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Susann-Cathrin Lang, Philipp Mayer, Andrew Hursthouse, Danijela Kötke, Ines Hand, Detlef Schulz-Bull, Gesine Witt



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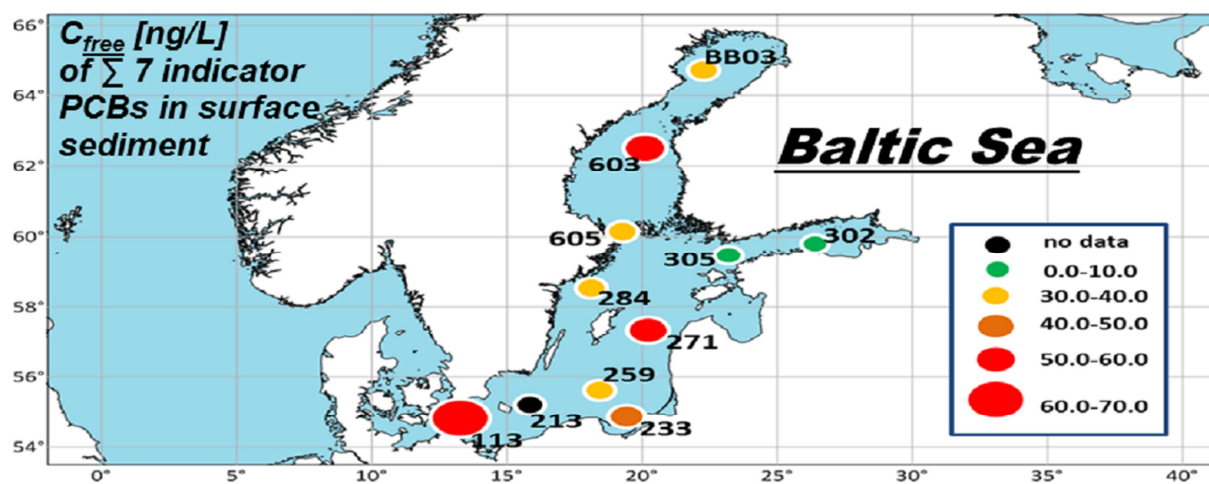
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# 1 **Assessing PCB pollution in the Baltic Sea - an equilibrium** 2 **partitioning based study**

3

## 4 **Authors' names**

5 Susann-Cathrin Lang<sup>1,2,‡,\*</sup>, Philipp Mayer<sup>3</sup>, Andrew Hursthouse<sup>2</sup>, Danijela Kötke<sup>4</sup>, Ines  
6 Hand<sup>5</sup>, Detlef Schulz-Bull<sup>5</sup>, Gesine Witt<sup>1,‡</sup>

7

## 8 **Authors' addresses**

9 <sup>1</sup> University of Applied Sciences Hamburg, Department of Environmental Engineering,  
10 Ulmenliet 20, 21033 Hamburg, Germany

11 <sup>2</sup> Institute of Biomedical and Environmental Health Research, School of Science & Sport,  
12 University of the West of Scotland, Paisley Campus, Paisley PA 1 2BE, United Kingdom

13 <sup>3</sup> Technical University of Denmark, Department of Environmental Engineering, 2800  
14 Kongens Lyngby, Denmark

15 <sup>4</sup> Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Institute of  
16 Coastal Research, Max-Planck-Strasse 1, 21502 Geesthacht, Germany

17 <sup>5</sup> Leibniz Institute for Baltic Sea Research, Seestraße 15, 18119 Rostock, Germany

18 <sup>‡</sup> Corresponding author

19 <sup>\*</sup> Present address: Agilent Technologies, Hewlett-Packard-Str. 8, 76337 Waldbronn, Germany

20

21

## 22 **Keywords**

23 passive sampling; bioavailability; sediments; PCBs; chemical activity; baseline toxicity

24

25

## 26 **Abstract**

27 Sediment cores and bottom water samples from across the Baltic Sea region were analyzed  
28 for freely dissolved concentrations ( $C_{\text{free}}$ ), total sediment concentrations ( $C_{\text{T}}$ ) and the  
29 dissolved aqueous fraction in water of seven indicator PCBs. Ex-situ equilibrium sampling of  
30 sediment samples was conducted with polydimethylsiloxane (PDMS) coated glass fibers that  
31 were analyzed by automated thermal desorption GC-MS, which yielded PCB concentrations  
32 in the fiber coating ( $C_{\text{PDMS}}$ ). Measurements of  $C_{\text{PDMS}}$  and  $C_{\text{T}}$  were then applied to determine  
33 (i) spatially resolved freely dissolved PCB concentrations; (ii) baseline toxicity potential  
34 based on chemical activities (a); (iii) site specific mixture compositions; (iv) diffusion  
35 gradients at the sediment water interface and within the sediment cores; and (vi) site specific  
36 distribution ratios ( $K_{\text{D}}$ ). The contamination levels were low in the Gulf of Finland and  
37 moderate to elevated in the Baltic Proper, with the highest levels observed in the western  
38 Baltic Sea. The SPME method has been demonstrated to be an appropriate and sensitive tool  
39 for area surveys presenting new opportunities to study the in-situ distribution and  
40 thermodynamics of hydrophobic organic chemicals at trace levels in marine environments.

41

## 42 **Introduction**

43 The Baltic Sea as a shallow semi-enclosed sea is connected to the open ocean through the  
44 North Sea. The mean residence time of the sea water is between 25 and 40 years  
45 (Rheinheimer, 1996). This facilitates the accumulation of pollutants in the Baltic Sea, because  
46 only 2-3% of the contaminants entering can flow out through the North Sea (Brügmann,  
47 1993). Large parts of the catchment area are industrialised or in agricultural use. The coastal  
48 zone of the southern Baltic Sea is strongly influenced by anthropogenic inputs derived from  
49 industry, agriculture, tourism and shipping (Blanz et al., 1999). In addition, atmospheric

50 deposition from the catchment area and non-Europe countries, due to long-range transport of  
51 pollutants in air, seriously reinforces the level of contamination of the Sea. Kot-Wasik et al.,  
52 (2004), reported that in the middle of the 1980s approximately 30 000 t a<sup>-1</sup> of chlorinated  
53 organic compounds were discharged into the Baltic Sea from pulp mills. HELCOM identified  
54 162 hot-spots in the Baltic Sea region (1992), with 110 being removed to date. However, their  
55 past pollution load was often buried in soils or sediments and has not yet disappeared from the  
56 ecosystem (HELCOM, 2010).

57 The environmental sensitivity and the strong anthropogenic pressures of the region have been  
58 recognized by the littoral states for many decades (Janßen et al., 2013). In response, the  
59 European Union Marine Strategy Framework Directive (MSFD) aims to establish effective  
60 protection of the EU's marine waters by putting in place a common framework for marine  
61 policy. The main objective of the MSFD is to achieve or maintain a good environmental  
62 status (GES) of the EU's marine waters by 2020, which corresponds closely to the declared  
63 aims of the HELCOM Baltic Sea Action Plan (Ahtiainen et al., 2013). Since 1990, the main  
64 goal of HELCOM has been to re-establish ecological equilibrium conditions. The general  
65 situation is that, HELCOM identified decreasing contamination trends for a variety of  
66 compounds, but with residual accumulation still present (Liehr, 2006). The Baltic Sea Action  
67 Plan was adopted by the coastal countries and the European Community in November 2007;  
68 as a regional intergovernmental program, it introduces measures to protect and manage the  
69 marine environment based on the Ecosystem Approach. Thus, ecological objectives are used  
70 to define indicators and targets, effect-based nutrient input and monitor implementations  
71 (Backer et al., 2010).

72 Polychlorinated biphenyls (PCBs) are ubiquitous anthropogenic contaminants. They are  
73 widely distributed in the environment through, for example, inappropriate handling of waste  
74 material or leakage from transformers, condensers and hydraulic systems (HELCOM, 2013).  
75 They are still emitted into the atmosphere via vaporization and open burning of products

76 containing PCBs (U.S.EPA, 2007) due to their production and application worldwide. Even  
77 though PCB manufacture was banned in the 1980s (U.S.EPA, 2014), their release into the  
78 environment is still a challenge. PCB concentrations decline only very slowly in soils and  
79 sediments due to their high persistency and high sorption to the soil and sediment matrix  
80 (Rein et al, 2007). Once accumulated mainly in the lipid-rich tissue of organisms, PCBs have  
81 been shown to cause cancer and several serious non-cancer health effects (U.S. EPA, 2007).  
82 For that reason, PCBs are defined as priority pollutants by the U.S. EPA (U.S. EPA, 2012)  
83 and are included in the 2002 by OSPAR adopted list of chemicals for priority action (OSPAR,  
84 2013).

85 Assessments of HOCs and their risks have traditionally been based on total concentrations of  
86 contaminants in the sediment, which are poorly related to the bioavailability and toxicity of  
87 these pollutants (Mayer et al., 2014). Potential risks of adverse biological effects from  
88 sediment associated contaminants are better related to concentrations of freely dissolved  
89 chemicals in the sediment porewater (effective concentrations) (Mayer et al., 2014). Today it  
90 is known that the contaminant's total amount in the sediment is not a suitable measure since it  
91 addresses neither of the two aspects of bioavailability defined by Reichenberg and Mayer  
92 (2006): (1) Accessibility: The quantity of the contaminant in the system which can be made  
93 available for an organism (i.e. the fraction which is not "trapped" in the environmental  
94 matrix). (2) Chemical activity/fugacity: The contaminant's thermodynamic potential for  
95 spontaneous physicochemical processes such as partitioning between different compartments  
96 in an environmental system, including partitioning into biological tissues (bioaccumulation).

