

**TIME TREND STUDIES OF POLYBROMINATED DIPHENYL
ETHERS (PBDE) IN BIOLOGICAL MATERIAL FROM THE
SWEDISH ENVIRONMENT**

or

Pike do it flame retarded!

**Ulla Sellström^A, Amelie Kierkegaard^A, Cynthia de Wit^A, Bo Jansson^A
and Mats Olsson^B**

^AInstitute of Applied Environmental Research, Laboratory for Analytical Environmental
Chemistry, Stockholm University, S-171 85 Solna, Sweden.

^BSwedish Museum of Natural History, Section for Vertebrate Zoology,
Box 50007, S-104 05 Stockholm, Sweden.

INTRODUCTION

PBDE are widespread in the Swedish environment and are found in background areas without known local sources as well as in industrialised areas. The spatial trend of PBDE along the Swedish coast is similar to that of polychlorinated biphenyls (PCB) and the DDTs. PBDE seem to bio-magnify in fish consumers such as guillemots and seals¹.

The use of PBDE as flame retardants has increased since the early 1970s. For example, in Japan, the annual consumption of brominated organic compounds has increased from 2500 tons in 1975 to 22100 tons in 1987². It can therefore be expected that the concentrations of these compounds in the environment have increased during this period. Retrospective studies on a sediment core from the southern Baltic showing increasing concentrations support this theory³. The long-term fate of PBDE stored in sediments is however not well understood as far as decomposition and metabolism are concerned. Both increasing and decreasing trends of PBDE concentrations in eel from different rivers during the time period 1983-1989 have been reported from the Netherlands⁴.

The aim of this study was therefore to determine if the amounts of bioavailable PBDE have changed over time.

PCB

MATERIALS AND METHODS

Two studies were carried out. In the first, guillemot eggs (*Uria aalge*) from an island (Stora Karlsö) in the south of the Baltic Sea were chosen as the sample matrix. In the second study, pike (*Esox lucius*) from Lake Bolmen in the south part of Sweden, were analysed. Both these areas are considered background stations and are sampling stations within the Swedish environmental monitoring program.

Guillemot eggs were chosen because they have been shown to be a good matrix for time-trend studies of PCB and DDT in the Baltic sea^{5,6}. Pike is a stationary fresh water fish at a high level in the food web. It has also been shown to be a useful matrix for temporal trend studies of DDT and PCB in freshwater environments since the late 1960s.

The guillemot study was divided into two steps. In a preliminary study one egg from each of six different years between 1970 and 1989 was analysed. These eggs had previously been analysed for PCB and DDT and each was selected because it contained concentrations of PCB and DDT close to the mean of 10 eggs collected annually. Thus they were believed to be representative for the actual sampling years. In a next step, analysis was performed on pooled samples of 10 individual eggs from 4 other years within the same time period. For two specific years (1976 and 1989), 10 individual egg samples were analysed for each year. The pooled samples represent a weighted arithmetic mean value in one single analysis. The 10 single analyses result in both a mean and a measure of the individual variation.

Later, this study was complemented with analyses of pooled samples of several individuals from almost every year between 1969 and 1992. These samples have also been analysed for dioxins. Furthermore 10 individual eggs from 1992 were analysed for PBDE.

In the pike study, 10 individual samples from each of 5 years between 1971 and 1991 were analysed. These samples had previously been analysed for PCB and DDT within the Swedish environmental monitoring program.

All analyses were performed with GC/MS using chemical ionisation detecting negative ions (bromide ions).

Due to the lack of pure reference standards only three congeners were analysed. These are the major components in the technical flame retardant mixture Bromkal 70-5DE.

RESULTS AND CONCLUSIONS

The results from the analysis of single guillemot eggs indicate increasing concentrations from 1970 to 1989. However, the results from the 4 pooled samples and the 10 individ-

uals from 1976 and 1989 modify those in the preliminary study to a great extent. The 95 % confidence intervals from the two sets of individual samples overlap and there is no statistically significant difference between the two years (Student's t-test). The results indicate a fairly constant pollution load over the studied time period although the small number of analyses does not allow firm conclusions to be made. The pooled samples from 1969 to 1992 are currently being analysed. The first time-trend study of Baltic guillemot eggs clearly shows the difficulties involved in disclosing true time-trends for contaminants.

Preliminary results from the time-trend study of pike indicate a continuous increase in PBDE concentrations from the early 1970s to early 1990s. However, in order to measure the between year variation, pooled samples of several individuals from the missing years are currently being analysed. From 1974 to 1991 the concentrations increase from about 40 to about 180 ng/g lipid weight (sum of three congeners, mean of 10 individual samples). This difference is statistically significant (Student's t-test).

REFERENCES

1. Sellström U, Jansson B, Kierkegaard A, de Wit, C, Odsjö T and Olsson M. Polybrominated diphenyl ethers (PBDE) in biological samples from the Swedish environment. Accepted for publication in *Chemosphere* 1993.
2. Watanabe I, Tatsukawa R. Anthropogenic brominated aromatics in the Japanese environment. Proceedings from the Workshop on Brominated Aromatic Flame Retardants, Skokloster, Sweden 24-26 October, 1989; pp 63-71, Swedish National Chemicals Inspectorate.
3. Nylund K, Asplund L, Jansson B, Jonsson P, Litzén K, Sellström U. Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. *Chemosphere* 1992;24:1721-1730.
4. de Boer J. Brominated diphenyl ethers in Dutch freshwater and marine fish. Proceedings 10th Int. Symp. Dioxin '90, Bayreuth, Germany, 1990, Vol. 2:315-318.
5. Olsson M, Reutergårdh L. DDT and PCB pollution trends in the Swedish aquatic environment. *AMBIO* 1986;15:103-109.
6. Bignert A, Göthberg A, Jensen S, Litzén K, Odsjö T, Olsson M, Reutergårdh L. The need for adequate biological sampling in ecotoxicological investigations. A retrospective study of twenty years pollution monitoring. *Science of the Total Environment* 1993;128:121-139.