Altered PCB Congener Composition over Time in Herring from the Swedish Marine Environment – A Result of Atmospheric Degradation? Part III.

Mats Olsson[1], Anders Bignert[1], Sören Jensen[1], Ulla Eriksson[2] and Lillemor Asplund[2]

[1]Contaminant Research Group, Swedish Museum of Natural History, Box 50007
S-104 05 Stockholm, Sweden
[2]Laboratory for Analytical Environmental Chemistry, Institute of Applied Environmental
Research (ITM), Solna, Stockholm University
S-106 91 Stockholm, Sweden

Introduction

Earlier presented data from the Swedish Environmental Monitoring Programme on Contaminants in Biota (SEMPC) did not follow the predictions from the models for Global transport of volatile and semi volatile compounds presented by Wania and Mackay (1, 2, 3). These theoretically well founded models predict that the concentrations will decrease more slowly in remote cold areas than in tempered, southern areas after the discharges have ceased and that a faster decrease is expected in terrestrial environments than in marine environments. However, the Swedish data showed that the concentrations of various OCs decreased at a similar rate both in remote sub Arctic regions of Sweden and in locally polluted, tempered parts of the southern Baltic (4, 5) and there were no differences in the trends between terrestrial, freshwater or marine environment. However, recent field studies have confirmed that the concentrations in air of various CBs are controlled by temperature (6, 7, 8) which shows the importance of volatilisations. In the present study we use the Swedish time trend series on herring to study changes in some PCB congener composition over time.

Material and Methods

Ten to twenty specimens of herring (*Clupea harengus*), annually collected and analysed from four different sites (See Figure1) within SEMPC are used at this study. The material as well as methods for sampling, preparation and chemical analysis have been presented elsewhere (5). The following PCB congeners are recorded since 1987; CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180. See Figure 2. From the annual geometric mean values, log-linear regression analysis has been applied for the ratios between the various congeners and CB-153 regarded as a fairly stable congener in the environment. We have used the calculated annual change of the ratios (percent) to study whether the relative amount of the different congeners

have changed over time. Changes in ratios of the various congeners have only been presented in Table 1 if the changes over time are statistically significant ($p<0.05$).

Results and Discussion

The lack of significant changes for CB-28, CB-52 and CB-101 versus CB-153 at Harufjärden (Table 1) is most likely due to the large between-year variation because the concentrations of CB-28 and CB-52 are in the vicinity of the detection limit and for some years at this site we lack data on concentrations of lower chlorinated CBs. The rapid relative decreases of CB-180 at Fladen may indicate a change in exposure rather than a result of a degradation processes.
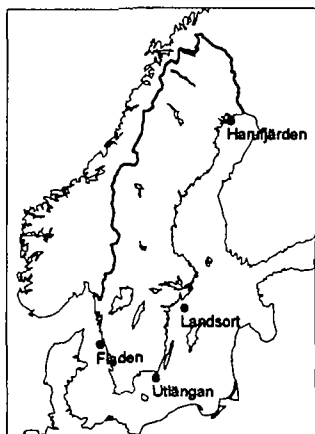
Comparing the spatial distribution pattern, the mean ratios of CB-28 and CB-52 to CB-153 indicate similar or even lower ratios in the north. The highest relative concentrations of the hepta-chlorinated CB-180, on the other hand, seems to be found in the north, a spatial variation which is statistically significant. This contradicts the expected gradient with a relative increase of lower chlorinated and more volatile compounds to the north. (1, 2, 3). However, regional variations in the use of various PCB products might partly explain these somewhat contradicting findings.

Figure 1. Sampling sites. Herring is sampled at these sites each year in the autumn.

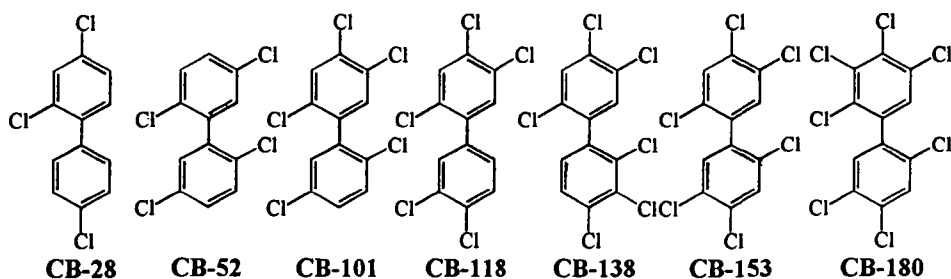CB-28 CB-52 CB-101 CB-118 CB-138 CB-153 CB-180

Figure 2. Chemical structures of analysed CB's.

Table 1. Annual change in ratios between CBs 28, 52, 101, 118, 138, 180 and 153 during the time period 1988-1995. * p< 0.05, ** p < 0.01, *** p < 0.001. The mean ratio for the entire study period is also indicated at the various sampling sites.

