SPATIAL TRENDS OF BROMINATED AND FLUORINATED ENVIRONMENTAL CONTAMINANTS IN GUILLEMOT EGGS (*Uria aalge*) FROM THE ARCTIC AND SUB-ARCTIC IN NORTH-WEST EUROPE.

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Introduction

The spatial distribution of organohalogens in the West-Nordic seems to be more complicated than previously theories predict. Previously, long range transport according to the global distillation theory is used to explain concentrations of environmental contaminants found in biota in the arctic and sub-arctic[1,2]. There is still much unknown about sources and distribution pathways of many actual environmental contaminants. Polybrominated diphenyl ethers (PBDEs) are commercially produced and are found in high concentrations in biota, both in the Arctic and sub-Arctic[3-6]. Several studies show concentrations of PBDEs in Europe and USA but there are only few studies related to these compounds in Iceland and large areas of the North-Atlantic. PBDEs can be metabolised to OH-PBDEs[7] but OH-PBDEs are also found as natural products, mainly formed by algae and sponges. MeO-PBDEs have so far only been found as natural products.

A whole range of polyfluorinated compounds have been identified as ubiquitous environmental contaminants[8-12]. For example, studies have presented concentrations in several food chains both in the Arctic and other areas[13,14]. This is the first major spatial trend study of fluorinated compounds for North-West Europe.

Material and Methods

Samples

Guillemot egg samples were taken from five locations in West-North Europe, Vestmannaeyjar in Iceland, Sandøy in the Faroe Islands, Svalbard, Hjelmsøya and Sklinna in Norway and Stora Karlsö, Sweden.

Method

For analysis of brominated and chlorinated compounds, the egg samples were extracted with the modified Jensen method[15], scaled down to 1 g sample. Lipids were determined gravimetrically and sample clean-up was performed according to Jörundsdóttir and coworkers[16]. The fluorinated compounds were extracted and cleaned-up accordingly to Tomy et al[17].

Instruments

Analysis and quantifications of PBDEs and MeO-PBDEs were performed on a Finnigan MAT SSQ 710 (ThermoFinnigan, San Jose, CA, USA) coupled with a Varian 3400 gas chromatograph with a septum equipped temperature programmable injector (SPI) and an CTC A200S autosampler. Helium was used as carrier gas and methane as reagent gas at 5.6 torr. The gaschromatograph was fitted with a

DB-5 HT capillary column (15 m, 0.25 mm i.d., 0.1 µm phase thickness, J&W Scientific, Folsom, CA, USA). The injector temperature program was as follows: 60°C (1 min) 150°C/min to 300°C (22 min). The oven temperature program was as follows: 80°C (1 min) with 15°C/min to 300°C and 2°C/min to 320°C. The ion source temperature was 200°C and the transfer line 290°C. The instrument was operated in the electron capture negative ionisation (ECNI) mode and the electron energy was 70 eV. The PBDE and MeO-PBDE congeners were analysed with selected ion monitoring (SIM) by scanning for the negative bromide ions, m/z 79 and 81.

For the analysis of fluorinated compounds, chromatographic separation was carried out on a Genisis C_{18} analytical column (50 mm, 2.1 mm i.d., 4 µm particle size; Grace Vydac, Jones Chromatography, USA) in a Agilent 1100 series HPLC system (Agilent Technologies, Palo Alto, CA, USA). The mobile phase consisted of water and methanol. The flow rate was 300 µl min^{-1} and the gradient started with 20% methanol and increased to 95% in 10 minutes and hold 2 min. Analyses were preformed API 2000 triple quadropol mass spectrometer (MDS Sciex, Ontario, Canada) in negative ion electrospray (ES) mode using multiple reaction monitoring. Optimized parameters were as follows; ion spray voltage -1250 V; curtain gas flow 15 arbitrary units (au); sheath gas flow 30 au; turbo gas flow 30 au; temperature 475ºC; and collision-assisted dissociation gas flow 8 au.

Results and discussion

A polychlorinated biphenyl (PCB) congener (CB-153), which is the PCB congener in highest concentration in biota, is used as a marker for the traditional distribution according to the global distillation theory. Stora Karlsö, is located in the Baltic Sea, which is considered one of the most contaminated marine environments found. The Baltic Sea is therefore an exposed area and the other locations, where there is no heavy industry, are considered remote and less contaminated areas. The concentration of CB-153 is 10 times higher in eggs from the Baltic compared to eggs from the North-Atlantic. Hexachlorbenzene does not follow this pattern and there are no significant concentration differences between the five locations.