97 It has been shown that measurements of  $C_{free}$ , rather than their estimations using generic  $K_d$   
98 values, can significantly improve the prediction of bioaccumulation (You, Landrum and  
99 Lydy, 2006; Mayer et al, 2014). Kraaij et al. (2003) predicted for instance internal  
100 concentrations of a few model HOCs in Tubificidae (benthic oligochaetes) as product of  $C_{free}$   
101 and bioconcentration factors. The strong agreement with measured biota concentrations

102 confirmed that bioaccumulation was the result of partitioning (not excluding oral uptake as an  
103 exposure route).

104 The measurement of  $C_{\text{free}}$  or chemical activity ( $a$ ) gives direct information about the direction  
105 of the diffusive mass transfer, which always takes place from areas of high to low  $C_{\text{free}}$   
106 concentration and chemical activity (Reichenberg and Mayer, 2006). Chemical activities in  
107 environmental media can be calculated by dividing  $C_{\text{free}}$  of a sparingly soluble compound in  
108 water by its respective subcooled liquid solubility ( $S_L$ ) (Schwarzenbach et al., 2003).

109 A number of studies have been carried out to investigate PCB sediment concentrations.  
110 Nevertheless, studies are mostly restricted to specific regions in the Baltic Sea and only a few  
111 studies have been investigating freely dissolved concentrations of PCBs in sediment pore-  
112 waters applying different types of passive sampling techniques (e.g. Cornelissen et al, 2008;  
113 Jahnke et al., 2012). The major advantages of passive sampling over “classical methods” are  
114 the simple sample preparation and considerably low detection limits especially regarding the  
115 highly hydrophobic substances that are enriched from water to polymer by 3-7 orders of  
116 magnitude. Passive sampling techniques are environmentally “green”, i.e. they are time and  
117 cost efficient and less resource lavish.

118 The aim of this study was to comprehensively investigate exposure, fate, partitioning,  
119 bioavailability, and baseline toxicity of selected PCBs. The study also makes substantial  
120 contribution to the assessment of sediment characteristics in terms of providing the first large-  
121 scale investigation of seven PCBs using an equilibrium sampling approach in Baltic Sea  
122 sediments. We identified (i) large scale horizontal gradients of  $C_{\text{free}}$  and chemical activity; (ii)  
123 gradients of diffusion within sediment cores as well as at the sediment-water interface; (iii)  
124 site specific distribution ratios ( $K_D$ ) and (iv) the baseline toxic potential. The approach used in  
125 this study provides a novel strategy to assess HOC contaminated sediments. It extends  
126 conventional approaches and techniques currently applied and delivers distinct insights in  
127 comparison to results obtained with classical analytical methods.



128

## 129 **Experimental section**

### 130 **Sampling**

131 Baltic Sea sediment cores were sampled in June and July 2008 during a cruise on the research  
132 vessel “Maria S. Merian”. The cores were obtained using a sediment multi corer and cut into  
133 2 cm thick slices on board. The samples were homogenized and aliquots were stored at -18 °C  
134 in pre-cleaned aluminum boxes and polyethylene (PE) containers until they could be  
135 analyzed. A total core with a length of 20 cm was sampled from eleven stations. Bottom water  
136 was sampled with the Kiel in-situ pump system (KISP, Aimes, Kiel, Germany) described by  
137 Petrick et al. (1996). KISP was fixed on a wire and lowered to preselected depth. After six  
138 hours of sampling approximately 360 L was processed and HOCs collected onto a XAD-2  
139 resin column. The loaded column was stored cool and dark until analysis. (For further  
140 information of the sampling procedure please refer to text S6 (SI)). Hydrographical-chemical  
141 parameters were obtained with a CTD rosette. A map showing the sampling locations is given  
142 in figure S1 (SI). Details, geographical positions and sampling depth of the stations are  
143 presented in SI, table S1.

144

### 145 **Chemicals and other materials**

146 A list of all materials and chemicals used as well as a description for treatment of glassware,  
147 solvents and other materials are given in text S1 (SI) and S2 (SI), respectively.

148

### 149 **Bulk sediment analyses**

150 The water content and the total organic carbon content (TOC) were determined for all  
151 sediment samples. In addition, black carbon (ROC) was measured for surface sediments. Text  
152 S3 (SI) describes the procedures.

153

**154 Chemical analyses of sediment and bottom water**

155 The sediment samples were analyzed for freely dissolved and total PCB sediment  
156 concentrations ( $C_T$ ) using equilibrium sampling and exhaustive extractions to yield  
157 concentrations for the seven indicator PCBs (PCB 28, 52, 101, 118, 138, 153 and 180). Figure  
158 1 presents the analytical procedure of sediment processing as a flow chart.

159 Solid phase micro-extraction (matrix-SPME) (Witt et al., 2009) was carried out to determine  
160 sediment porewater concentrations. The fibers were analyzed with a GC-MS system (7890A  
161 GC, 5975C MSD, Agilent Technologies) equipped with a cold injection system (CIS) for  
162 thermal desorption of the fibers and a GERSTEL Automated Liner EXchange system (ALEX)  
163 for fully automated sample processing. Calculated freely dissolved concentrations were  
164 temperature corrected from 20 °C (laboratory) to 4 °C (field) using the Van't Hoff equation  
165 and actual fiber coating thicknesses were measured with laser scanning confocal technology.  
166 A detailed description of the analytical procedure (SPME experiments, GC-MS analyses,  
167 measurement and calculation of  $C_{free}$  as well as important requirements) is given in the Text  
168 S4 (SI).

169 Total sediment concentrations were determined by application of accelerated solvent  
170 extraction (ASE) to the sediment samples, followed by a SPE (solid phase extraction) clean-  
171 up of the extract and subsequent analyses via GC-MS. The analytical procedure is described  
172 in text S5 (SI).

173 Dissolved bottom water PCB concentrations were analyzed by extracting the loaded XAD-2  
174 columns with solvents, a subsequent clean-up step and measurement of the compounds of  
175 interest with GC-MS. A precise summary of the analytical procedure is presented in text S6  
176 (SI).

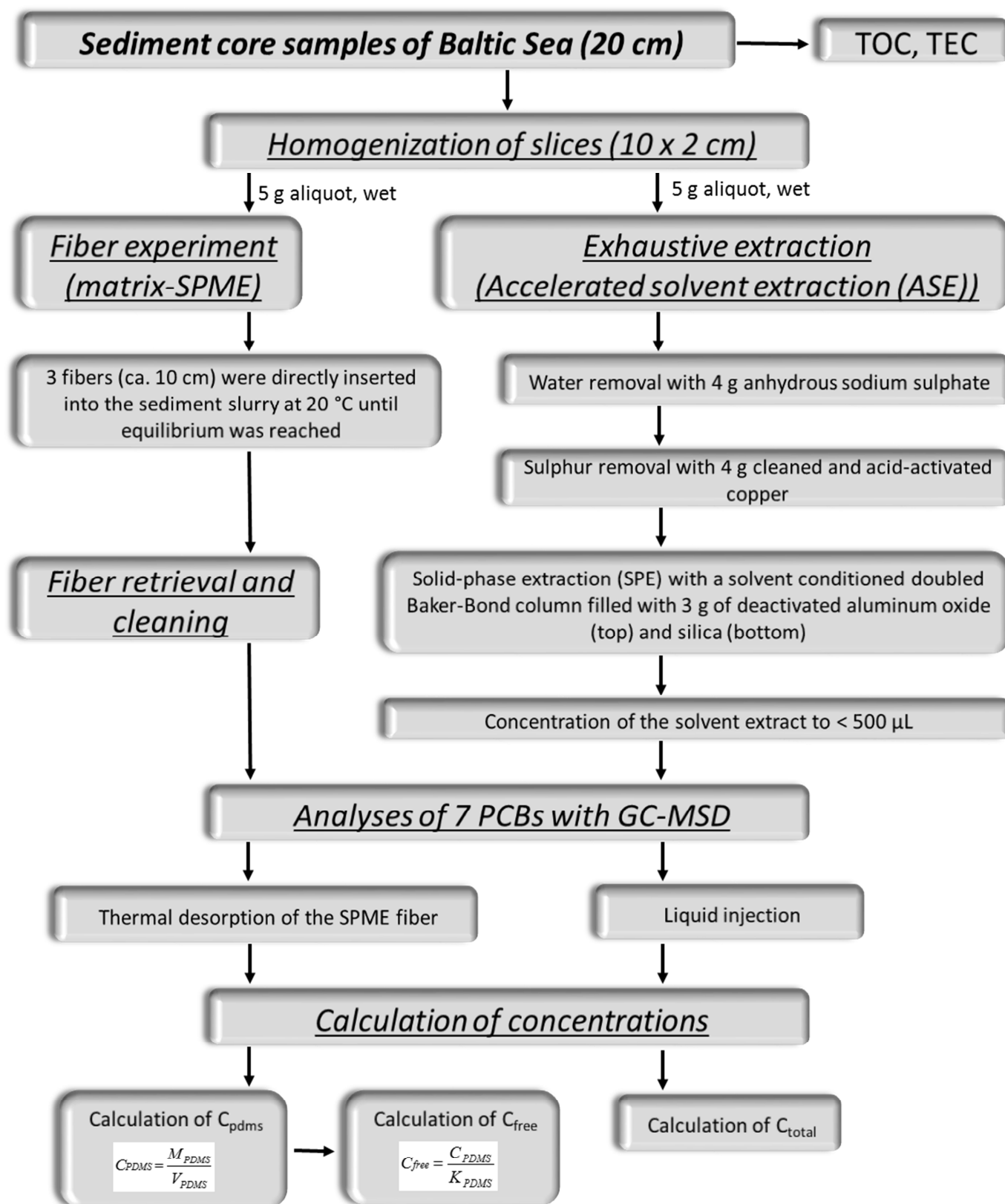
177

**178 Quality control and assurance (QA/QC):**

179 Method validation was performed by assessing measurement precision (10 times replicate of a  
180 standard solution), linearity (multipoint calibration, 3 replicates) and system solvent blanks of  
181 the analytical system. Evaluation of processing blanks, repeatability of the sample processing  
182 procedure (reference material and sample), recovery rates of the analytes (based on internal  
183 standard processing) and accuracy (standard reference sediment) were used to predict final  
184 uncertainty of the analytical results.

