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1 **Determination of multi-class polyaromatic compounds in sediments by a simple**  
2 **modified matrix solid phase dispersive extraction**

3

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22

23

24

25 **Abstract**

26 A simple, efficient matrix solid phase dispersive extraction (MSPD) method was optimized to  
27 analyse simultaneously polycyclic aromatic hydrocarbons (PAHs) and polychlorobiphenyls  
28 (PCBs) from sediments, and was compared to microwave-assisted extraction (MAE). New  
29 dispersing agents were tested to improve MSPD extraction. 3-chloropropyl-bonded silica  
30 particles, in addition to Florisil, increased significantly the polyaromatics desorption capacity.  
31 A compromise was found for eluting both families of compounds from sediments, using a  
32 small volume of hexane/acetone. Low procedural detection limits could be reached (0.06-0.22  
33 ng g<sup>-1</sup> and 0.3-1.1 ng g<sup>-1</sup> for PAHs and PCBs, respectively). Mean total extraction recoveries  
34 were good for PAHs (>67%, depending on the sediment) and for PCBs (>89%), with good  
35 precision (6-9% and 4-10% inter-day precision for PAHs and PCBs, respectively). Higher  
36 recoveries for PCBs could be reached in comparison with formerly developed sonication or  
37 Soxhlet extraction methods, but also with MAE. MSPD offered significant decrease of sample  
38 amount, of solvent consumption and allowed more efficient cleaning of the sediment matrix,  
39 leading to less matrix effects compared to MAE, removing lots of interfering compounds  
40 without additional purification step. The robustness of the MSPD methodology could be  
41 demonstrated extracting quantitatively sediments from different sources and with various  
42 mineralogical characteristics.

43

44 **Key words:**

45 Extraction and purification; Green sample preparation; Polychlorobiphenyls; Polycyclic  
46 aromatic hydrocarbons; Sediments; Solid phase dispersion.

47

## 48 **1. Introduction**

49 The analysis of toxic polyaromatic compounds in environmental solid samples is essential to  
50 monitor and manage the risks for human health and ecosystems. Methods for determining  
51 regulated toxic polyaromatic compounds such as polycyclic aromatic hydrocarbons (PAHs) or  
52 polychlorobiphenyls (PCBs) therefore became routine. Standardized methods for the analysis  
53 of PAHs or PCBs in soils or sediments exist [1, 2]. Analytical methods generally involve  
54 several steps: first, extraction from the solid environmental matrix is required, Soxhlet being  
55 considered as a standard method. However it is a long and solvent-consuming extraction  
56 method. Sonication, which is simpler and faster, can be also used but it is generally  
57 considered as less efficient than Soxhlet. Alternative methods are proposed, which are as  
58 efficient (or more) and faster than Soxhlet, such as pressurized liquid extraction, microwave-  
59 assisted extraction, supercritical fluid extraction, but that necessitate high investment and  
60 apparatus maintenance costs [3 - 5]. Second, samples often require clean-up, due to the  
61 presence of interfering compounds in the extracts because extraction methods are not enough  
62 selective. Potential interferences, which may bias the quantification of the target compounds,  
63 can be removed using solid phase extraction or columns packed with sorbents, selective  
64 pressurized liquid extraction or specifically functionalized purifying materials [6 - 9]. The last  
65 step is the separation and quantification, which is generally achieved through gas  
66 chromatography coupled to mass spectrometry (GC-MS or GC-MS/MS), liquid  
67 chromatography coupled to a fluorimetric detector for PAHs, or GC coupled to electron  
68 capture detector for PCBs [10 - 13].

69 Nowadays, faster, low cost, less complicated processes and among all, multi-residual sample  
70 treatment methods are required to increase analytical throughputs. So matrix solid phase  
71 dispersive (MSPD) extraction has been regarded for the past few years as an interesting  
72 alternative to the long and complex sample preparation methods, because it allows extraction,

