

PLANAR PCB LEVELS AND PATTERNS IN AQUATIC AND TERRESTRIAL MUSTELIDS IN RELATION TO FOOD SOURCES

Leonards, P.E.G.^A, Broekhuizen, S.B., Van Hattum, v. B.^A, de Voogt, P.C., Brinkman, U. A. Th.^D, Van Straalen, N. M.^E, Cofino, W. P.A.

^A Institute for Environmental studies, Free Univeristy, De Boelelaan 1115, 1081 HV Amsterdam, The Netherlands.

^B Institute for Forestry and Nature Research, P.O. 2901, Arnhem, The Netherlands

^C Department of Environmental and Toxicological Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.

^D Department of Analytical Chemistry, Free Univeristy, De Boelelaan 1083 HV Amsterdam, The Netherlands.

^E Department of Ecology and Ecotoxicology, Free Univeristy, De Boelelaan 1087, 1081 HV Amsterdam.

One of the factors probably responsible for the decline of seal and otter populations in Europe is the accumulation of PCBs in these animals. Especially non-ortho and mono-ortho substituted PCB congeners are assumed to have serious effects on the reproduction of piscivorous birds and mammals as seals and mustelids^{1,2}. These congeners have effects similar to dioxins and furans. In most studies non-ortho and mono-ortho substituted PCB congeners have been investigated in the aquatic ecosystem. Less attention has been given to the terrestrial ecosystem. This study focused on aquatic (otter) and terrestrial (polecat, stoat, weasel and pine marten) mustelids from a selected area in The Netherlands. The levels and patterns of di-ortho, mono-ortho and non-ortho PCB congeners in liver of otter, polecat, stoat, weasel and pine marten were compared. Also PCB levels and patterns in the food sources of these animals were investigated. The second aim of this study was to make a comparison of the toxic equivalent concentration between aquatic and terrestrial mustelids.

PCB

Non-ortho (IUPAC nr. 77, 81, 126, 169), mono-ortho (IUPAC nr. 105, 114, 118, 156, 157, 167, 189) and 13 di-ortho substituted PCB congeners were determined in liver of otter (*Lutra lutra*, n=5), polecat (*Mustela putorius*, n=4), stoat (*Mustela erminea*, n=5), weasel (*Mustela nivalis*, n=3) and pine marten (*Martes martes*, n=4). All animals were road victims, and collected in the period 1984-1992 in a selected area in The Netherlands (Friesland). The analytical method in summary; ¹³C labeled non-ortho PCBs were added before saponification with 40% KOH and ethanol. After hexane extraction and clean-up with alumina and H₂SO₄ silica a silica column fractionation was performed to separate the analyte from interfering pesticides. Separation of the di-ortho from the mono- and the non-ortho PCBs was accomplished using a cosmosil PYE-5 HPLC column, according to the method of Haglund et al.³. The di-ortho and mono-ortho fractions were measured with GC-ECD and the non-ortho fraction with GC-ion trap detection. Recoveries were determined as 97 ± 9 (n=22) for the di-ortho and mono-ortho, and 88 ± 20 (n=22) for the non-ortho congeners.

Despite differences in food sources between the studied mustelids, all mustelids showed a similar PCB pattern (Fig. 1, except for PCB 118, 187). This implies that PCB patterns primarily seem to be determined by metabolic processes rather than diet related factors. PCB congeners with one to five chlorine atoms were either absent, or found in very low concentrations in all mustelids, probably as a result of metabolism such as has been observed for mink⁴.

To investigate if the position of free vicinal H-atoms are important for the capability of metabolism, as has been seen by cetaceans⁵, PCB congeners in otter liver, and the main food source of the otter, viz. fish were classified according to the position of the vicinal H-atoms⁵. Fig. 2 shows that PCB congeners with vicinal H-atoms in the *o,m* or *p,m* position were lower in otter than in fish, which indicates the capability of metabolism. This was also found in harbor seals but not in cetaceans; cetaceans have a low capacity of biotransformation of congeners with free H-atoms on the *p,m* position⁵. PCB congeners without free vicinal H-atoms are found in higher ratios in otter than in fish (Fig. 2), and therefore accumulate in otter.