185 Precision of the measurement method was determined with  $< 10\%$  for uncorrected and ISTD  
186 (internal standard) corrected area responses for the 7 PCBs. Linear regression of the  
187 calibration curves yielded coefficients of determination ( $R^2$ )  $> 0.990$  and target PCBs were  
188 not detected in solvent blanks.

189 Method detection and quantification limits of the optimized methods (MDLs and MQLs) were  
190 calculated using the average PCB target responses in processing blanks plus 3 times (MDL)  
191 or 10 times (MQL) the standard deviation. MQLs were between 5 and 18  $\text{pg } \mu\text{L}^{-1}$  PDMS for  
192 PCBs. MDLs were lower than 10  $\text{pg } \mu\text{L}^{-1}$  PDMS for all target compounds. Final mean  
193 standard recoveries of internal and external PCB target compounds of standard test solutions  
194 were  $90\% \pm 15\%$ . For an average of eight sediment samples being extracted via ASE one  
195 blank was processed and analyzed simultaneously. Mean standard recoveries of the internal  
196 standard solutions added to each sample were calculated for all target compounds with  $82\% \pm$   
197  $7\%$ . Additionally, the standard reference materials EC-4 as well as QPH 058 and QPH 059  
198 (QUASIMEME, Laboratory Performance Studies, <http://www.quasimeme.org/>) were equally  
199 processed with the samples and checked for recovery. The measured concentrations for the  
200 single compounds were in all cases in the range of certified values ( $\pm$  certified uncertainty).  
201 Finally, the maximum uncertainty of the analytical results was predicted to be  $\pm 30\%$ .



202

203 **Figure 1:** Diagram presenting the steps of the analytical procedure of sediment processing.

204

205 **Results and Discussion**

## 206 **Sediment characteristics**

207 The TOC content of Baltic Sea sediment cores ranged from 1.4% - 11.5% (w/w, dry).  
208 Concomitant with progressive diagenesis at greater sediment depths, i.e. the decomposition of  
209 the sedimentary organic matter under oxic, sub-oxic and anoxic conditions by micro-biota and  
210 its mineralization, a decrease of TOC was observed. Average TOC values from the measured  
211 triplicates for each sampling station and depth are presented in detail in Table S2 (SI).  
212 Besides TOC, black carbon (ROC) is suggested to play a major role in the sorption of  
213 hydrophobic organic contaminants (Jonker and Koelmans, 2002; Lohmann et al., 2005;  
214 Cornelissen et al., 2005; Staniszevska et al., 2011). Depending on the measurement method  
215 and definition the TOC can be interpreted to include the two components ROC and OC  
216 (organic carbon) fraction, i.e.  $OC + ROC = TOC$  (Accardi-Dey and Gschwend, 2002). ROC  
217 contents ranged between 0.043% and 0.225% (w/w, dry) for the sediment layer of 2 - 4 cm  
218 (individual values can be found in the SI). Jahnke et al. (2012) determined the ROC to be  
219 approximately 0.2% in surface sediments of the Stockholm Archipelago after applying the  
220 method of Gustafsson et al. (1997) for soot quantification, which closely corresponds to the  
221 data from the Åland Sea (605) recorded herein.

222

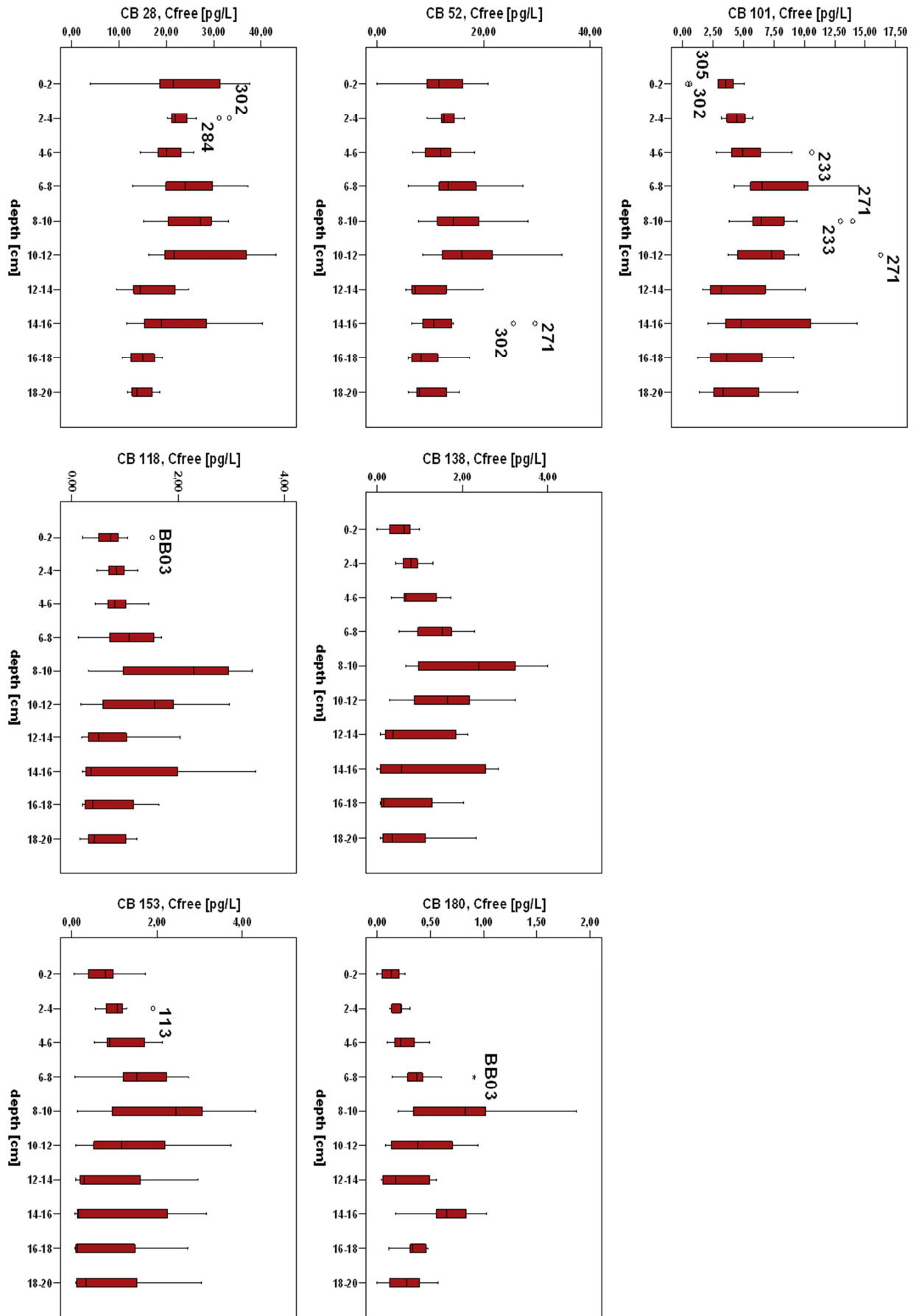
## 223 **Composition of the sum of $C_{free}$ in surface sediments and spatial distribution**

224 The most hydrophobic PCBs (CB 118 - CB 180) yielded very low concentrations compared to  
225 the less hydrophobic PCBs (CB 28 - 101). The PCB distribution pattern was similar among  
226 the sampling stations (see Box-plot, Figure 2). CB 28 and 52 yielded markedly higher  
227 variability of  $C_{free}$  for the sediment depth 0 - 2 cm in contrast to the other PCBs. For CB 118  
228 an outlier was observed at the Bothnian Bay (site BB03). CB 101 concentrations were notably  
229 lower at the Gulf of Finland (site 302 and 305) compared to the other stations. Box-plots of  
230 PCB distribution patterns and therefore  $C_{free}$  concentration ranges for all sediment depths at  
231 the eleven investigation sites are given in figure S2 (SI).

232 Jahnke, et al (2012), studied freely dissolved concentrations in surface sediments along an E-  
233 W transect from central Stockholm towards the outer Stockholm Archipelago (in the region of  
234 site 605 (Åland Sea)) and found decreasing trends in this direction. Their results for 7 PCB  
235 congeners are in good agreement with the data presented in this study. Within congener  
236 concentration variability, in some cases CB 28 and CB 52 were up to 3 - 7 higher in this study  
237 and for CB 101, 118, 153, 138 and 180 up to 10 times higher in their study. The lower  
238 concentrations of the higher chlorinated PCBs at the Åland Sea were consistent with their  
239 decreasing trends towards the open Baltic Sea.