73 clean-up and filtration in a single step and reduces drastically the analysis time and the  
74 consumption of toxic solvents. MSPD has been developed to extract toxic persistent  
75 contaminants such as PAHs, PCBs, organochlorine or organophosphorous compounds more  
76 particularly from solid or semi-solid biological samples or fatty foods [12, 14-17]. But  
77 methodologies have been also developed for environmental matrices such as soils, sediments  
78 or sewage sludges, which are known to accumulate these persistent lipophilic contaminants  
79 [10, 11, 18]. MSPD involves the grinding of the solid matrix with dispersing agents, which  
80 could be liquids in its original conception but now, solid abrasive particles are used that play  
81 two roles [19]. Particles are added to disrupt the sample structure and favour desorption of the  
82 lipophilic contaminants from the sample organic matter and re-adsorption on the attracting  
83 particles surface; thereafter the lipophilic contaminants are better eluted with appropriate  
84 solvent mixtures. Other particles are added to favour adsorption of the polar interfering  
85 compounds and prevent their elution, which constitute the purifying step. In general, the most  
86 used sorbents for PAHs and PCBs are C<sub>18</sub> bonded particles [10, 11, 20, 21] and cleaning  
87 sorbents are silica or Florisil particles [18].

88 The aim of the present work was to optimise a multiresidual MSPD extraction method for the  
89 simultaneous extraction and purification of two families of contaminants, PAHs and PCBs,  
90 from sediment samples. Very few works report the use of MSPD as a powerful, simple and  
91 low cost extraction method for sediments analysis. Moreover, as no work reports the use of  
92 novel additives to enhance desorption of both PAHs and PCBs from sediments, new  
93 dispersing agents were tested with different combinations of eluting solvents. The MSPD  
94 method was tested and validated on real sediments (of which different reference materials)  
95 and its benefits and drawbacks were compared with those of the more classical microwave-  
96 assisted extraction (MAE). In particular, benefits on the sample purification, though matrix  
97 effects quantification, were compared. Moreover, the robustness of the method was

98 demonstrated extracting quantitatively various sediments with different mineralogical  
99 characteristics and from different sources.

100

## 101 **2. Materials and methods**

### 102 2.1 Chemicals and samples

103 Hexane, toluene, dichloromethane, acetone, all of HPLC grade, were provided by VWR  
104 (Fontenay sous Bois, France). Octan-1-ol (HPLC grade), sodium sulfate (purity >99%), 3-  
105 chloropropyl functionalized silica (37-62  $\mu\text{m}$  particulate diameter ( $d_p$ ), 6 nm pore diameter)  
106 and 4-benzylchloride functionalized silica ( $d_p= 37\text{-}74 \mu\text{m}$ , 6 nm pores) were provided by  
107 Sigma-Aldrich (Saint-Quentin-Fallavier, France). Septra Florisil ( $d_p=180 \mu\text{m}$ , 8.5 nm pores),  
108 Septra silica gel ( $d_p=50 \mu\text{m}$ , 6.5 nm pores) and Septra C<sub>18</sub> bonded silica ( $d_p=50 \mu\text{m}$ , 6.5 nm  
109 pores) were furnished by Phenomenex (Le Peck, France).

110 Perdeuterated phenanthrene (PheD10) and perylene (PerD12), used as internal standards (IS)  
111 for GC-MS, and perdeuterated fluoranthene (FltD10) and benzo[*a*]pyrene (BaPyrD12), used  
112 as surrogate standards (SS), were provided by Sigma-Aldrich. PCB156, used as SS for PCBs,  
113 was furnished by Sigma Aldrich. A solution of 7 PAHs (phenanthrene (Phe), fluoranthene  
114 (Flt), pyrene (Pyr), benzo[*b*]fluoranthene (BbFlt), benzo[*k*]fluoranthene (BkFlt),  
115 benzo[*a*]pyrene (BaPyr), benzo[*ghi*]perylene (BPer), all furnished by Sigma Aldrich), was  
116 prepared at 100 mg L<sup>-1</sup> in acetone. A solution containing the 16 priority PAHs (defined by US-  
117 EPA, Table S1 in supplementary materials) at 2000 mg L<sup>-1</sup> and a solution of 7 PCBs (PCB28,  
118 PCB52, PCB101, PCB138, PCB153, PCB180, PCB209) at 10 mg L<sup>-1</sup>, were furnished by  
119 Sigma Aldrich.