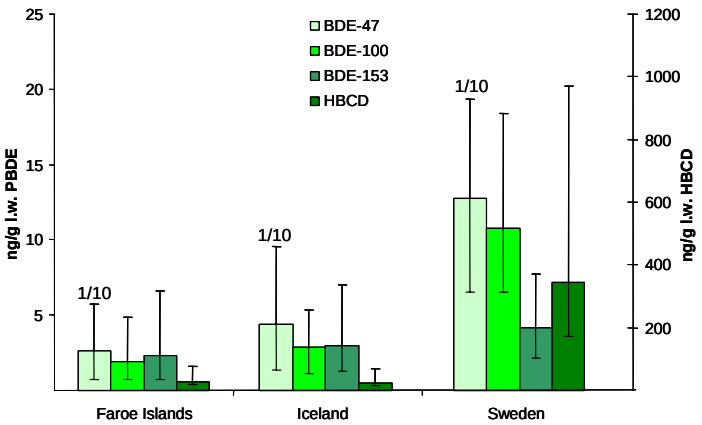

Figure 1. Concentrations (ng/g fat) and range of three polybrominated diphenyl ethers, BDE-47, BDE-100 and BDE-153, plus hexabromocyclododecane (HBCDD) in guillemot egg from the Faroe Islands, Iceland and the Baltic proper. IMPORTANT: Please note that the levels of BDE-47 is presented as 1/10 of its actual concentration to enable visualisation. Concentrations found in Norwegian eggs are not shown here.

PBDEs can not be treated as a single group where different congeners show different concentration gradient from west to east. The difference between the Baltic Sea and the North-Atlantic varies from two-times higher concentrations in the Baltic up to five times higher concentrations (Figure 1). Hexabromcyclododecane on the other hand shows a similar pattern as CB-153. There are no good explanations for the difference in the brominated group. In the North-Atlantic, the concentration of HBCDD is similar to BDE-47, but in the Baltic Sea the concentration of HBCDD is higher than for any of the PBDE congener.

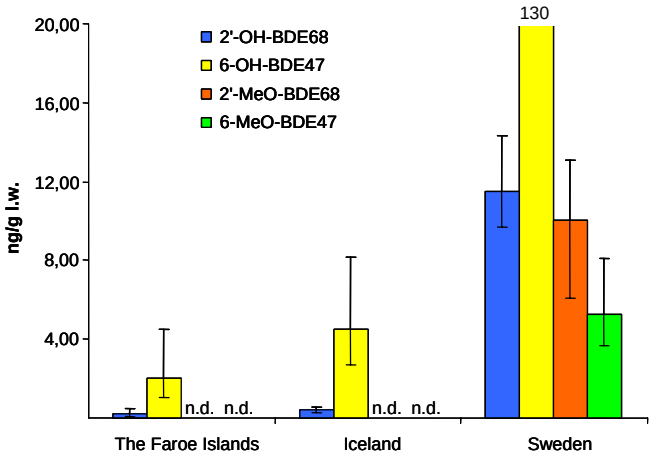

Figure 2. Concentrations (ng/g fat) and range of OH-PBDEs and MeO-PBDEs analysed in guillemot egg from the Faroe Islands, Iceland and the Baltic proper. Concentrations found in Norwegian eggs are not shown here. n.d. stands for not detected.

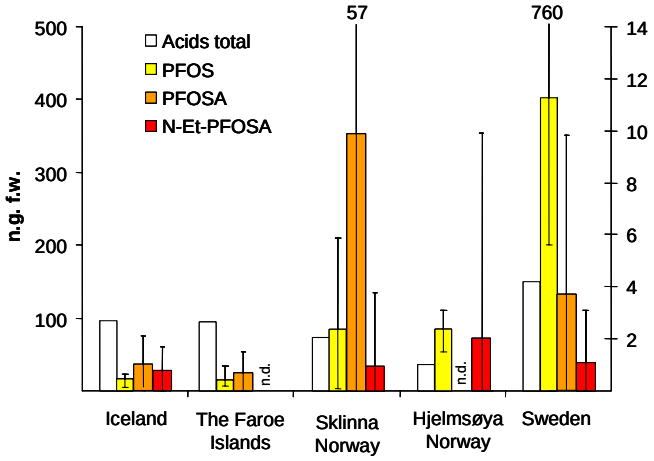

Figure 3. Concentrations with range of some polyfluorinated compounds in guillemot eggs from the West-Nordic presented on fresh weight basis. Please note that there are two y-axes, one for the acids and PFOS (left side of the graph) and one for PFOSA and N-Et-PFOSA (right side of the graph). n.d. stands for not detected.