Converting the concentration of the mono-ortho and non-ortho PCBs to 2,3,7,8-TCDD AHH-toxic equivalent concentrations⁶ (TEQ) shows that the highest toxic equivalent concentration was found in the otter, which was extremely high, TEQ 440 to 6000 pg/g wet weight. At the moment the otter is extinct in The Netherlands and in decline in other Europe countries. In terrestrial mustelids the TEQ ranged from 120- 1256 pg/g wet weight. Surprisingly these concentrations are in the same

range (110-3800 pg/g wet weight) as in marine mammals from the Pacific⁷. Comparing the ratio PCB 126/153 (Fig. 3) between the mustelids shows that polecats have the lowest ratio and weasel and stoat the highest. The lowest ratio of the polecat is still ten times higher than that found in harbor seal blubber⁵.

In conclusion, the present results indicate that mustelids can metabolise PCB congeners with vicinal H-atoms in the *o,m* and *m,p* position in combination with one chlorine atom at the ortho position; including the non-ortho PCB 77.

The total concentrations of PCBs in otters from The Netherlands are comparable with the concentrations found in otters from high contaminated areas elsewhere in Europe. Most surprising are the high concentrations of PCBs in the terrestrial mustelids. The high TEQ concentrations found in this study indicate that bioaccumulation of toxic PCBs in terrestrial food-chains may be an underestimated phenomenon.

