LEVELS OF PBDES AND SOME NOVEL BFRS IN GERMAN WADDEN SEA SEDIMENTS

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Introduction

North Sea tidal flats are subject to changes induced by natural processes typically occurring in this environment and by influences of human activities. This study focuses on the Jade Bay, which forms part of a large tidal flat system in North West Germany. For a comprehensive assessment of natural sciences and cultural aspects of the Jade Bay area the multidisciplinary project *Baseline study Jade Bay* was set up by the State of Lower Saxony. The project will bring together geological, biological and chemical data as well as a record of human settlement covering a time span from the Holocene to Present. Partners involved include the Institute for Chemistry and Biology of the Marine Environment (ICBM) of the University of Oldenburg, the Lower Saxony Institute for Historical Coastal Research, the Marine Science Department of the Senckenberg Institute, the Wadden Sea National Park Administration of Lower Saxony and the Lower Saxony Water Management and Coastal Defence and Nature Conservation Agency. Detailed objectives and the complete set of chemical parameters are presented at *http://www.jade.icbm.de/en/*.
So far, only a few data are available on levels of brominated flame retardants (BFRs) in sediments from the German Wadden Sea[1] but none from the Jade Bay area. Here we show the results of a survey on 23 polybrominated diphenyl ethers (PBDEs) and six novel BFRs determined in Wadden Sea surface sediments collected in the inner Jade Bay, Germany, using a fully optimised and validated GC-ECNI-MS method.

Material and methods

Surface samples were taken in January 2009 using a Van-Veen box corer. The position of sampling sites is shown in Fig. 1. Station JB09-38 is located in a small marina at the city of Wilhelmshaven, whereas the remaining four stations are not directly influenced by human activities. Stations JB09-17/-21/-22/-38 are classified as intertidal mudflats (more than 50% of particles <63 µm), whereas station JB09-16 represented a mixed mud/sand tidal flat (5-50% of particles <63 µm). There is no significant riverine input into the bay.

Analyses of PBDEs, pentabromotoluene (PBT), pentabromoethylbenzene (PBEB), hexabromobenzene (HBB), brominated biphenyls (BB153, BB209) and 1,2-bis(tribromophenoxy)ethane (BTBPE) were performed as described previously[2] with some modifications. In brief, 10 to 20 g of sediment were extracted with toluene at 125°C and 14 MPa using an ASE 200 accelerated solvent extractor (Dionex GmbH, Idstein, Germany) followed by gel permeation chromatography and multi-layer silica gel column chromatography clean-up. The purified extracts were evaporated to a final volume of 100 µl using an automatic evaporation device (Flowtherm Optocontrol, Barkey GmbH & Co. KG, Leopoldshöhe, Germany).
Quantification of PBDEs and BFRs was performed by high-resolution capillary gas chromatography-electron capture negative ionisation mass spectrometry (GC-ECNI-MS) in the selected ion monitoring mode under the following conditions: GC 7890A / MSD 5975 inert XL EI/CI MSD (AGILENT, Palo Alto, CA, U.S.A.) equipped with autosampler MPS2 (CTC Analytics AG, Zwingen, Switzerland) and PTV injector CIS 4 plus (GERSTEL, Mülheim/Ruhr, Germany); capillary column: Rtx-CLPesticide (Restek, Bellefonte, PA, U.S.A.), 30 m x 250 µm, film thickness: 0.25 µm; pressure-pulse injection: 50 psi (1 min); injection volume: 2 µl; carrier gas: helium; CI ion source reagent gas: methane; ion source temperature: 200°C. For quantification of BDE209 the highly specific ions at *m/z* = 484.7 and *m/z* = 486.7 were monitored. For all other BFRs, ions specific to bromine at *m/z* = 79 and *m/z* = 81 were recorded. The monofluorinated brominated diphenyl ethers F-BDE28, F-BDE100 and F-BDE160, F-BDE181 and $^{13}C_{12}$-labelled BDE209 were used as internal standards. Quality control included recovery tests, regular analyses of procedural blanks, blind replicate samples as well as participation in international interlaboratory studies on the

determination of PBDEs. Standards were purchased from Chiron AS (Trondheim, Norway) and Wellington Laboratories Inc. (Guelph, Ontario, Canada).