120 A model sediment was prepared by mixing 73 g silt (collected from surface formations  
121 covering the chalk plateau in Normandy, France), 5 g sand (SIKA, Hostun, France), 19.5 g  
122 kaolinite (IMERYS, Poigny, France) and 2.5 g organic matter (VEOLIA, France). The particle

123 size distribution of this model sediment was approximately the same than the one  
124 corresponding to a dredged sediment collected from the disposal site of a French harbor. 100  
125 g of the model sediment were spiked with 2.5 mL of the solution containing the 7 PAHs (2.5  
126  $\mu\text{g g}^{-1}$  dry weight (dw) each PAH) and 5 mL of the solution containing the 7 PCBs (0.5  $\mu\text{g g}^{-1}$   
127 (dw) each PCB), and was mixed under a fume hood for 12 h in the dark, for solvent  
128 evaporation. The mixture was left in the dark at 4°C at least three weeks, mixing it regularly,  
129 to favour the interactions between the spiked contaminants and the model sediment, in order  
130 to better reflect naturally contaminated matrices where sorption is stronger with ageing. A  
131 dredged sediment, naturally contaminated with PAHs and PCBs, was collected from a storage  
132 site of a French harbor at Tancarville, in the Seine River estuary (Normandy, France). It was  
133 freeze-dried, crushed, and then stored at -20°C. Three reference sediment materials, CNS391  
134 (containing certified amounts of PAHs and PCBs), CRM104 (containing certified amounts of  
135 PAHs) and BCR-536 (containing certified amounts of PCBs) were obtained from Sigma-  
136 Aldrich. Another reference sediment, Wepal-SETOC-717 (containing certified amounts of  
137 PAHs and PCBs) was purchased from LGC (Teddington, UK). All of them were stored at -  
138 20°C.

139

## 140 2.2 Extraction procedures

### 141 2.2.1 Matrix solid phase dispersive extraction

142 Dry sediment (0.5 g) was spiked with 15  $\mu\text{L}$  of the three SS (at 100  $\text{mg L}^{-1}$ ) and 1 g sodium  
143 sulfate was added. 1 g Florisil and 0.5 g of the best dispersing agent (3-chloropropyl-bonded  
144 silica particles) were added and the mixture was ground with a pestle for 10 min. A co-column  
145 containing 1 g Florisil was introduced at the bottom of a 12 mL polypropylene SPE tube with  
146 a polyethylene frit (20  $\mu\text{m}$ ) (Phenomenex) and the solid mixture, blended previously, was put  
147 above it, covered by another frit. The whole sediment column and co-column were slightly

148 pressed. The analytes were eluted with 5 mL of the best mixture acetone/hexane 50/50 (v/v),  
149 using a semi-automated SPE extraction system from Phenomenex. The eluates were  
150 evaporated to dryness (after adding 60  $\mu$ L octanol, as solvent keeper) with a MiVac duo  
151 concentrator (Genevac, Ipswich, UK). The remaining volume was then completed to 1.5 mL  
152 with toluene, before the subsequent analysis in GC-MS.

153

### 154 2.2.2 Microwave assisted extractions

155 Microwave assisted extractions (MAE) were performed using a MARS X equipment (CEM  
156 Corporation, Matthews, USA). Dry crushed sediment (5 g) was spiked with 15  $\mu$ L of the three  
157 SS (at 100 mg L<sup>-1</sup>) and was introduced in a Teflon PTFE flask with 20 mL acetone and 20 mL  
158 toluene and heated using a power of 1200 W at 130°C for 30 min [22]. After cooling,  
159 extracted solutions were filtered with PTFE filters (0.2  $\mu$ m) from Fisher Scientific (Illkirch,  
160 France). Thereafter, the extracts were evaporated to dryness (after adding 60  $\mu$ L octanol) with  
161 a MiVac duo concentrator. The remaining volume was then completed to 1.5 mL with toluene,  
162 before the subsequent analysis in GC-MS.

163

### 164 2.3 GC-MS analysis

165 For GC-MS analyses, 10  $\mu$ L of the two IS were added to 990  $\mu$ L of the MAE or MSPD  
166 extracts. PhenD10 was the IS for PAHs from naphthalene to chrysene and for PCBs, while  
167 PerD12 was used for higher molecular weight PAHs. Then 1  $\mu$ L of the sample was injected in  
168 the splitless mode at 285°C and separated with the column Zebron ZB-SemiVolatiles (60 m  
169 length $\times$ 0.25 mm i.d. $\times$ 0.25  $\mu$ m film thickness) from Phenomenex. The oven program started at  
170 60°C (1.2 min) to 190°C (at 40°C min<sup>-1</sup>) followed by an increase to 240°C (at 4°C min<sup>-1</sup>) and  
171 finally to 305°C (at 6°C min<sup>-1</sup>) during 12 min, under a constant carrier gas flow of 1.4 mL  
172 min<sup>-1</sup>. The temperature of the transfer line was set at 300°C and the detection was conducted