240

241 **Distribution of  $C_{\text{free}}$  in sediment cores**



243 **Figure 2:** Box-plots for the 7 measured PCBs as depth profiles, including the  $C_{\text{free}}$   
244 concentration values [ $\text{pg L}^{-1}$ ] for all sampling stations of the Baltic Sea in each box. Each box  
245 displays the median, the 10-, 25-, 75- and 90-percentile as well as the extreme value (asterisk)  
246 and outlier (circle) for the compound of interest.

247  
248 Figure 2 displays box-plots as depth profiles for the 7 PCBs, including the  $C_{\text{free}}$  data for all  
249 Baltic Sea sampling stations in each box. Highly elevated freely dissolved PCB  
250 concentrations were mainly found in deeper sediment layers (8 - 16 cm). Since PCB  
251 manufacture was banned around the 1980s, a rapidly decreasing environmental concentration  
252 could be expected to be reflected in the upper sediment layers by lower concentrations. Even  
253 though their release in the environment is on-going through burning of PCB containing  
254 products and strong environmental persistence. In most cases PCBs were not elevated in the  
255 upper sediment layers. However, increasing concentration levels towards the upper sediment  
256 layers were observed for PCBs in the northern Baltic Sea. A clear increase was observed for  
257 station 603 (Bothnian Sea), whereas slightly elevated  $C_{\text{free}}$  levels were found at the Bothnian  
258 Bay (BB03) for CB 101 and CB 118. Individual depth profiles for the sediment cores and  
259 measured PCBs are displayed in figure S3 (SI).

### 261 **Baseline toxicity**

262 The sum of chemical activities, calculated from the single  $C_{\text{free}}$  values of the individual  
263 compounds is an indicator of the baseline toxic potential of a mixture (Di Toro et al., 2000).  
264 Baseline toxicity, also referred to as narcosis, is the minimal toxicity a single compound can  
265 cause when crossing membranes (Escher and Schwarzenbach, 2002). Mixtures can include  
266 thousands of individual compounds and even if all these compounds are below the threshold  
267 level of specific toxicity, the underlying cumulative baseline toxicity might determine the  
268 overall toxic effect (Escher et al., 2002).



269 In this study baseline toxicity or rather the contribution to the baseline toxicity potential of a  
270 mixture was evaluated for the sum of seven PCBs. The PCB mixture showed moderate  
271 variations between the sites and was below lethality in any case. In most cases the  
272 contribution of the sum of PCBs to the baseline toxic potential was approximately a factor of  
273 thousand below the effective activity range (EA50, between 0.01 and 0.1). At this chemical  
274 activity range baseline toxicity is lethal (Reichenberg and Mayer, 2006).

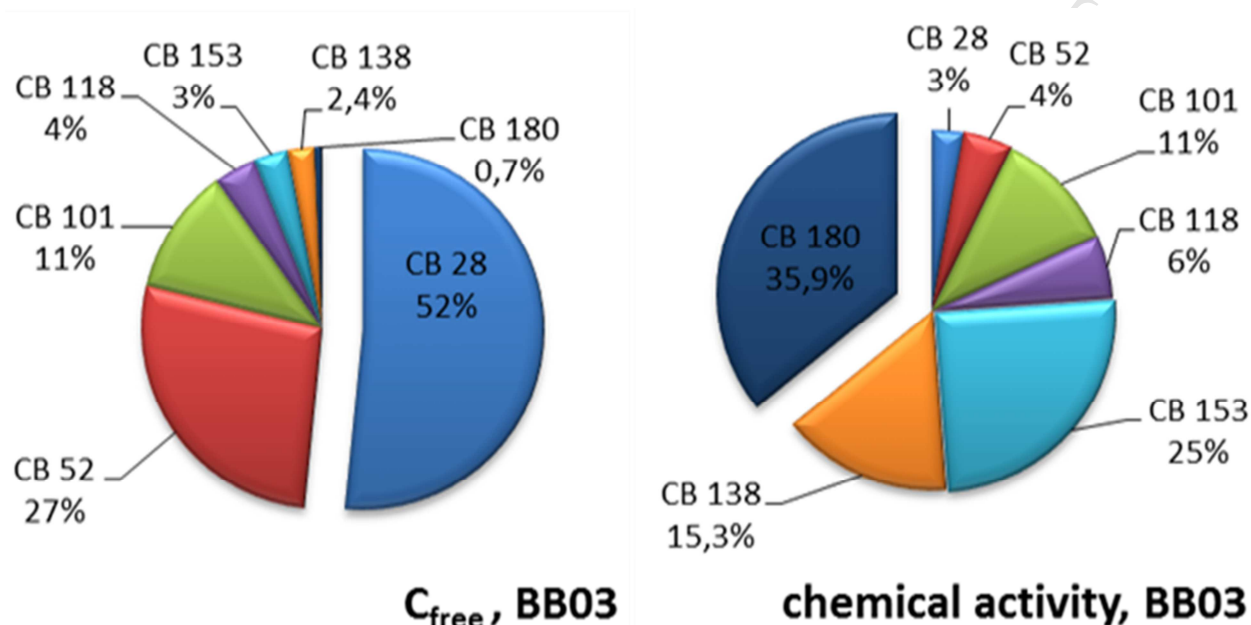
275 Values for the sum of chemical activities (seven PCBs) for all sediment depths at the  
276 sampling stations and the mean, maximum and minimum value for each station are presented  
277 in table 3 (SI). Within the sediment cores the highest chemical activities were mostly found in  
278 the middle or deeper sediment layers, suggesting that an organism experiences lower  
279 exposure from PCBs in surface sediment layers. Depth profiles of the sum of chemical  
280 activities of the seven PCBs for all sampling stations can be found in figure S4 (SI).

281

### 282 **Comparison of the composition of $C_{\text{free}}$ and chemical activity**

283 A comparison of the variation in molecular composition of the 7 PCBs as a percentage of  $C_{\text{free}}$   
284 and chemical activity for station BB03 at a sediment depth of 0 - 2 cm is given in Figure 3.  
285 Although the percentage composition of  $C_{\text{free}}$  and chemical activity varied moderately  
286 between the sampling stations, the general distribution of the PCBs was consistent for a depth  
287 of 0 - 2 cm. Lower chlorinated PCBs had only a minimal contribution to the chemical activity  
288 and therefore to baseline toxicity. In contrast, higher chlorinated PCBs which contributed less  
289 to  $C_{\text{free}}$ , predominated the contribution to the overall exposure when expressed as chemical  
290 activity. This example clearly demonstrates the relevance of not only freely dissolved  
291 concentrations, but also on the properties of a single compound when assessing baseline  
292 toxicity from chemical activities of a contaminant mixture. Thus, the baseline toxicity of PCB  
293 mixtures is not only controlled by the concentration but also by the properties and  
294 characteristics of the individual compounds. In this context, it is relevant to be mentioned,

295 that freely dissolved PCBs concentrations were found to be 2 - 3 orders of magnitude lower  
 296 than PAHs concentrations (Lang et al., 2015). Nevertheless, the sum of chemical activities  
 297 and hence the contribution to the baseline toxic potential was only one order of magnitude  
 298 lower for PCBs compared to PAHs.



299  
 300 **Figure 3:** Comparison between the contributions of 7 individual PCBs to  $C_{free}$  and chemical  
 301 activity in percentage for the surface sediment layer (0 - 2 cm) at site BB03 (Bothnian Bay,  
 302 Baltic Sea).

303

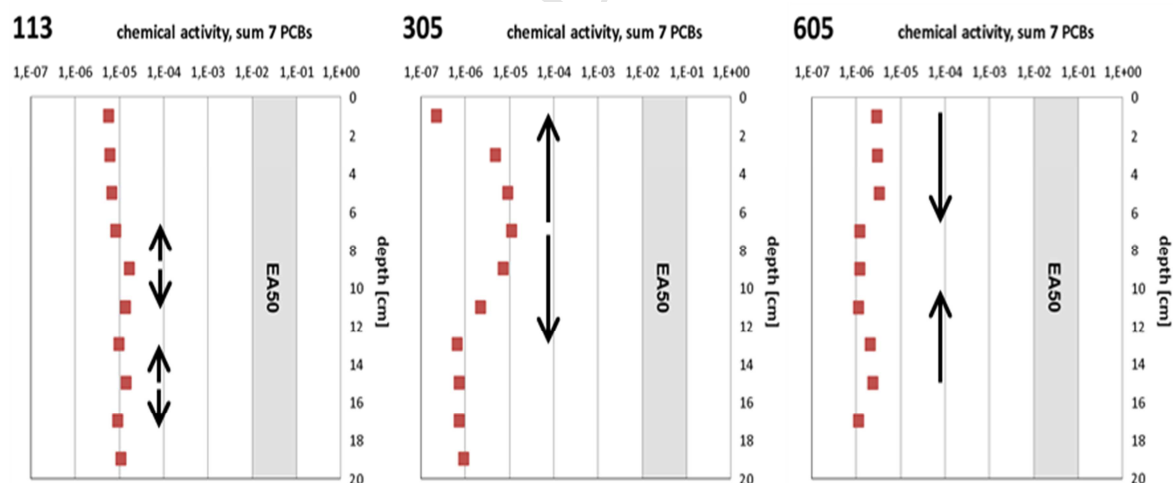
### 304 Diffusion gradients

305 An indicator for diffusive mass transfer of contaminants is also the chemical activity  
 306 (Reichenberg and Mayer, 2006). Diffusion always takes place from high to low chemical  
 307 activity. Diffusion gradients, i.e. the direction of contaminant mass transfer in the sediment  
 308 can be seen in the vertical profiles of the chemical activities. In addition, the diffuse mass  
 309 transfer at the sediment water interface was investigated for PCBs to address the question  
 310 whether the Baltic Sea sediments act as diffusive source or as diffusive sink to the water  
 311 column.

