

## MONITORING OF PBDE, METHOXYLATED PBDE AND PCB IN BLUE MUSSELS FROM THE SWEDISH COAST LINE

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### Abstract

Methoxylated polybrominated diphenyl ethers (MeO-PBDEs), polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) have been analysed in the Swedish Environmental Monitoring Programme on Contaminants in Biota (SEMP). In this contribution we report on the results of PBDE and MeO-PBDEs in blue mussels (*Mytilus edulis*) for years 2001-2005. High levels of MeO-PBDEs (300-1100 ng/g l.w.) were found in the Baltic Sea. The levels of 6-MeO-BDE-47 were 60-500 times higher in the mussels from the Baltic Sea compared to mussels from the west coast of Sweden. The levels of BDE-47 are considerably lower (about 3 ng/g l.w.) and quite similar at all three locations both from the Swedish west coast and the Baltic Sea. The high levels of MeO-PBDE in the blue mussels from the Baltic Sea may indicate a specific MeO-PBDE source (e.g. natural production by algae and/or cyanobacteria). Furthermore, the Baltic Sea is a semi-enclosed water body heavily influenced by nutrients and frequently affected by algal blooms, a condition that may contribute to the high levels of MeO-PBDE found.

### Introduction

The brominated flame retardant, polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) are well known man made ubiquitous environmental contaminants. During the last years, methoxylated polybrominated diphenyl ethers (MeO-PBDEs) and hydroxylated polybrominated diphenyl ethers (OH-PBDEs) have been found in fish and seals from the Baltic Sea<sup>1,2,3,4</sup>. The origin of MeO-PBDEs and OH-PBDEs are somewhat less clear. To our knowledge, neither MeO-PBDEs nor OH-PBDEs are commercially produced, nor have they been reported as impurities in brominated technical products, or formed as by-products in any industrial process. However, OH-PBDEs can originate from metabolism of PBDE<sup>5,6</sup> but both OH-PBDEs and MeO-PBDEs are also well known natural products in the marine environment<sup>7</sup> and MeO-PBDEs have been isolated from whale blubber and determined to be of natural origin by measurements of the <sup>14</sup>C content<sup>8</sup>. OH-PBDEs and MeO-PBDEs have also recently been found in the red algae (*Ceramium tenuicorne*) and cyanobacteria from the Baltic Sea<sup>9,10</sup> indicating natural production.

The Baltic Sea is a semi-enclosed brackish water body heavily influenced by nutrients and environmental contaminants and is frequently affected by algal blooms<sup>11,12</sup>. The environmental situation in the Baltic Sea is followed yearly by the Swedish Environmental Monitoring Programme on Contaminants in Biota (SEMP). The marine part of this program monitors water chemistry, algae and cyanobacteria occurrences, vulnerable species and levels of environmental contaminants. PCB and DDT have been analysed in the programme since the 1970s<sup>13</sup>. The programme includes several species: blue mussels, herring, perch, cod, from several locations along the Swedish coast line, and guillemot eggs from Stora Karlsö (Baltic Sea Proper). All sites included in SEMPC are reference sites without any known local sources of pollution. The monitoring programme includes PBDEs since 2000. In this contribution we report on the results for blue mussels from 2001 to 2005. The aim of this presentation is to compare the PBDEs, MeO-PBDE and PCB concentrations in blue mussels (*Mytilus edulis*) from three Swedish coastal sites.

### Materials and Methods

**Samples** Blue mussels (*Mytilus edulis*) were collected from three locations along the Swedish coast, from Kvädöfjärden (58° 2' N, 16° 46' E) in the Baltic Proper, Fladen (57° 14' N, 11° 50' E) in the Kattegat and Väderöarna (58° 31' N, 10° 54' E) in the Skagerack (Figure 1). All sites were reference sites within the SEMPC with no known local sources of pollutants and are thus believed to be representative of a larger area. Sampling was conducted in autumn each year between 2001-2005. Pooled samples of 20 mussels were prepared and stored frozen until analysis. Five different pooled samples from each location were analysed each year. One sample from Kvädöfjärden, 2004 showed an extremely low fat content, less than 18% of the mean fat content in the rest of the samples and was therefore excluded from the statistical evaluation of the data.