Results and discussion

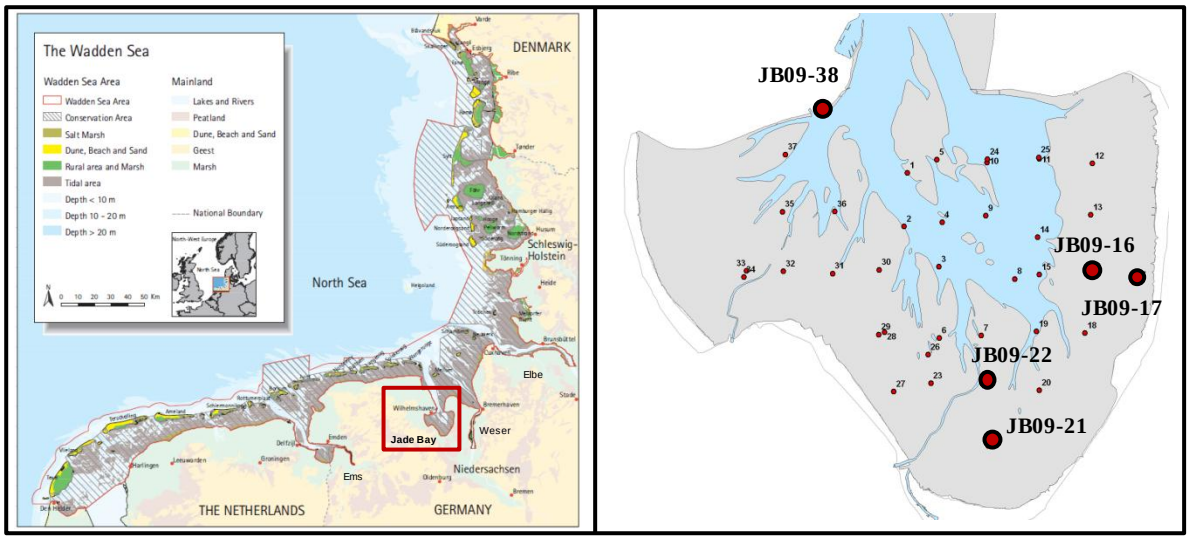

Fig. 1: Sampling stations (Wadden Sea map: *http://www.waddensea-secretariat.org/QSR-2009/index.htm*)

In sediments collected in the Jade Bay area, BDE209 was the prevalent compound (Tab. 1). Besides BDE209, low concentrations of BDE28, BDE47, BDE49, BDE66, BDE99, BDE100, BDE183, BDE196 and BDE197 were detected in all samples. In four out of five samples, BDE153, BDE206 and BDE207 were found at minor concentrations. The levels of the remaining congeners were below the limit of detection (LoD <0.0001-0.0008 ng/g dw) or the limit of quantification (LoQ <0.0003-0.02 ng/g dw). Highest levels of BDEs were found at the small marina at Wilhelmshaven (JB09-38). Tidal currents indicated JB09-38 as a sink for suspended particulate matter and explain the relatively high PBDE levels found at this station. BTBPE was present in all samples and concentrations ranged from 0.007 ng/g dw to 0.15 ng/g dw. In sample JB09-21 PBT, PBEB, BB153 and BB209 were found in trace amounts. HBB was not detected in any of the sediments.

For the major BDE congeners BDE209, BDE47 and BDE99, these results are in good agreement with previously measured PBDE levels in sediments of the German Bight[1] (and unpublished results). The authors reported results of a 4-year study on PBDEs in sediments sampled at various locations in the German North Sea including samples from the German Wadden Sea. Median concentrations of BDE209, BDE47, and BDE99 ranged from 0.03 to 6.5 ng/g dw, 0.05 to 0.11 ng/g dw and 0.06 to 0.13 ng/g dw, respectively. The fairly low BDE47 and BDE99 concentrations seen in both studies may reflect that a voluntary self commitment of German plastic and textile additives producers to abandon the use of PBDEs in their products has been in place since 1986 and that technical penta- and octa-BDE have been banned on the European market since 2003.

Information on PBDE concentrations in Wadden Sea sediments is scarce. Zegers *et al.*[4] analysed a dated sediment core from the Dutch Wadden Sea. In Tab. 2 concentrations of the top-most layer of this core (year 1995±2) are shown. Only those congeners determined in our study as well were included. BDE47 and BDE99 levels detected in the Dutch Wadden Sea are in the same order of magnitude as those found in the Jade Bay sediments, except at station JB09-38 (Tab. 2). BDE209 concentrations at stations JB09-16, -17 and -22 show similar concentrations of BDE209 as presented by Zegers *et al.*[4], whereas sediments taken at JB09-21 and -38 yield significantly higher values (factor 3.5 and 9).

Table 1: Concentrations of PBDEs and novel BFRs in Jade Bay sediments [ng/g dw]