312 Figure 4 displays the activity profiles of the sum of seven PCBs for site 113 (Arkona Sea),  
 313 305 (Gulf of Finland) and 605 (Åland Sea). The black arrows indicate the direction of  
 314 contaminant diffusion within the depth profile from high to low chemical activity. PCB  
 315 activity profiles for the other stations without indicative arrows are given in figure S4 (SI) and  
 316 individual values in table S3 (SI).

317 Station 113 represents a profile determined by a low range of chemical activities over the  
 318 entire depth and therefore low diffusion gradients. Site 305 (Gulf of Finland) showed a  
 319 maximum chemical activity at a sediment layer of 6 - 8 cm and a diffusion trend towards the  
 320 upper and deeper sediment layers. Site 605, represents a diffusion pattern directed to mid  
 321 sediment layers and was not observed at any other site. Profiles with low variations in  
 322 chemical activities were also found for stations 213, 233 and 259. All other stations revealed a  
 323 clearly identifiable maximum in middle up to deeper sediment layers with a varying diffusion  
 324 trend towards upper and deeper sediment layers.

325



326

327 **Figure 4:** Vertical profiles of the sum of chemical activities for three Baltic Sea sampling  
 328 sites (113, 305 and 605) calculated from seven PCBs for each depth. Small and large black  
 329 arrows indicate small-scale and overall diffusion trends, respectively.

330

331 **Sediment to water activity ratios:** Chemical activities of sediment porewater (surface layer,  
332 0 - 2 cm depth) were plotted against chemical activities of the bottom water for PCBs (figure  
333 S5 (SI)). Calculated activity ratios ( $a_{PW}/a_{BW}$ ) between sediment porewater (PW) and bottom  
334 water (BW) indicate whether sediments act as diffuse source or sink. The grey line in the  
335 diagrams indicates similar activities ( $a_{PW}/a_{BW} = 1$ ) in sediment porewater and bottom water,  
336 which implies a similar energetic state between these compartments where no spontaneous  
337 diffusion processes occur. A ratio of  $a_{PW}/a_{BW} > 1$  suggests that the sediment acts as a source  
338 of PCBs to the water body, while a ratio of  $a_{PW}/a_{BW} < 1$  suggests that the sediment acts as a  
339 sink.

340 In a few cases the chemical activities of the 7 PCBs were almost equal (thermodynamic  
341 equilibrium,  $a_{PW}/a_{BW} = 1$ ) or lower (disequilibrium,  $a_{PW}/a_{BW} < 1$ ) in the sediment compared to  
342 the chemical activities in the bottom water. Exceptional diffusive flux, directed from water to  
343 sediment ( $a_{PW}/a_{BW}$ : 0.26 - 1.04) were found at site 302 and 305 (Gulf of Finland) for CB 118,  
344 CB 138 and CB 153 and at station 284 (Western Gotland Sea) for CB 180 and the sediment  
345 was assumed to act as a sink. In all other cases the ratios were:  $a_{PW}/a_{BW} > 1$ , which implies the  
346 sediment to act as a diffuse source for PCBs. Calculated chemical activity ratios of sediment  
347 porewater to bottom water ( $a_{PW}/a_{BW}$ ) for the seven different PCBs at the 11 sampling stations  
348 are given in table S4 (SI).

349 In a previous study (Cornelissen et al., 2008), mean  $a_{PW}/a_{BW}$  ratios close to one were  
350 calculated for 14 PCBs at five locations in the open northern Baltic Sea region. They  
351 concluded equilibrium conditions between sediment porewater and overlying water in the  
352 open Baltic Sea, which implies no overall diffusive flux of PCBs. Further, Jahnke et al  
353 reported higher chemical activities of PCBs in lake and Baltic Sea sediment compared to biota  
354 and water (Jahnke et al, 2012; Jahnke et al, ES&T 2014; Jahnke et al, ESPI 2014 ).

355

356 **Site specific distribution ratios ( $K_D$ )**

357 It is also known that black carbon (ROC, a part of the TOC) – like organic carbon - is an  
358 important sorbent for PCBs in the Baltic Sea (Gustafsson et al., 1997; Gustafsson et al., 2001;  
359 Cornelissen and Gustafsson, 2005b). ROC was measured in addition to TOC, to investigate its  
360 impact on the sorption behavior of the compounds in Baltic Sea sediments. An assessment of  
361 correlation between  $K_D$  values ( $= C_T/C_{free}$  [L Kg<sup>-1</sup> dw]) and ROC as well as TOC yielded  
362 positive results. The  $K_D$  values were plotted against TOC and ROC and regional differences  
363 of the sorption capacity and sorptive strength of the sediments were identified.  $K_D$  values and  
364 plots of  $K_D$  against TOC and ROC for individual PCBs can be found in table S5 (SI) and in  
365 figure S7 (SI), respectively.

366 A strong correlation with TOC was found for all PCBs in the northern Baltic Sea region ( $R^2$ :  
367 0.84 - 0.94). In contrast, a moderate correlation with ROC was observed ( $R^2$ : 0.46 - 0.82) for  
368 this region. The correlation with ROC was also lower and inverse compared to TOC,  
369 suggesting that the major sorbent for PCBs is TOC in the northern Baltic Sea region. Jahnke  
370 et al. (2012) confirmed TOC as the major sorbent for PCBs in the Stockholm harbor and  
371 Archipelago, with  $R^2$  values between 0.49 - 0.70 for six PCBs. Compared to the northern  
372 Baltic Sea region, the southern Baltic Sea region yielded low to moderate correlation  
373 coefficients between  $K_D$  values and both TOC and ROC. The  $R^2$  values between TOC and  $K_D$   
374 ranged from 0.05 - 0.89, but with CB 101, 138 and 180 showing  $R^2$  values  $< 0.1$  and CB 28,  
375 52, 118, 153  $R^2$  values between 0.52 and 0.89. In contrast,  $R^2$  values for ROC and  $K_D$  ranged  
376 between 0.004 - 0.74, with CB 28, 52 and 118 showing  $R^2$  values  $< 0.22$  and CB 101, 138,  
377 153, 180  $R^2$  values between 0.61 and 0.74. For this region, the correlation with ROC was also  
378 inverse, but reverse of that in the northern Baltic Sea region. The results for the southern  
379 Baltic Sea region suggest a compound dependent sorption to ROC and TOC. CB 28, 52, 118  
380 and 153 are more likely associated with TOC and CB 101, 138, 153 and 180 are more closely  
381 associated with ROC, while CB 153 showed similar  $R^2$  values with TOC and ROC. In the  
382 case of PCBs, station 271 (Gotland Deep) did not associate with any regional trends. With

383 very high TOC content (11.1%) and the highest  $K_D$  values across all sites it remained  
384 exceptional.

385 An earlier study presented by Konat and Kowalewska (2001) showed trends and fate of PCBs  
386 in sediments of the southern Baltic, identifying main sources of contamination as floods and  
387 heavy rains washing these compounds from land to the sea, while PCB pollution is not  
388 directly attributable to specific human activity. Further they concluded that algae and algal  
389 detritus play an important role in the transport and distribution of PCBs in the southern Baltic,  
390 because of high correlation of PCBs with chlorophyll as derivatives. The northern Baltic Sea  
391 region in contrast, was directly influenced by industrial PCB discharge, before hot spots in  
392 this area were controlled (HELCOM, 2012 and 2013).

393 In a PCB survey of the U.S. EPA (2007) difference between urban and rural atmospheric  
394 pollution by PCBs was observed. The higher chlorinated PCBs, typically associated with the  
395 particle phase, were found at higher concentration in urban sites, whereas at rural sites, the  
396 PCB mixture had more PCB congeners with lower chlorination, typically associated with the  
397 gas phase. The distinct origin and input of PCBs between the two regions may explain the  
398 differences in sorption behaviour to TOC and ROC in general, whereas the northern Baltic  
399 Sea region could be described as dominated by rural inputs in contrast to the urban and  
400 industrial influenced southern Baltic Sea.

401  
402 A plot of  $K_D$  against  $K_{OW}$  (Figure S6 (SI)) gives evidence of higher sorption strength of the  
403 sediments in the western Baltic Sea and Baltic Proper compared to the Gulf of Finland and  
404 northern Baltic Sea. The sediments of the Gotland Deep (station 271) have highest sorption  
405 strength for PCBs compared to all other sites. At the northern Baltic Sea region, highest  $K_D$   
406 values were observed for station BB03. Compared to site 603 and 605, station BB03 showed  
407 a higher TOC content and sediment concentrations, while  $C_{free}$  was only slightly elevated. In  
408 the Gulf of Finland, station 305 revealed only slightly higher  $K_D$  values than site 302 and

409 freely dissolved concentrations were similar at both sites. However, total sediment  
410 concentrations were approximately double compared to those at site 305, while the TOC  
411 content was nearly half of the one at site 302. Thus, this would suggest that PCBs are more  
412 available for partitioning into the porewater at site 302, while the sorption strength is higher at  
413 site 305. In the southern Baltic Sea region lowest  $K_D$  values were observed at the Gdansk  
414 Deep (233). Compared to site 113, 213 and 259, total sediment concentrations were lowest,  
415 while  $C_{free}$  was similar for all stations indicating lower sorption strength and therefore a  
416 possibly higher bioavailability of the sediment bound PCBs in this region.