173 in full SCAN for identification and in selected ion monitoring (SIM) for better sensitivity  
174 (Table S1). Calibration curves were established using 6-7 levels of concentrations, from 0.05  
175 to 3 mg L<sup>-1</sup>, using the internal calibration methodology, and all the correlation coefficients  
176 were >0.990. The limits of detection (LOD), calculated as three times the signal-to-noise ratio  
177 (S/N=3) were in the range 0.1-0.6 µg L<sup>-1</sup> for PAHs and 0.4-0.8 µg L<sup>-1</sup> for PCBs (Table S1).  
178 The limits of quantification (LOQ) calculated as ten times the signal-to-noise ratio (S/N=10)  
179 were in the range 0.4-2 µg L<sup>-1</sup> for PAHs and 1.3-2.6 µg L<sup>-1</sup> for PCBs (Table S1). For  
180 determining matrix effects in GC-MS, the CNS391 certified sediment was spiked with PAHs  
181 and PCBs solutions from 0.2 to 3 mg L<sup>-1</sup> and extracted by MAE and MSPD (sections 2.2.1  
182 and 2.2.2).

183

## 184 2.3 Statistical analysis

185 Statistical analyses were carried out using the Microsoft XLSTAT 2013 software (Microsoft  
186 Inc. USA). ANOVA tests were performed to compare two means through the variances of two  
187 independent populations using the Fishers' distribution and one p-value to support or reject  
188 the null hypothesis.

189

## 190 **3. Results and discussion**

### 191 **3.1 Optimisation of conditions for MSPD extraction from a model sediment**

#### 192 3.1.1 Influence of the nature of dispersing agents

193 The first step in the optimisation of the MSPD methodology was to find the best combination  
194 of additives and dispersing agents introduced in a model sediment spiked with a mixture of 7  
195 PAHs and 7 PCBs. The model sediment, which was of the same mineralogical composition  
196 than a real sediment from Tancarville (France) (section 2.1) was used because it could be  
197 considered as a blank matrix without any pollution from PAHs and PCBs. PAHs and PCBs are

198 non-polar semi-volatile organic compounds (Table S2). For improving their extraction in  
199 matrices as sediments, soils or sewage sludges, a drying agent can be added, *e.g.* anhydrous  
200 sodium sulfate. The presence of water can interfere for the extraction of the non-polar  
201 compounds and can cause the co-elution of the polar ones [23]. So 1 g sodium sulphate was  
202 added to 0.5 g sediment to ensure better drying.

203 Cleaning sorbents, used to trap the polar interfering compounds, are generally silica or Florisil  
204 particles [24]. Sample/sorbent ratios typically range from 1/1 to 1/4 [18]. In this study, Florisil  
205 or silica gel were used in the ratio 1/2 (0.5 g sediment /1 g cleaning sorbent). At first sight, the  
206 recoveries obtained for PAHs were higher when using silica rather than Florisil, but  
207 unfortunately with higher relative standard deviations (some exceeding 15%). In addition, it  
208 appeared that blank samples, obtained from the MSPD extraction of the non-spiked model  
209 sediment, contained higher amounts of PAH impurities when silica was used as dispersing  
210 agent and for constituting the co-column put above the blended sediment. As Florisil gave  
211 lower interferences, it was chosen as a dispersing and cleaning agent.

212 The sample and the associated contaminants can be also dispersed over the surface of a  
213 bonded-phase support material or nanotube adsorbents that can favour, through hydrophobic  
214 interactions, their transfer from the disrupted solid matrix [25]. Only a small variety of solid  
215 supports have been used for extracting PAHs or PCBs from solid matrices through MSPD [26,  
216 27]. Even if authors considered that silica-based materials have been extensively studied [6],  
217 it was not particularly the case for PAH and PCB MSPD extractions from soils or sediments.  
218 So new functionalised silica particles have to be tested and compared to the effects of Florisil  
219 alone or to the more “classical” C<sub>18</sub> bonded-silica particles, in order to enhance the transfer  
220 and the further elution of these compounds from sediments. 3-chloropropyl- (3-ClPr) and 4-  
221 benzylchloride- (4-BCl) grafted silica were chosen for their possible intermolecular attraction  
222 between chlorinated atoms with PCBs and/or their possible  $\pi/\pi$  attraction through phenyl