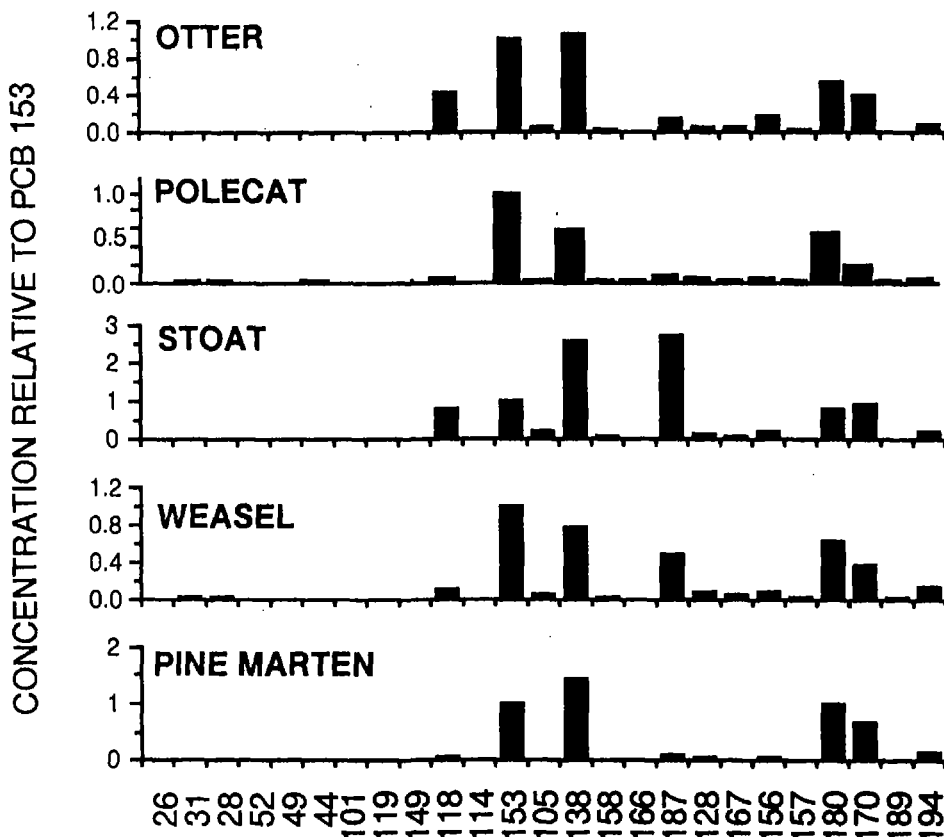


Fig. 1: PCB pattern in different mustelids

PCB

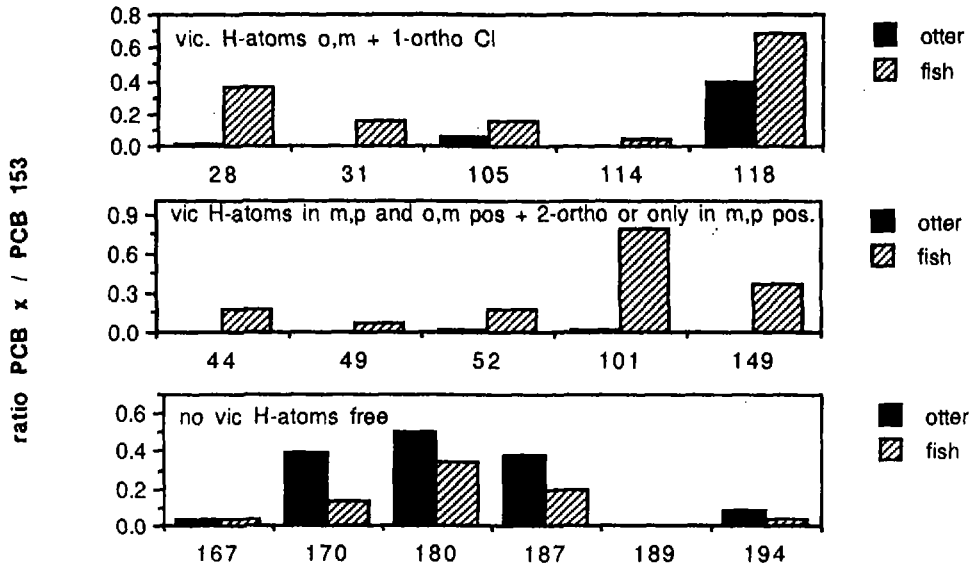


Fig. 2: PCB patterns in otter liver and fish muscle. PCB congener expressed as ratio of PCB x / PCB 153 (according to Boon et al, 1992).

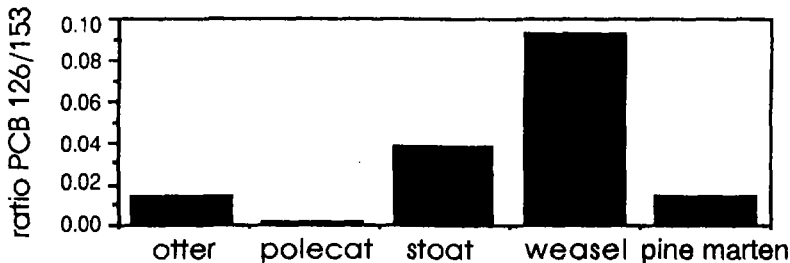


Fig. 3: Ratio of PCB 126/153 in all mustelids species

References

- Safe S. Polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs): Biochemistry, toxicology, and mechanism of action. *Crit Rev Toxicol* 1984;13:319-393.
- Aulerich R J, Bursian J, Breslin W J, Olson B, Ringer R K. Toxicological manifestations of 2,4,5,2',4',5'-, 2,3,6,2',3',6', and 3,4,5,3',4',5'- hexachlorobiphenyl and aroclor 1254 in mink. *Journal Toxicol Environ Health* 1985;15:63-79.
- Haglund P, Asplund L, Järnberg U, Jansson B. Isolation of toxic polychlorinated biphenyls by electron donor acceptor high performance liquid chromatography using a 2-(1-pyrenyl)ethyltrimethylsilylated silica column. *J Chromatogr* 1990;507:389-398.
- Bergman Å, Athanasiadou M, Bergek S., Haraguchi K., Jensen S., Klasson Wehler E. PCB and PCB methyl sulfones in mink treated with PCB and various PCB fractions. *Ambio* 21 (8). 1992:570-576.
- Boon J.P., Arnhem E., Jansen S., Kannan N, Petrick G., Schulz D., Dulker J.C., Reijnders P.J.H., Goksøyr A. The toxicokinetics of PCBs in marine mammals with special reference to possible interactions of individual congeners with the cytochrome P450-dependent monooxygenase system -an overview-. In persistent pollutants in marine ecosystems. SETAC special publication series. Pergamon press, England. 1992; p 119-159.
- Goldstein J.A. and Safe S., In :Kimbrough and Jensen 1989:267.
- Tanabe S, Kannan N, Subramanian An, Watanabe S, Tatsukawa R. Highly toxic coplanar PCBs: Accurrence, source, persistency and toxic implications to wildlife and humans. *Environ Pollut* 1987;47:147-163.