417

## 418 **Conclusions**

419 This study provides the first comprehensive dataset on freely dissolved concentrations and  
420 contaminant chemical activities of PCBs in Baltic Sea sediments. The SPME ALEX GC-MS  
421 method used for this basin-scale investigation proved to be a suitable and efficient tool to  
422 measure  $C_{free}$ . The method is straightforward provided some application conditions are  
423 considered. Measurements of  $C_{free}$  from seven indicator PCBs at the main sedimentation  
424 basins of the Baltic Sea allowed for the investigation of spatial gradients among and within  
425 the sites. Furthermore, the baseline toxic potential was successfully assessed. Highly  
426 hydrophobic substances were characterized by rather low levels for  $C_{free}$  and high levels of  
427 chemical activity. This means that whilst the contribution of such substances to the pool of  
428 freely dissolved molecules is often negligible, their contribution to the baseline toxic potential  
429 may be of high relevance. Moreover, this study clearly shows that  $C_{free}$  and chemical activity  
430 are important exposure parameters for expressing bioavailability and predicting baseline  
431 toxicity and physico-chemical processes like diffusion. The obtained results can be directly  
432 applied within a quantitative thermodynamic exposure assessment framework. On this basis,  
433 the presented results should be considered when assessing environmental risk and remedial  
434 actions. Further investigations should involve other HOCs of concern, such as PCDD/Fs,

435 PBDEs, PAHs and BFRs. It seems especially relevant to estimate and sum-up the contribution  
436 of mixture constituents to the baseline toxicity of complex mixtures, including priority  
437 pollutants as well as other hydrophobic chemicals. Reproducing and linking freely dissolved  
438 concentrations of HOC mixtures measured in the sediment pore-water to aquatic toxicity  
439 testing via passive dosing (Smith et al. 2010a, Smith et al. 2010b, Schmidt et al., 2013) which  
440 ensures constant exposure concentrations in bioassays over time, allows then for an  
441 ecotoxicological assessment under nearly `true` field conditions.

442

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447 campaign.

448

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ACCEPTED MANUSCRIPT

## List of figure captions of the main manuscript:

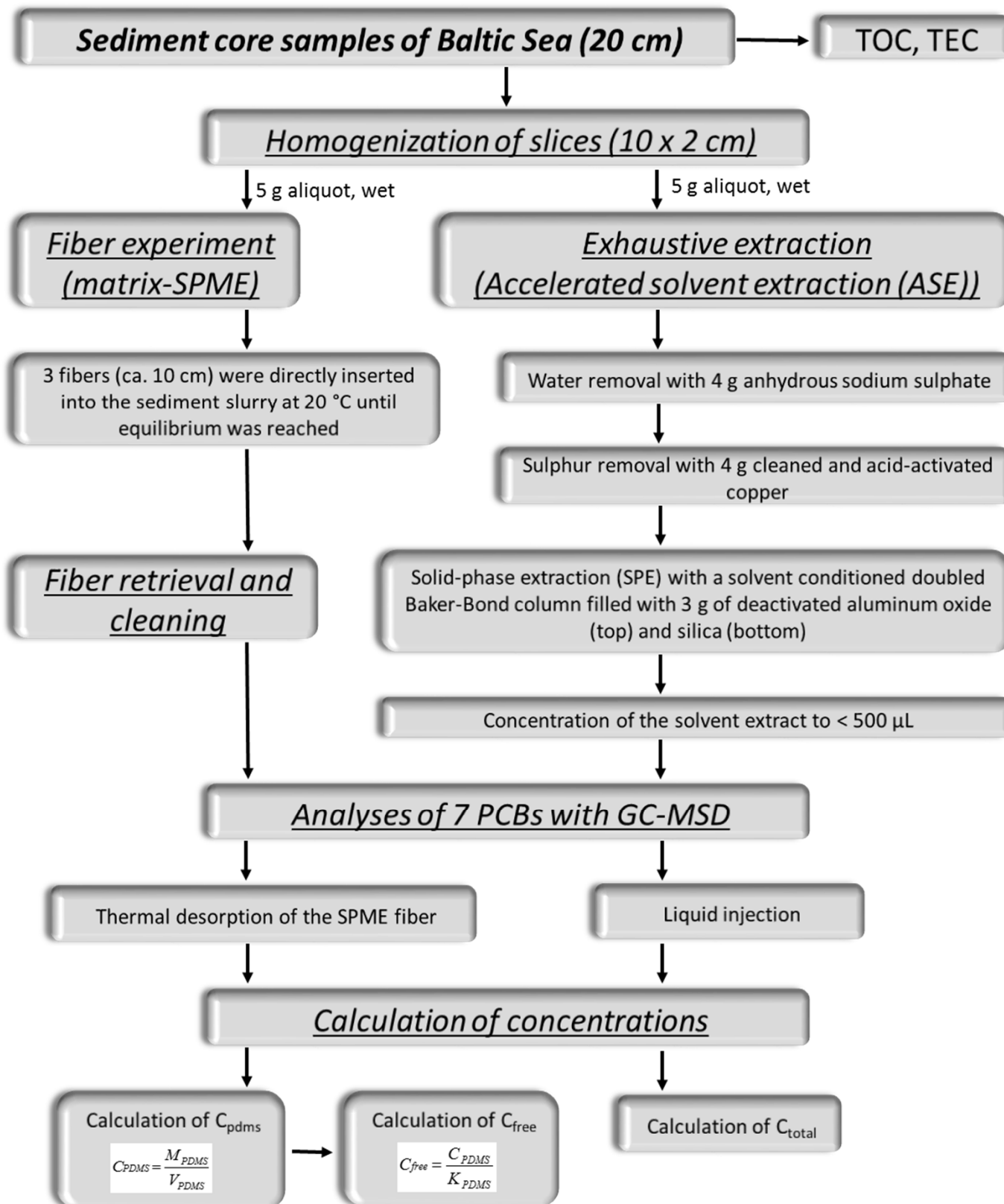
**Figure 1:** Diagram presenting the steps of the analytical procedure of sediment processing.

