Materials

#### Samples

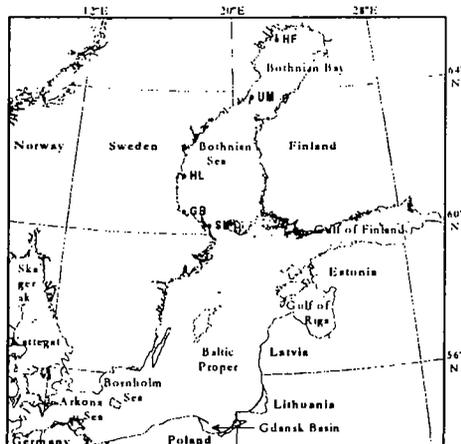


Figure 1. Sampling locations in the Baltic Sea.

Surface bottom sediment, amphipod, and isopod samples were grab sampled at different coastal locations in the northern part of the Baltic Sea (Fig. 1). The sampling locations were Simpnaäs (SN), Gävlebukten (GB), Hornslandet (HL), Umeå (UM), and Harufjärden (HF). The samples were taken from the second sediment accumulation bottom from the coastline at all locations in order to measure background levels. Fourhorned sculpins were caught in fishing nets and sediment traps were placed in Simpnaäs and Harufjärden collecting settling particulate matter (SPM) over a period of 12 months. The following samples were taken: surface bottom sediments (n=16), SPM (n=3) amphipods (n=14), isopods (n=18), and fourhorned sculpins (n=13). The sampling period started in autumn 1991 and ended in spring 1994.

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## Extraction and clean-up

All samples were placed in pre-extracted cellulose thimbles and Soxhlet extracted 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. Before extraction three  $^{13}\text{C}$ -labelled non-ortho-PCBs (IUPAC#77, #126, #169) were added as internal standards. The clean-up was carried out by means of dialysis with semi-permeable membranes, SPMDs, to reduce the bulk of the lipids using cyclopentane<sup>10</sup>. The dialysis extract was further cleaned-up by elution on a silica column with n-hexane and fractionated on an HPLC aminopropylsilica column<sup>11</sup>. A fraction from the column containing dicyclic aromatic compounds was introduced to an HPLC column containing activated carbon to achieve a final separation of the planar PCNs from the ortho-substituted PCBs by gradient elution with a mixture of methylene chloride in n-hexane and toluene. PCNs were backflushed from the column with 80 mL toluene<sup>12</sup>.

## HRGC-HRMS analysis

The samples were injected in a splitless mode on a Hewlett Packard 5890 GC coupled to a VG Analytical 70-250S mass spectrometer. A 60 m Rtx-5 (0.32 mm i.d., 0.25  $\mu\text{m}$  film thickness) GC column was used. Electron impact was used at 30 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-CNs) were monitored. The identification of PCNs was based on literature data<sup>13</sup> and on a Halowax 1014 mixture.

## Results and Discussion

### Total PCN levels

The analyses of the surface sediment samples show that the average load of total PCNs differs approximately by one order of magnitude between the sample locations (Table 1). High PCN levels were found in sediments outside Stockholm, 840 pg/g dw. Low levels were found outside Umeå, 87 pg/g dw. These background sediment levels are in agreement with other studies<sup>13</sup>.

**Table 1.** Total PCN levels in collected autumn samples.

Sampling site	Total PCN levels				
	SPM (pg/g dw)	Sediment (pg/g dw)	Amphipod (ng/g lw)	Isopod (ng/g lw)	Fourhorned sculpin (ng/g lw)
Harufjärden (HF)	340	330	69	18	0.54
Umeå (UM)	*	87	12	8.4	1.3
Hornslandet (HL)	*	730	23	5.2	0.91
Gävlebukten (GB)	*	490	17	*	1.4
Simpnäs (SN)	300	840	32	7.5	1.2