Congener/compound	JB09-16	JB09-17	JB09-21	JB09-22	JB09-38
BDE17	<NG	<NG	<NG	<NG	<NG
BDE28	0.003	0.004	0.006	0.004	0.017
BDE47	**0.012**	**0.025**	**0.050**	**0.023**	**0.131**
BDE49	0.003	0.005	0.011	0.005	0.030
BDE66	0.002	0.005	0.010	0.004	0.019
BDE71	<NG	<NG	<NG	<NG	<NG
BDE77	<NG	<NG	<NG	<NG	<NG
BDE85	0.011	<NG	<NG	<NG	<NG
BDE99	**0.008**	**0.024**	**0.041**	**0.055**	**0.098**
BDE100	0.002	0.004	0.007	0.006	0.018
BDE138	<NG	<NG	<NG	<NG	<NG
BDE153	<BG	0.004	0.008	0.005	0.022
BDE154	<BG	<BG	0.005	0.004	0.009
BDE179	<NG	<NG	0.004	<NG	0.009
BDE183	0.004	0.006	0.016	0.007	0.026
BDE188	0.005	<NG	0.003	<NG	0.007
BDE196	0.007	0.013	0.043	0.019	0.087
BDE197	0.004	0.007	0.014	0.006	0.029
BDE202	<NG	0.005	0.009	<NG	<NG
BDE203	<NG	0.006	0.008	<NG	0.015
BDE206	0.015	0.039	0.090	<NG	0.232
BDE207	0.010	0.021	0.039	<NG	0.097
BDE209	**0.309**	**1.344**	**3.390**	**0.675**	**8.953**
PBT	<NG	<NG	0.010	<NG	<NG
PBEB	<NG	<NG	0.003	<NG	<NG
HBB	<NG	<NG	<NG	<NG	<NG
BB153	<NG	<NG	0.007	<BG	<NG
BTBPE	**0.007**	**0.022**	**0.052**	**0.028**	**0.147**
BB209	<NG	0.035	0.061	<NG	0.126

LoD < 0.0001-0.0008 ng/g dw; LoQ <0.0003-0.02 ng/g dw

Wadden Sea sediments were also included in a study by Sellström *et al.*[5] (Tab. 2). Station Weser is in close vicinity of the Jade Bay while Wadden Sea 10 is located in the Dutch Wadden Sea. Moreover, de Boer *et al.*[6] presented PBDE concentrations in sediments from the Eastern (Station 15) and Western (Station 16) Dutch Wadden Sea. BDE47 and BDE99 levels differed at the two sampling sites and are much higher than those reported in this and the above mentioned studies (Tab. 2).

Lopez *et al.*[3] analysed BFRs in five sediments from the Scheldt estuary containing PBT from 0.01 to 0.33 ng/g dw and 0.25 and 0.31 ng/g dw BTBPE, respectively. These findings are consistent with the levels of PBT and BTBPE at the highest contaminated site JB09-38.

Table 2: PBDE concentrations in Dutch and German Wadden Sea sediments [ng/g dw]

Reference	Station	BDE47	BDE99	∑47+99	BDE209
This study	JB09-16	**0.011**	**0.008**	**0.02**	**0.31**
	JB09-17	**0.025**	**0.024**	**0.05**	**1.35**
	JB09-21	**0.050**	**0.041**	**0.09**	**3.40**
	JB09-22	**0.023**	**0.055**	**0.09**	**0.68**
	JB09-38	**0.131**	**0.098**	**0.23**	**9.00**
Zegers[4]	[a]	**0.05**	**0.05**	**0.1**	**1.00**
Sellström[5]	Wadden Sea 10[b]			**0.08**	**0.13**
	Station Weser			**0.04**	**3.30**
de Boer[6]	Station 15[c]	**1.0**	**0.66**	**1.66**	**10.00**
	Station 16[c]	**1.0**	**0.22**	**1.22**	**10.00**

[a]Top-most layer of a sediment core from the Dutch Wadden Sea; [b]Dutch Wadden Sea; [c]Dutch Wadden Sea

Table 3: Patterns of octa- to deca-BDEs in technical formulations and Jade Bay sediments

Congener	Percentage of octa- to deca-BDEs		Percentage of octa- to deca-BDEs in sediments				
	Saytex 102 E	Bromkal 82 ODE	JB09-16	JB09-17	JB09-21	JB09-22	JB09-38
BDE196	***nd***	**0.46**	**1.96**	**0.90**	**1.19**	**2.67**	**0.93**
BDE197	***nd***	**0.03**	**1.16**	**0.48**	**0.39**	**0.81**	**0.31**
BDE203	***nd***	**0.07**	***nd***	**0.41**	**0.23**	***nd***	**0.16**
BDE206	**2.19**	**5.13**	**4.35**	**2.73**	**2.50**	***nd***	**2.47**
BDE207	**0.24**	**4.1**	**2.87**	**1.50**	**1.08**	***nd***	**1.03**
BDE209	**96.8**	**91.6**	**89.66**	**93.99**	**95.76**	**96.46**	**95.12**

[d]modified from LaGuardia *et al.*[7]; *nd* = not detected; [e]congeners found in technical deca formulations and sediments

The patterns of octa- to deca-BDEs in the sediments taken in the Jade Bay show slight differences compared to the pattern seen in the deca-BDE technical products Saytex 102E and Bromkal 82 ODE in particular with regard to the percentages of BDE196, BDE197 and BDE207 (Tab. 3). However, so far we have no evidence that these differences might be due to degradation of BDE 209.

The predominance of deca-BDE, the presence of non-BDE-based BFRs and the declining BDE47 and BDE99 levels seen in the studied sediments should be considered in future monitoring programmes, which should focus on deca-BDE and novel BFRs utilised as replacement products for technical penta- and octa-BDEs.

Acknowledgements

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