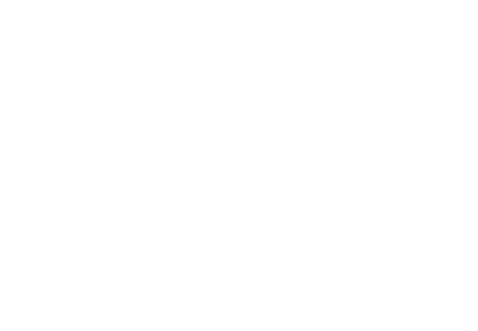
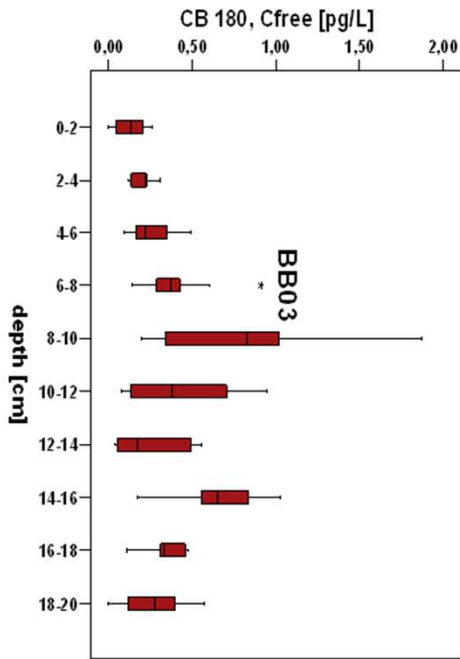
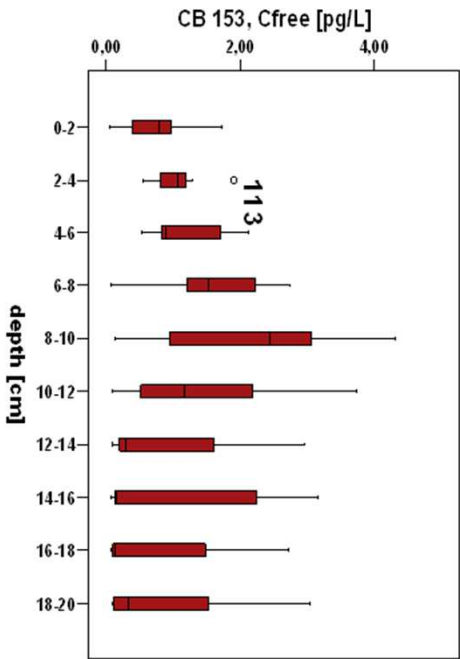
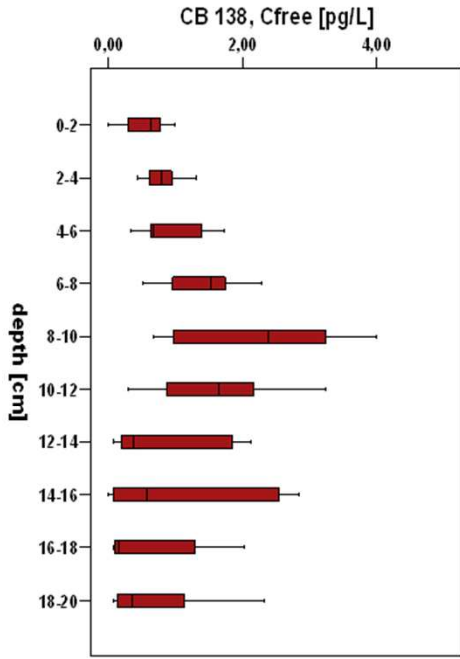
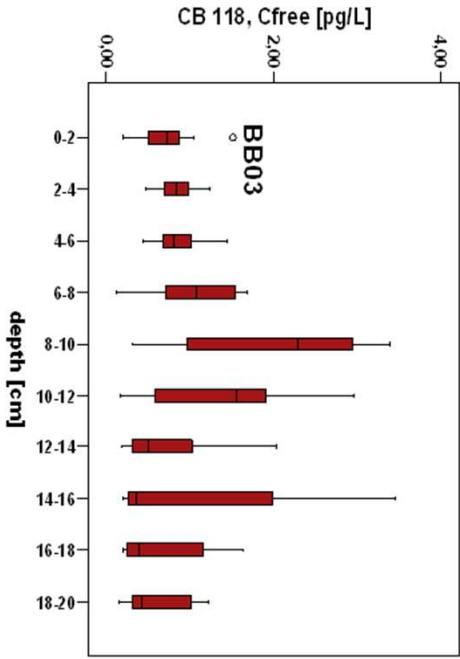
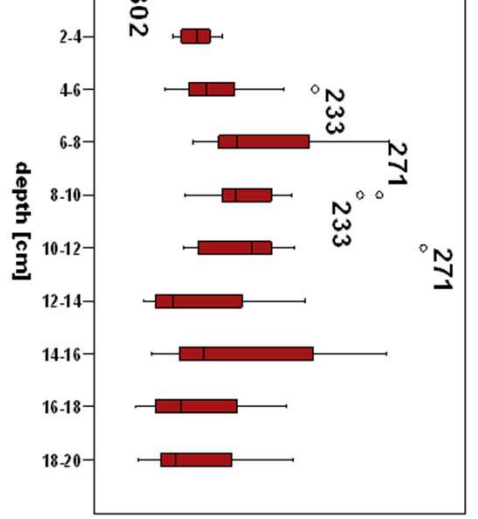
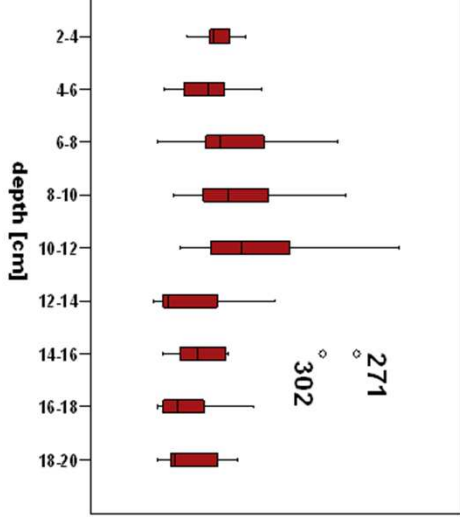
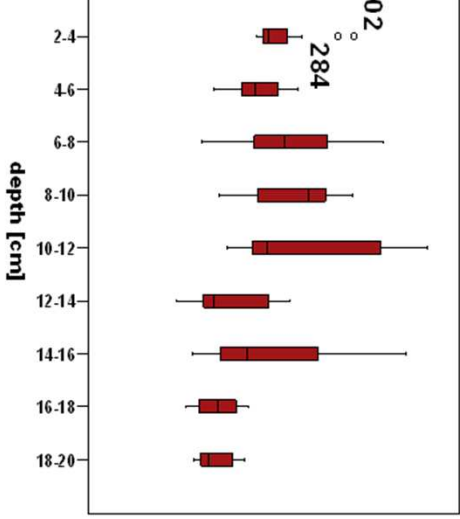
**Figure 2:** Box-plots for the 7 measured PCBs as depth profiles, including the  $C_{\text{free}}$  concentration values [ $\text{pg L}^{-1}$ ] for all sampling stations of the Baltic Sea in each box. Each box displays the median, the 10-, 25-, 75- and 90-percentile as well as the extreme value (asterisk) and outlier (circle) for the compound of interest.

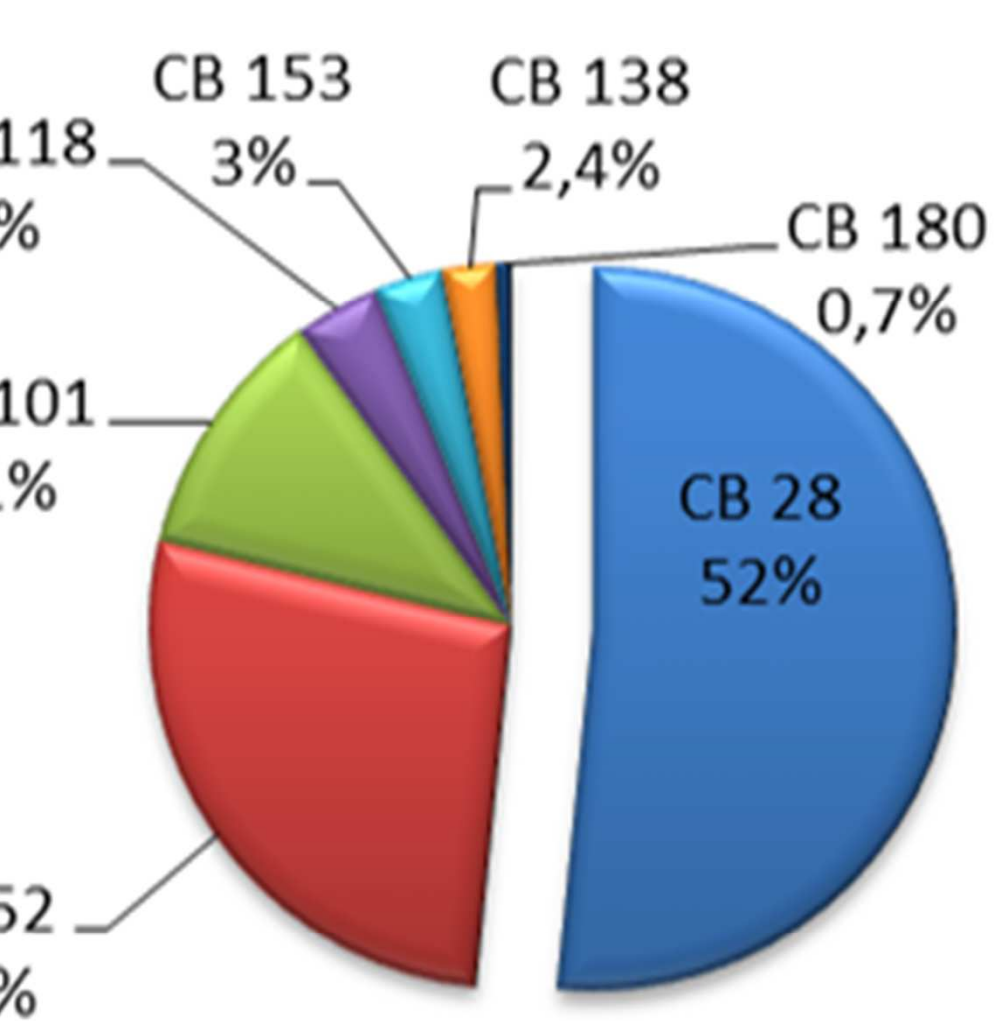
**Figure 3:** Comparison between the contributions of 7 individual PCBs to  $C_{\text{free}}$  and chemical activity in percentage for the surface sediment layer (0 - 2 cm) at site BB03 (Bothnian Bay, Baltic Sea).

**Figure 4:** Vertical profiles of the sum of chemical activities for three Baltic Sea sampling sites (113, 305 and 605) calculated from seven PCBs for each depth. Small and large black arrows indicate small-scale and overall diffusion trends, respectively.