\* Not sampled

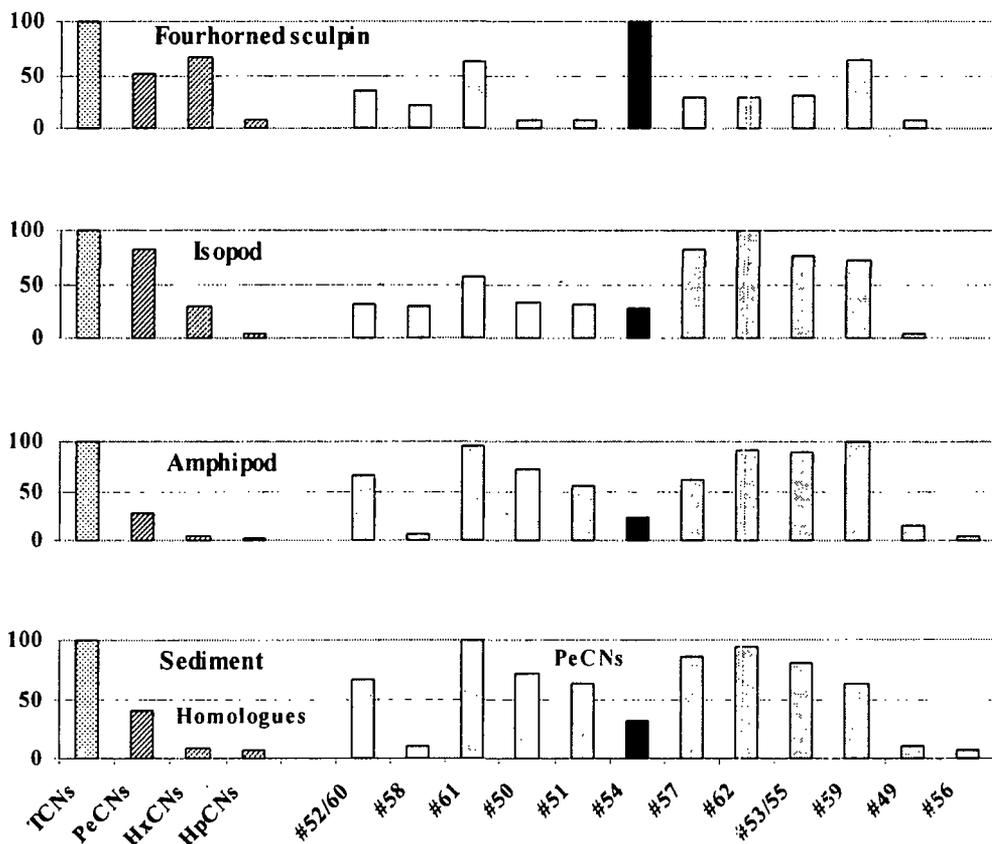
The difference in the levels between the stations is less pronounced in biota and the total level decreases going from the bottom to the top of the benthic food chain. The PCN content in the lipids in the fourhorned sculpins (~1 ng/g lw) is very similar in all analysed samples. Reported total PCN levels in herring caught in the Baltic Sea were typically in the range of 1-25 ng/g lw<sup>13</sup>. There is no characteristic North (Harufjärden) - South (Simpnäs) trend in the data as might be expected. The settling particulate matter (SPM) in the sediment traps at Harufjärden and Simpnaäs (sampling period 1992/1993) contain similar amounts of total PCNs. These results suggest that the air deposited PCNs during this period of time have been of the same size at the sampling locations.

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## Homologue profiles

Low chlorinated naphthalenes are found in the food chain base. Higher chlorinated homologues accumulate in the top of the chain (Fig. 2, left).



**Figure 2.** Relative levels (%) of PCN-homologues and PeCNs in the food chain outside Umeå.

The amphipod samples show no major deviation in homologue distribution from the sediments they live in. This is probably caused by the limited capacity of the amphipods to metabolise PCNs. When moving upwards in the food chain the homologue profile becomes more dominated by higher chlorinated homologues. This might indicate higher metabolic activity and/or diffusive clearance in the isopods and the sculpins of the lower chlorinated congeners compared to the amphipods in the benthic food chain.

## PeCN patterns

The PeCN pattern seems to shift from a sediment-like pattern (amphipod) to a non-sediment-like pattern (sculpin) when moving from the bottom to the top of the food chain (Fig. 2, right). Furthermore, the relative concentration of PCN#54 (1,2,3,6,7-PeCN), increases upwards in the

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food chain. This increase suggests that PCN#54 might be less metabolised than other pentachlorinated isomers in these organisms.

## BMFs

In general, low biomagnification factors,  $BMFs = C_{\text{Fourhorned sculpin}}/C_{\text{Amphipod}}$ , are found in the studied benthic food chain indicating that many congeners are metabolised and/or eliminated at a higher trophic level in the food chain. BMFs for PCN homologues are in the range 0.01 – 0.3 (Fig. 3, left).