**Chemicals** The PBDE standards were purchased from AccuStandards (New Haven, CT, USA) and MeO-PBDE standards were gifts from Göran Marsh and Åke Bergman (Stockholm University). The method used for synthesis is described elsewhere<sup>14</sup>. Dechlorane 603 (Hooker Chemical Corop) was used as internal standard, *n*-Hexane (LiChrosolv) and acetone (SupraSolv) were from Merck, (Darmstadt, Germany) and 2,2,4-trimethylpentane and diethyl ether (HPLC-grade) were from Lab-Scan (Dublin, Ireland). Sulphuric acid (98%) was from Fisher (Waltham, USA), while phosphoric acid (85%, pro analysis) and sodium chloride both were from Merck (Darmstadt, Germany).



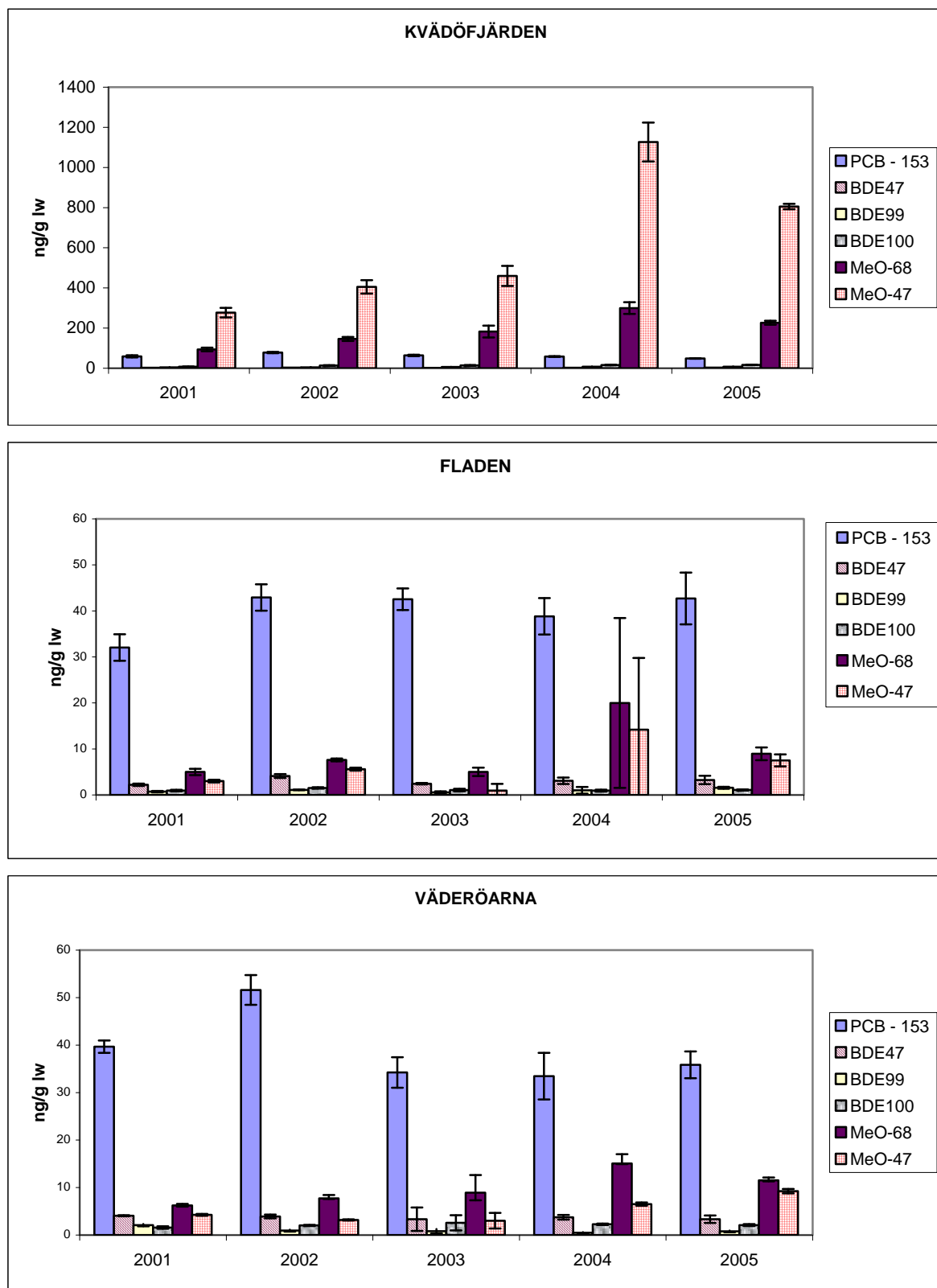
**Figure 1:** Samplesites  
<sup>1</sup>Kvädöfjärden; <sup>2</sup>Fladen; <sup>3</sup>Väderöarna.