CB ratios	Harufjärden % / ratio	Landsort % / ratio	Utlängan % / ratio	Fladen % / ratio
28/153	n.s. / 0.047	-13* / 0.085	-25** / 0.081	-15* / 0.115
52/153	n.s. / 0.142	-10* / 0.188	-12** / 0.215	n.s. / 0.164
101/153	n.s. / 0.467	-5.9* / 0.547	-6.6*** / 0.636	-4.9* / 0.507
118/153	-9.6** / 0.423	-9.2** / 0.569	-9.3** / 0.582	-11** / 0.548
138/153	-3.5 * / 0.937	-4.1** / 0.940	-3.8*** / 0.946	-3.6* / 0.957
180/153	n.s. / 0.401	n.s. / 0.295	n.s / 0.260	-10* / 0.201

The results in table 1 clearly indicates that the fastest change in ratio is found for CB-28/CB-153, the tri chloro-biphenyl, and the higher chlorination degree the slower relative decrease in concentration is found. This variation in environmental decreases for CBs of various chlorination degree is in accordance with the calculated tropospheric lifetimes due to reaction with OH-radical (9). However, both CB-101 and CB-118 are penta chlorobiphenyls and both CB-138 and CB-153 are hexa-chloro biphenyls but CB-118 decrease faster than CB-101 and CB-138 decrease in concentration faster than CB-153.

Calculated values for Henry´s law Constants (10) indicate a higher volatility for CB-101 than CB-118 and similarly a higher volatility for CB-153 than for CB-138. These conditions do not indicate that a higher volatility will explain the different changes in decrease over time.

Polychlorinated biphenyls are known to loose chlorine when exposed to sunlight and higher chlorinated CBs will loose chlorine faster than low chlorinated CBs and then preferentially in the *ortho* position (11). Thus CB-153 show fast photo dechlorination at the *ortho* position to form CB-118. Ultraviolett degradation do therefore not explain the relatively faster degradation of lower chlorinated CBs compared to CB-153.

Both CB-118 and CB-138 have vicinal hydrogen atoms in one ring, and CB-28 and CB-52 in both rings. CBs with vicinal hydrogen are more rapidly degraded by enzymatic reactions (12). This fact would thus indicate that an enzymatic degradation can be responsible to the faster decrease of CB-28 and CB-52 but also to the relatively faster decrease of CB-138 relative to CB-153. However, vicinal hydrogenes in *meta* and *para* position in particular is known to facilitate degradation of CB congeners (14) but CB-101, having this quality, decline slower than the isomer CB-118 in our time series. Furthermore, our recent results comparing

biologically more active aquatic systems with less active aquatic systems do not indicate that enzymatic reactions will explain the rate of degradation over time (13).

The fate of the single CB congener is complicated and several processes might be involved. As an example, higher chlorinated CBs might be dechlorinated by photolysis, increasing the possibilities for further degradation by OH-radical reactions but also increasing the possibilities for enzymatic degradation. This complexicity makes studies on environmental fate very difficult for a group of compounds like PCBs.

To what extent various isomers of CBs (same number of chlorines) differ in the expected tropospheric life time due to chemical atmospheric reactions is not known by us. However, results from a pilot study comparing penta CBs indicate that CB-101 is degraded much faster by OH-radicals in water solution than CB-118 (15). Our present experiences both from temporal trend studies and experimental studies thus indicate that the position of the chlorine atoms might be important. Tentatively, our results might indicate that atmospheric degradation of various organochlorines are the major cause of observed decreases in environmental concentrations of compounds regarded as persistent compounds. These first time trend studies using various CB congeners will be expended also to other matrices and environments.

References
1. Wania, F. and Mackay, D.; *Ambio* **1993**, 22, 10.
2. Wania, F. and Mackay, D.; *Environ. Sci. Technol.* **1996**, 30, 390.
3. Wania, F. and Mackay, D.; The global fractionation of persistent organic pollutants. NILU:TR 10/96, **1996** Norwegian Institute for Air Research, Kjeller-Norway.
4. Olsson, M., Bignert, A., Odsjö, T., Persson, W., Litzén, K., Eriksson, U., Häggberg, L. and Alsberg, T.; *Organohalogen Compounds* **1997**, 33, 99.
5. Bignert, A., Olsson, M., Persson, W., Jensen, S., Zakrisson, S., Litzén, K., Eriksson, U., Häggberg, L. and Alsberg, T.; *Environmental Pollution* **1998**, 99, 177.
6. Halsall, C.J., Lee, R.G.M., Coleman, P.J., Burnett, V., Harding-Jones, P. and Jones, K.C.; *Environ. Sci. Technol.* **1995**, 29, 2368.
7. Lee, R.G.M. and Jones, K.C.; *Organohalogen Compounds* **1997**, 33, 275.
8. Hillery, B.R., Basu, I. and Hites, R.A.; *Organohalogen Compounds* **1997**, 33 270.
9. Atkinson, R. *Environ. Sci. Technol.* **1987**, 21, 305.
10. Brunner, S., Hornung, E., Santl, H., Wolff, E. and Piringer, O. G.; *Environ. Sci. Technol.* **1990**, 24, 1751.
11. Lepine, F.L. and Masse, R.; *Env. Health Prospect* **1990**, 89, 183.
12. Safe, S.; *Crit. Rev. Toxicol.* **1994**, 24, 87.
13. Bignert, A., Greyerz, E., Olsson, M., Roos, A., Asplund, L. and Kärsrud, A.-S. Similar Decreasing Rate of OCs in Both Eutrophic and Oligotrophic Environments - A Result of Atmospheric Degradation? Part II in Dioxin '98 (submitted).
14. Borlakoglu, J. and Walker, C. *Eurp. J. Drug. Metab. Pharmacokinet.* **1989**, 14, 127-131.
15. Jensen, S., Lind, J. and Merényi, G. and Olsson, M.; Manucript in preparation 1998.