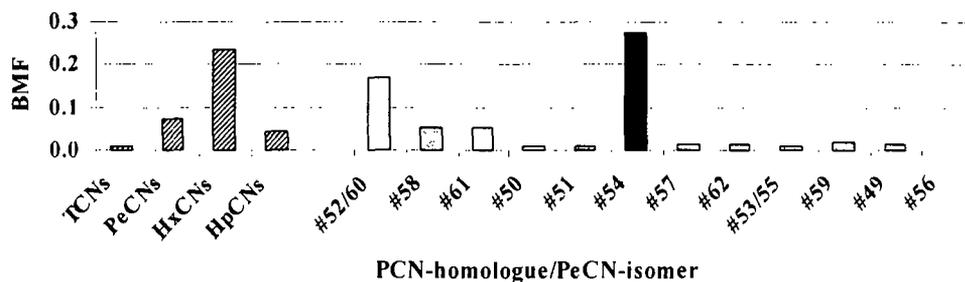


Figure 3. Calculated BMFs for PCN homologues and PeCN isomers in samples from SN.

HxCNs biomagnify to a higher degree than the other homologues. PeCN isomers ( $BMFs = 0.010 - 0.27$ ) can be divided into three categories depending on the BMF values (Fig. 3, right). One PCN isomer, PCN#54, the only 2,3,6,7-chlorine substituted PeCN isomer, shows the highest BMF value. PeCN isomers with intermediate BMF values are PCN#52, #60, #58, and #61. This group of PCN congeners does not have adjacent carbon atoms unsubstituted with chlorine. Low BMF values are found for the remaining PeCN isomers, isomers which have adjacent carbon atoms unsubstituted with chlorine. PCN#55 belongs to the intermediate group but co-elutes with PCN#53 on a DB-5 type capillary GC column. The low BMF value indicates that the eluting peak mainly consists of PCN#53. Separation of these two isomers on a Rt- $\beta$ DEXcst capillary GC column has shown the absence of PCN#55 in Halowax 1014<sup>14</sup>.

## Acknowledgments

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## References

1. Järnberg U., Asplund L., Wit C., Grafström A.-K., Haglund P., Jansson B., Lexén K., Strandell M., Olsson M., and Jonsson B. (1993) *Environ. Sci. Technol.* 27, 1364-1374.
2. Jansson B., Asplund L., and Olsson M. (1984) *Chemosphere*. 13, 33-41.
3. Ishaq R., Karlson K., and Näf C. (2000) *Chemosphere*. 41, 1913-1925.
4. Falandysz J., Strandberg L., Bergqvist P.-A., Kulp S.-E., Strandberg B., and Rappe C. (1996) *Environ. Sci. Technol.* 30, 3266-3274.
5. Harner T., and Bidleman T. F. (1997) *Atmos. Environ.* 31, 4009-4016.
6. Hanberg A., Waern F., Asplund L., Haglund E., and Safe S. (1990) *Chemosphere* 20, 1161-1164.
7. Engwall M., Brunström B., and Jakobsson E. (1994) *Arch. Toxicol.* 68, 37-42.
8. Imagawa T., Yamashita N., and Miyazaki A. (1993) *J. Environ. Chem.* 3, 221-230.
9. Kannan K., Kawano M., Kashima Y., Matsui M., and Giesy J. P. (1999) *Environ. Sci. Technol.* 33, 1004-1008.
10. Strandberg B., Bergqvist P.-A., and Rappe C. (1998) *Anal. Chem.* 70, 526-533.
11. Colmsjö A. L., Zebühr Y., and Östman C. E. (1987) *Chromatographia*. 24, 541-544.

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## OTHER POPs OF CONCERNS I

12. Lundgren K., Bergqvist P-A., Haglund P., and Rappe C. (1992) *Organohalogen Compd.* 8, 103-106.
13. Järnberg U. (1997), Analytical methods for studying polychlorinated naphthalene congener profiles and levels in the environment (*Thesis*), Stockholm University, ISBN 91-7153-6582.
14. Helm P., Jantunen L., Bidleman T., and Dorman F. (1999) *J. High Resolut. Chromatogr.* 22, 639-643.