223 rings, forces that could increase the attraction between the adsorbate and the adsorbent  
224 compared to the London dispersion forces alone developed by the C<sub>18</sub> grafts. Fig. 1 shows the  
225 mean recovery yields (n=3) obtained for the sum of the 7 PAHs ( $\Sigma_7$ PAHs) and the 7 PCBs  
226 ( $\Sigma_7$ PCBs) extracted from the spiked model sediment, comparing the effects of Florisil alone,  
227 or in combination with C<sub>18</sub>-, 4-BCl- or 3-ClPr- bonded silica particles. Comparing the use of  
228 Florisil alone and the addition of 3-ClPr-functionalized silica, the mean recoveries were  
229 significantly increased (p-value=0.044 < 0.05), from 55±2% to 62±4% for the  $\Sigma_7$ PAHs and  
230 from 79±1% to 87±4% for the  $\Sigma_7$ PCBs (p=0.037). Individually, adding 3-ClPr-functionalized  
231 particles to Florisil (compared to Florisil alone) allowed increasing significantly the  
232 recoveries of Flt, Pyr, BbFlt, BkFlt, BPer, PCB52, PCB101 and PCB138 (p-values<0.05).  
233 Adding C<sub>18</sub> bonded particles to Florisil did not significantly favoured the mean extractions of  
234 PAHs and PCBs (55±2% and 86±5%, respectively) (p>0.05). Adding 4-BCl-bonded particles  
235 to Florisil slightly favoured the mean extractions of PAHs and PCBs (57±1% and 79±2%,  
236 respectively), but not significantly (p>0.05). Moreover, the improving effect of 3-ClPr- over  
237 C<sub>18</sub>-bonded silica particles was significant for the  $\Sigma_7$ PAHs (62±4% vs 55±2%, p=0.044) while  
238 it was not significant for the  $\Sigma_7$ PCBs (87±4% vs 86±5%, p>0.05). Individually, adding 3-  
239 ClPr-functionalized particles to Florisil rather than C<sub>18</sub> particles allowed increasing  
240 significantly the recoveries of Phe, Pyr and BPer (p-values<0.05). Consequently, 3-ClPr-  
241 functionalized silica was added to the cleaning sorbent Florisil to improve the simultaneous  
242 MSPD extraction of PAHs and PCBs from the sediment matrix.

243

### 244 3.1.2 Influence of the eluting solvent and grinding time

245 It has been demonstrated that mixtures of hexane/acetone were suitable solvents for eluting  
246 PAHs from cartridges containing blended soils, but mixtures of hexane/dichloromethane were  
247 generally more appropriate for eluting PCBs [18, 28, 29]. In the case of a multiresidual

248 analysis, the best solvent had to be found for eluting quantitatively both PAHs and PCBs. Fig  
249 2 shows various tested solvents or solvent mixtures: pure hexane and the mixture  
250 hexane/dichloromethane 50/50 (v/v) were the worst solvents for eluting both PAHs and PCBs  
251 from the model sediment, with mean recoveries of  $12\pm 2\%$  and  $39\pm 2\%$  for the  $\Sigma_7$ PAHs,  
252 respectively, and  $59\pm 2\%$  and  $72\pm 3\%$  for the  $\Sigma_7$ PCBs, respectively. Pure dichloromethane was  
253 appropriate for eluting PCBs ( $83\pm 1\%$ ) but not for PAHs ( $46\pm 2\%$ ). The mixtures containing  
254 hexane/acetone 50/50 or 25/75 (v/v) were the best for eluting the two families of compounds,  
255 with not significantly different mean recoveries ( $p>0.05$ ). The mixture containing less acetone  
256 was chosen in order to limit the elution of polar interfering compounds. The influence of the  
257 elution volume on the mean recoveries was also evaluated. Recoveries tended to slightly  
258 decrease with the elution volume increase, in the 5-15 mL range (Fig. S1a). Elution with 5 mL  
259 of the best solvent mixture was significantly better for PAHs ( $p=0.011$ ) than using 15 mL, or  
260 than using 10 mL for PCBs ( $p=0.006$ ).

