Hydroxylated polybrominated diphenyl ethers in Baltic Sea biota

Natural production, food web distribution and biotransformation

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Abstract

Hydroxylated polybrominated diphenyl ethers (OH-PBDEs) are naturally produced in aquatic ecosystems e.g. by algae. Many OH-PBDEs have been observed to be highly bioactive and to cause adverse effects through several pathways, e.g. via disrupting oxidative phosphorylation (OXPHOS). The levels of some OH-PBDEs have increased in Baltic biota over the past decades. This may be associated with the nutrient enrichment of the Baltic Sea, which has favored growth of some of the OH-PBDE producers.

Ceramium tenuicorne has been suggested to be a producer of OH-PBDEs in the Baltic Sea, which is supported by the results presented in this thesis. The levels of OH-PBDEs were observed to fluctuate greatly in *C. tenuicorne* over the summer season, and to correlate with the levels of pigments in the algae. However, the observed congener pattern in *C. tenuicorne* questioned theories regarding the mechanism of their biosynthesis. The results indicate a much more selective pathway for biosynthesis than previously suggested for the production of OH-PBDEs.

One of the most abundant OH-PBDEs in *C. tenuicorne*, 6-OH-BDE137, has previously been observed to be toxic to bacteria, fungi, and crustaceans. Furthermore, Baltic gammarids seemed to change their feeding preferences towards less grazing on *C. tenuicorne* during the production peek of OH-PBDEs in the alga. This suggests that OH-PBDEs may serve as allelochemical defense agents for *C. tenuicorne*.

The transport and fate of OH-PBDEs through a Baltic food chain was also studied, including *C. tenuicorne*, *Gammarus* spp., three-spined stickleback (*Gasterosteus aculeatus*), and perch (*Perca fluviatilis*). A small portion of the OH-PBDEs were observed to be methylated in the alga, or by associated bacteria. The methylated OH-PBDEs biomagnified in the food chain up to perch, in which they were converted back to the OH-PBDEs via demethylation. The OH-PBDEs and their methylated counterparts were also partially debrominated in the food chain, which resulted in high concentration of 6-OH-BDE47 in the perch. This congener is the most toxic OH-PBDE with regards to OXPHOS disruption.

Another biotransformation of OH-PBDEs was identified in Baltic Sea blue mussels (*Mytilus edulis*). High concentrations of OH-PBDEs were conjugated with lipophilic moieties, e.g. fatty acids. This increases the residence time of the OH-PBDEs in the mussels. Mussels have been suggested to conjugate steroids with fatty acids as a means to regulate hormone levels. The conjugation of OH-PBDEs to fatty acids may occur due to intrusion into this pathway. Methods were developed to include quantification of conjugated OH-PBDEs in the analysis of mussels.

OH-PBDEs were also quantified in blood from Baltic Sea grey seals (*Halichoerus grypus*). Seals originating from the Baltic proper were observed to be more highly exposed to 6-OH-BDE47 than seals from the Gulf of Bothnia. However, the levels of OH-PBDEs were generally low. A major effort was invested into securing these results, including development of a new analytical method. Blood obtained from dead seals is a difficult matrix for quantification of OH-PBDEs, and previous attempts using an established method yielded unsatisfactory results.

Keywords: *OH-PBDEs, Baltic Sea, Biosynthesis, Environmental fate, Wildlife exposure, Metabolism, Analytical methods, Ceramium tenuicorne, Blue mussel, Gammarus spp., Stickleback, Perch, Grey Seal.*

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