MeO-PBDEs were not found in samples from the North-Atlantic. Metabolism may therefore play a particular role contributing to OH-PBDEs found in these samples. Another factor verifying this is the difference in concentrations of OH-PBDEs between the North-Atlantic and the Baltic Sea, being much higher than for the PBDE compounds in the former environment.

There is very little known about spatial trends of perfluorinated compounds in the West-Nordic and this is one of the first studies presenting spatial trend results. Perfluorinated compounds like PFOS, PFOA and other perfluorinated carboxylic acids show a very different distribution pattern. The pattern is different from brominated and chlorinated compounds, and there is an extreme difference in between the fluorinated group. Therefore the fluorinated group has to be treated on individual basis.

Conclusions

The spatial trends of organohalogen compounds seems to be more complicated than previous theories predict depending much on physical and chemical properties, sources and other factors. Even though the traditional compounds like PCBs show a very distinctive pattern, this pattern can not be transferred directly on other substance groups.

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References

1. Bignert, A., Olsson, M., Persson, W., Jensen, S., Zakrisson, S., Litzén, K., Eriksson, U., Häggberg, L. and Alsberg, T. *Environ. Pollut.* 1998, *99,* 177-198.
2. Fenner, K., Scheringer, M., MacLeod, M., Matthies, M., McKone, T., Stroebe, M., Beyer, A., Bonnell, M., Le Gall, A. C., Klasmeier, J., Mackay, D., Van de Meent, O. D., Pennington, D., Scharenberg, B., Suzuki, N. and Wania, F. *Environ. Sci. Technol.* 2005, *39,* 1932-1942.
3. Elliott, J. E., Wilson, L. K. and Wakeford, B. *Environmental science & technology* 2005, *39,* 5584-5591.
4. Fängström, B., Athanasiadou, M., Athanassiadis, I., Bignert, A., Grandjean, P., Weihe, P. and Bergman, Å. *Chemosphere* 2005, *60,* 836-843.
5. Fängström, B., Strid, A., Grandjean, P., Weihe, P. and Bergman, Å. *Environmental Health: A global Access science source* 2005, *4:12*.
6. Muir, D. C. G., Backus, S., Derocher, A. E., Dietz, R., Evans, T. J., Gabrielsen, G. W., Nagy, J., Norstrom, R. J., Sonne, C., Stirling, I., Taylor, M. K. and Letcher, R. J. *Environ. Sci. Technol.* 2006, *40,* 449-455.
7. Malmberg, T., Athanasiadou, M., Marsh, G., Brandt, I. and Bergman, Å. 66, 3836-3841. 2004. Berlin, Germany. Organohalogen Compounds.
8. Giesy, J. P. and Kannan, K. *Environ. Sci. Technol.* 2001, *35,* 1339-1342.
9. Holmström, K., Järnberg, U. and Bignert, A. *Environ. Sci. Technol.* 2005, 80-84.
10. Kannan, K., Koistinen, J., Beckmen, K., Evans, T., Gorzelany, J. F., Hansen, K. J., Jones, P. D., Helle, E., Nyman, M. and Giesy, J. P. *Environ. Sci. Technol.* 2001, *35,* 1593-1598.
11. Kannan, K., Franson, J. C., Bowerman, W. W., Hansen, K. J., Jones, P. D. and Giesy, J. P. *Environ. Sci. Technol.* 2001, *35,* 3065-3070.
12. Sinclair, E., Mayack, D. T., Roblee, K., Yamashita, N. and Kannan, K. *Arch. Environ. Contam. Toxicol.* 2006, *50,* 398-410.
13. Bossi, R., Riget, F. F., Dietz, R., Sonne, C., Fauser, P., Dam, M. and Vorkamp, K. *Environmental Pollution (Amsterdam, Netherlands)* 2005, *136,* 323-329.
14. Martin, J. W., Smithwick, M. M., Braune, B. M., Hoekstra, P. F., Muir, D. C. G. and Mabury, S. A. *Environ. Sci. Technol.* 2004, *38,* 373-380.
15. Jensen, S., Häggberg, L., Jörundsdóttir, H. and Odham, G. *J. Agric. Food Chem.* 2003, *51,* 5607-5611.
16. Jörundsdottir, H., Norström, K., Olsson, M., Pham-Tuan, H., Hühnerfuss, H., Bignert, A. and Bergman, Å. *Environ. Pollut.* 2006, *141,* 226-237.
17. Tomy, G., Halldorson, T. and Tittlemier, S. 67, 787-789. 2005. Toronto, Canada. Organohalogen compounds.