261 The influence of the grinding time has generally received little attention in MSPD  
262 optimisation steps [25]. However the first disruption and dispersion step might appear  
263 important in the context of the utilization of the 3-ClPr-functionalized silica as dispersing and  
264 attracting agent. A slight increase of the mean recovery yields with an increase of the grinding  
265 time was observed in the 2-10 min range (Fig. S1b). Despite the low improvement, 10 min  
266 grinding was significantly more favourable than grinding 2 or 8 min for extracting PAHs  
267 ( $p=0.010$  and  $p=0.038$ , respectively) and PCBs ( $p=0.001$  and  $p=0.015$ , respectively).

268 In the optimised conditions with 10 min grinding (section 2.2.1), mean recoveries of  $67\pm 2\%$   
269 could be reached for the  $\Sigma_7$ PAH and  $109\pm 2\%$  for the  $\Sigma_7$ PCBs. Unlike PCBs, the mean  
270 recovery of total PAHs could not be considered quantitative even after the optimisation of  
271 MSPD extraction. Indeed a specific degradation of BaPyr after spiking was noted after several  
272 weeks of sediment/contaminants equilibration (section 2.1), which was not the case for PCBs.

273 The low recovery of BaPyr (52%, Table 1) contributed to decrease the overall results for  
274 PAHs. It was already observed in other studies that BaPyr could be more particularly  
275 biodegraded in acidic soils unlike other high molecular weight PAHs [30].

276

## 277 **3.2 Performances of the MSPD procedure and comparison with MAE**

### 278 3.2.1 Performances of the optimised MSPD method

279 In the optimal conditions, mean recoveries, repeatability (or intra-day precision) and  
280 reproducibility (or inter-day precision) of the MSPD method were evaluated by analysing  
281 spiked model sediments (n=5). Considering the intra-day study, the mean relative standard  
282 deviations (RSD) were 4% and 3% for the  $\Sigma_7$ PAHs and  $\Sigma_7$ PCBs, respectively. RSDs were  
283 ranging from 2% for BkFlt to 5% for BaPyr and from 2% for PCB28 to 4% for PCB138.  
284 Considering the inter-day study (Table 1), the mean RSDs for the  $\Sigma_7$ PAHs and  $\Sigma_7$ PCBs were  
285 both 7%. RSDs were ranging from 6% for BaPyr to 9% for Flt and from 4% for PCB209 to  
286 10% for PCB138. Mean recoveries of the surrogate standards were  $100\pm 2\%$  for FltD10,  
287  $97\pm 3\%$  for BaPyrD12 and  $105\pm 4\%$  for PCB156 (n=5), that showed that PAHs were better  
288 recovered when they were freshly spiked rather than spiked for several weeks.

289 The procedural limits of detection (LOD) and quantification (LOQ) of the whole extraction  
290 method were evaluated from the analysis of a blank sample. The non-spiked model sediment  
291 was extracted with the optimised MSPD process to determine the sample noise near the peaks  
292 of interest. LODs and LOQs were then estimated as the average response (n=3) for each  
293 spiked analyte multiplied by three times or ten times the standard deviation of the blank  
294 sample noise, respectively. Table 1 gives the procedural LODs and LOQs. LODs were  
295 compared with literature data obtained from similar environmental matrices for PAHs, but  
296 from biological or food samples for PCBs. LODs were ranging from 0.08 to 0.22 ng g<sup>-1</sup> (dw)  
297 for PAHs, that was better than the values found in the study using also a MS detector (Table

298 1) [20]; LODs were lower in the studies that analysed PAHs with a fluorescence detector,  
299 more sensitive than MS [18, 27]. LODs were ranging from 0.3 to 1.1 ng g<sup>-1</sup> (dw) for PCBs,  
300 which was better than in the study of Ziarrusta *et al.* but lower than in the study of Roscales *et*  
301 *al.* who determined PCBs in food samples (Table 1) [16, 26].

302 Table 1 shows also the analysis of the model sediment without spiking it, considered as the  
303 blank sample. It can be noted that no PCBs could be detected, which was not the case for  
304 some PAHs. But measured values for PAHs were generally under the LOQs that showed very  
305 low interference on the previous results.