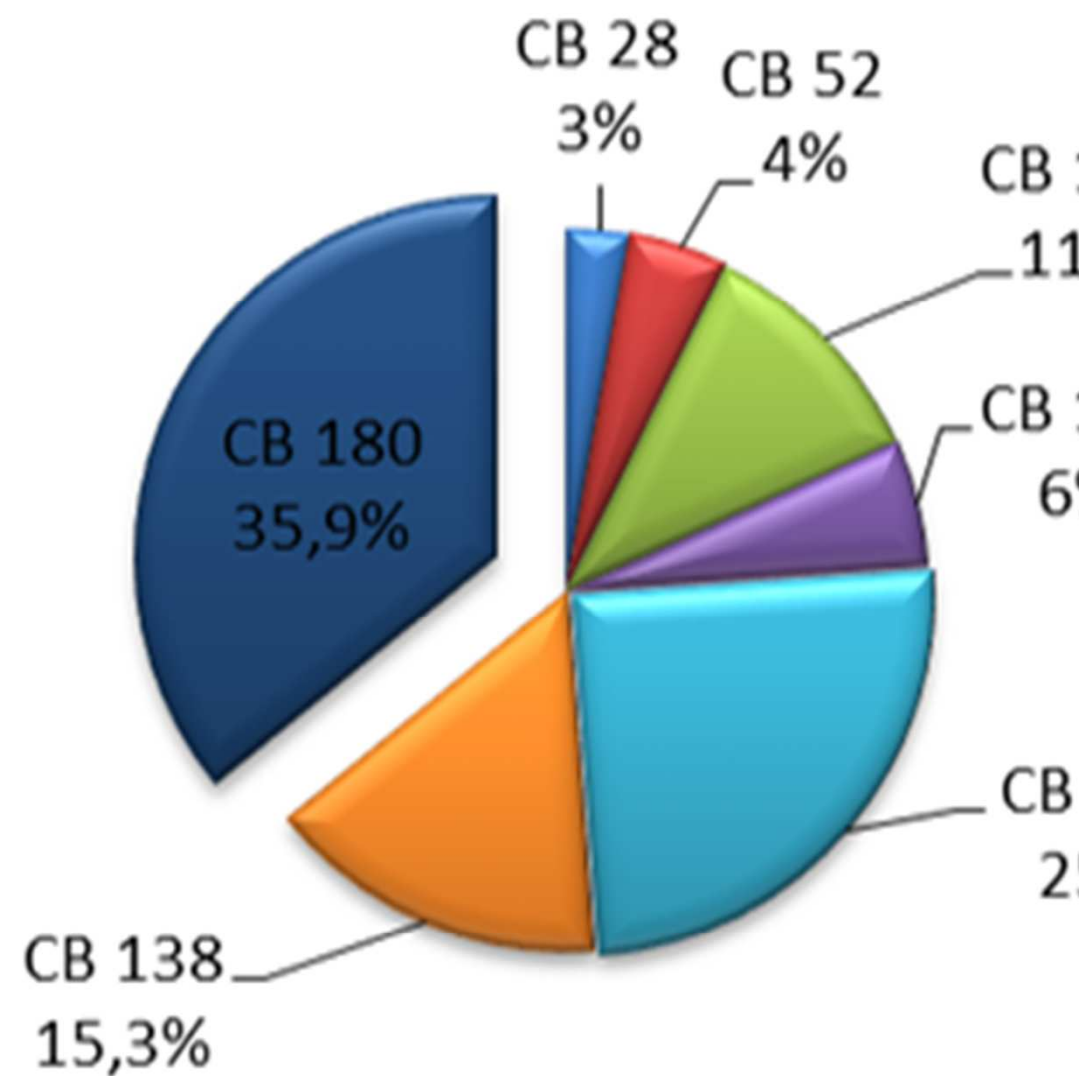






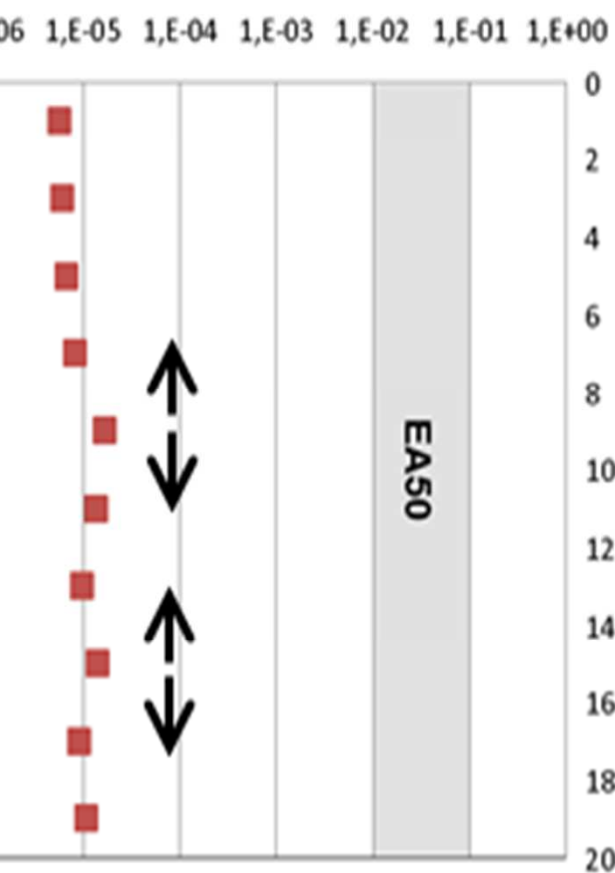


$C_{\text{free}}$ , BB03



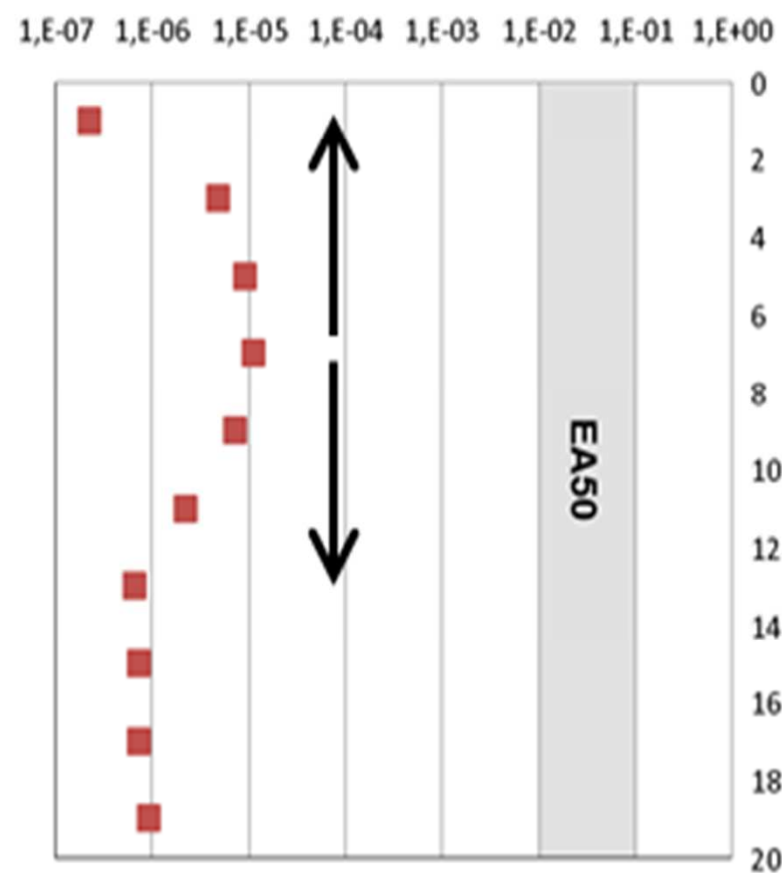
chemical activity, BB03

chemical activity, sum 7 PCBs



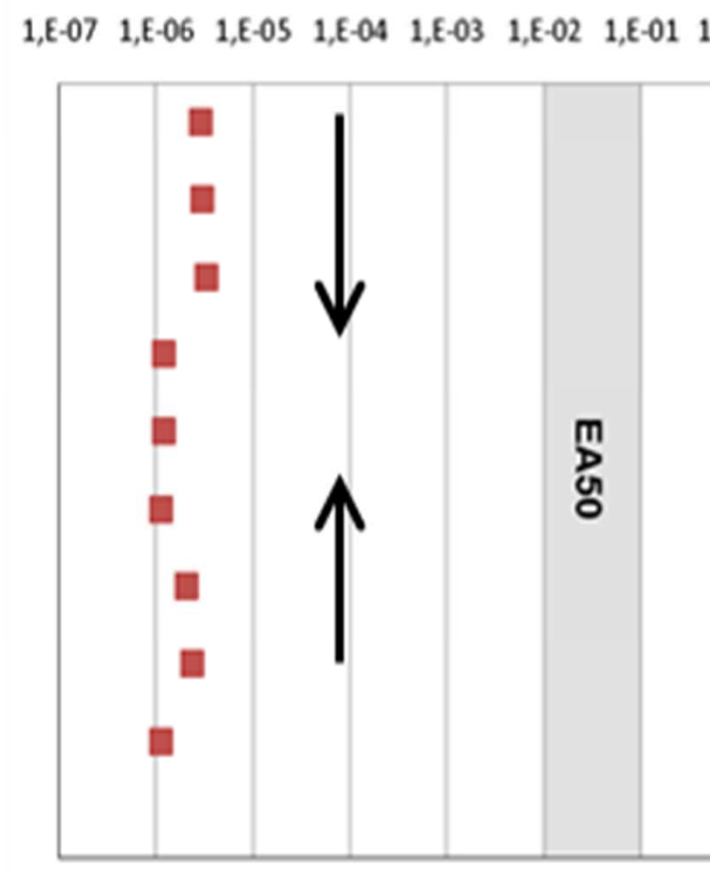
305

chemical activity, sum 7 PCBs



605

chemical activity, sum 7 PCBs



## 1 **Highlights**

- 2 • The baseline toxicity of the PCB mixture was below lethality at all sampling sites
- 3 • Expressed as chemical activity - higher chlorinated PCBs contributed most to
- 4 exposure
- 5 • The sediment was assumed to act as a sink for PCBs in some individual cases
- 6 • Sorption capacity/sorptive strength of sediments for PCBs revealed regional
- 7 differences