**Analytical method** The blue mussel homogenates (10g) were extracted with *n*-hexane/acetone followed by *n*-hexane/diethyl ether and cleaned up by treatment with concentrated sulphuric acid according to the method described by Jensen *et al.* 1983<sup>15</sup>. Chromatographic separation was carried out on a DB-5 MS capillary column (30m x 0.25 mm i.d., 0.25 µm particle size; J&W Scientific, Palo Alto, CA, USA). Helium was used as carrier gas and the injector temperature was held at 270°C. The GC-oven temperature program was; 80°C (2 min), 25°C/min to 200°C 4°C/min to 315 (5 min). The samples were analysed by GC/MS using electron capture negative ionisation (ECNI) with ammonia as reaction gas. The analyses were performed with a Finnigan SSQ 7000 (ThermoFinnigan, Bremen, Germany). The ion source and the transfer line were set at 180°C and 300°C respectively. The mass fragments monitored were *m/z* 79 and 81 for PBDE and MeO-PBDEs and *m/z* 237 and 239 for the internal standard Dechlorane. The BDE congeners analysed were: BDE-47, BDE-99, BDE-100 and the MeO-BDE congeners: 6-methoxy-2-2',4,4'-tetraBDE (6-MeO-BDE-47) and 2'-methoxy-2,3',4,5'-tetraBDE (2'-MeO-BDE-68).

### Results and Discussion

The levels of 6-MeO-BDE-47 were 60-500 times higher in blue mussels from the Baltic Sea (Kvädöfjärden) compared to the west coast (Fladen and Väderöarna) (Figure 2). The levels of BDE-47 and CB-153 are quite similar at all three locations both from the Swedish west coast and the Baltic Sea and no significant differences can be detected (Figure 2). The same spatial trend with high levels in the Baltic Proper and lower levels on the west coast has been observed for MeO-PBDEs in another recent study<sup>16</sup>.

Although Figure 2 seems to indicate increasing temporal trends for MeO-PBDEs, it is too early to carry out statistical tests considering the large between-year variation and the few number of years yet available.



**Figure 2** Concentrations of BDE-47, -99, -100, MeO-BDE-47, MeO-BDE-68 and CB-153 (ng/g l.w.) in blue mussels from the Swedish coast mean values and 95% confidence intervals.

**Table 1** Ratio of 6-MeO-BDE-47 to BDE-47 in the blue mussels from the Swedish coast.

Year	2001	2002	2003	2004	2005
Kvädöfjärden	120	130	210	430	270
Fladen	1.0	0.8	0.9	1.7	2.8
Väderöarna	1.4	1.4	0.4	4.6	2.3

The ratio of 6-MeO-BDE-47 to BDE-47 is about 100 times higher in blue mussels from the Baltic Sea compared to mussels from the west coast of Sweden (Table 1). For this reason, metabolism of BDE-47 in the blue mussels, via OH-BDE or directly, is not a likely source of 6-MeO-BDE-47. Another potential source of OH-PBDEs may be reactions between OH radicals and PBDEs in the atmosphere<sup>17</sup>. MeO-PBDEs could then possibly be formed by methylation in e.g. the sediments by microorganisms. However, OH radical formation is highly unlikely as a major source for the MeO-BDEs found in the Baltic Sea biota considering that the 6-MeO-BDE-47 to BDE-47 ratio in the blue mussels differs by a factor 100 between the east and west coast of Sweden. Therefore the high MeO-PBDE concentrations in mussels from the Baltic Sea indicate specific OH-/MeO-PBDE sources in the Baltic Sea. One such source could be natural production of OH-PBDE and/or MeO-PBDE in e.g. algae and/or cyanobacteria. Another factor that may influence the difference in concentrations of MeO-PBDEs in the Baltic Sea compared to the west coast of Sweden could be that the marine environment at the west coast is less favourable for the accumulation of these substances. Recently OH- and MeO-BDEs have also been detected in red algae and cyanobacteria from the Baltic Sea<sup>9,10</sup> but further research is required to definitively establish the origin of the MeO-PBDEs in the Baltic Sea.

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