306

### 307 3.2.3 Comparison of MSPD and MAE extraction methodologies

308 The optimised MSPD extraction was compared with microwave-assisted extraction (MAE),  
309 which has been validated with a certified reference sediment (CRM104) for the extraction of  
310 PAHs. Excepting naphthalene, all the PAHs were quantitatively extracted (78-132%) using  
311 MAE (Table S3), with a mean recovery of the 16 priority PAHs of 101% compared to the  
312 certified values (recently revised in a certificate dated 2017). It can be noted that even if MAE  
313 gave excellent results for extracting PAHs from the naturally contaminated CRM104  
314 sediment, it gave significantly lower results ( $p=0.01$ ) than MSPD for extracting the spiked  
315 model sediment, with a mean extraction recovery of  $59\pm 3\%$  (instead of  $67\pm 2\%$  for MSPD)  
316 and recoveries ranging between 45-68% for individual PAHs. As mentioned previously, PAHs  
317 were measured 3-5 weeks after they were spiked on the model sediment and they were  
318 probably subject to slight biodegradation, and more particularly BaPyr which recovery was  
319 the lowest.

320 The MSPD methodology was then tested on a real sediment, initially the CNS391 reference  
321 material. Table 2 gives the recoveries obtained from the MSPD and MAE extraction  
322 methodologies and the deviations with the certified values indicated on the certificate (dated

2013). It must be noted that Naph was removed from the discussion because its value, obtained from three different extraction tools (optimised MSPD, validated MAE and conventional Soxhlet (8 h extraction with 100 mL dichloromethane) extractions), was considerably lower (mean recoveries less than 10%) than that mentioned by the CNS391 certificate. However, for the CRM104 certified reference material, MAE gave significantly better results for Naph (Table S3). The discrepancy with the CNS391 certified value might be explained observing the date of the CNS391 certificate, where data were listed in 2013, and the certificate has not been reconsidered for many years, whereas the CRM104 certificate was regularly updated. It is well known that the lower molecular weight PAHs can be volatilized or degraded, even in cold and dry storage conditions, and it was probably the case for Naph in CNS391 material.

The total amount of the  $\Sigma_{15}$ PAHs ( $3415 \text{ ng g}^{-1}$ ) obtained from MSPD was lower than that mentioned on the CNS391 sediment certificate ( $3985 \text{ ng g}^{-1}$ ) (Table 2). Some values of individual PAHs were not in the intervals of prediction of the certificate (8/15) and had mean extracted amounts lower than the certified values. However, spiked SS recoveries were quantitative, with  $100\pm 4\%$  and  $88\pm 9\%$  recoveries for FltD10 and BaPyrD12, respectively. As mentioned previously, the furnished certificate, dated 2013, was perhaps no more consistent with the PAH levels measured in a sediment material bought recently, where degradation/evaporation could have happened. However, the mean extraction level of the  $\Sigma_{15}$ PAHs using MSPD remained satisfactory, with a mean loss of 14.3% compared to the certified values (Table 2). To verify this hypothesis, MSPD results were crossed with those obtained from the validated MAE methodology. It appears from Table 2 that, as for MSPD extraction, lots of results obtained from MAE extraction of PAHs from CNS391 were not in the intervals of prediction of the certificate (5/15). However, spiked SS recoveries were quantitative, with  $99\pm 4\%$  and  $92\pm 8\%$  recoveries for FltD10 and BaPyrD12, respectively. The

348 total amount of the  $\Sigma_{15}$ PAHs ( $3063 \text{ ng g}^{-1}$ ) extracted through MAE was lower than that  
349 mentioned on the CNS391 certificate, with a mean loss of 23.1%. But it is important to note  
350 that excepting 3 values, MSPD and MAE results matched together. As shown in Table 2,  
351 MSPD was overall better than MAE for extracting PAHs, with a gain of 10.3%. In fact, MAE  
352 was slightly less efficient than MSPD for extracting low molecular weight PAHs but slightly  
353 better for some high molecular weight PAHs. However, compared to the values of the  
354 certificate, the mean extraction level of the  $\Sigma_{15}$ PAHs using MAE (77%) was less satisfactory  
355 than MSPD (86%).

356 Table 2 shows that the total amount of the  $\Sigma_6$ PCBs (PCB209 was not considered here, because  
357 it is generally missing from naturally contaminated sediments), extracted by MSPD ( $377 \text{ ng g}^{-1}$ ),  
358 was much higher than the total amount listed in the certificate ( $295 \text{ ng g}^{-1}$ ). The extraction  
359 of the PCBs was higher using the MSPD method whatever the PCB, from the less chlorinated  
360 (3 Cl) to the more chlorinated (7 Cl), with a mean extraction gain of 28.1% compared to the  
361 certified values. The spiked SS PCB156 was quantitatively extracted, with  $112 \pm 10\%$   
362 recovery. Only one value of PCB (PCB180) did not enter in the interval of prediction of the  
363 certified sediment. The results achieved from the extraction of PCBs were compared with the  
364 MAE extraction of the reference material, performed in the same conditions than those  
365 applied for PAHs. Table 2 shows that results obtained using MAE were higher than those  
366 listed in the certificate, with a mean gain of 8.6%. The spiked SS PCB156 was quantitatively  
367 extracted, with  $100 \pm 8\%$  recovery. Compared to the values of the certificate, the mean  
368 extraction level of the  $\Sigma_6$ PCBs using MAE (109%) was less satisfactory than MSPD (128%).

369 In fact, the results listed in the certificate for CNS391 were obtained from conventional  
370 extraction methods, developed in the beginning of the 90's: the results are a combination of  
371 ultrasound-assisted extraction (method 3550A of US-EPA) or Soxhlet extraction (method  
372 3541 of US-EPA). However, when examining these methods, it is mentioned that the method

373 3550A may extract less than 50% of the organochlorine compounds and that the method 3541  
374 may not be really appropriate when concentrations of PCBs are too low. So, it is not so  
375 surprising that the MSPD extraction method allowed achieving concentration values markedly  
376 higher than the values given by the CNS391 certificate of analysis.

377 If the optimised MSPD methodology appeared better than MAE for extracting PAHs and  
378 PCBs, it must be underlined that MSPD required considerably smaller sediment size to be  
379 analysed (0.5 g vs 5 g for MAE) and offered saving in terms of solvent consumption (5 mL vs  
380 40 mL for MAE). But the most important advantage was the capacity of MSPD to purify the  
381 extracts. Fig. 3 shows two chromatograms of extracts obtained from MAE and MSPD  
382 extractions of the CNS391 sediment. Fig. 3a shows that the interfering compounds are more  
383 important on the chromatogram obtained after MAE than after MSPD extraction, which  
384 presented a cleaner chromatogram particularly in the 6-16 first minutes of the analysis, with  
385 less baseline drift (Fig. 3b). The same remark could be obviously done on chromatograms  
386 obtained in full SCAN mode, where the extracts were cleaner after MSPD extraction (Fig.  
387 S2).

388 To confirm the good ability of MSPD purification, matrix effects (ME) of MSPD and MAE  
389 extraction methods were compared, using CNS391 sediment, by comparing the slopes of the  
390 standard solutions calibration curves with that of matrix-matched standard solutions. ME were  
391 observed for both extraction methods: as shown in Table 3, lower slopes for matrix-matched  
392 standard solutions suggest ion-suppression in GC-MS due to the CNS391 sediment matrix.  
393 Ion-suppression for PAHs was in the range 9.6-33.3% using MSPD (mean value: 20.9%) and  
394 13.4-31.9% using MAE (mean value: 26.1%). Ion-suppression was lower for PCBs, being in  
395 the range 10.8-25.9% using MSPD (mean value: 17%) and 15.1-26.7% using MAE (mean  
396 value: 22.4%). With only three exceptions, all the PAHs/PCBs ME were higher using MAE  
397 than MSPD extraction. So MSPD appeared as a more selective extraction method than MAE,

398 with lesser matrix effects. MS ionization suppression for the MSPD method was also  
399 demonstrated smaller than the QuEChERS extraction method for pesticides in fruits [31].

400

#### 401 3.2.4 Robustness of the MSPD method with application on various contaminated sediments

402 Obviously, the robustness of the MSPD extraction method must be confirmed by its  
403 application on other naturally contaminated sediments with different characteristics. CNS391  
404 material is a freshwater sediment, but BCR-536 is a harbour sediment with high contents of  
405 fine clayey particles (22.8%) and organic matter (12%), and Wepal-SETOC-717 is a marine  
406 sediment with low content of organic matter (approximately 2.5%), moderate levels of clays  
407 (10%) but higher levels of salts. Environmental matrices rich in fine particles (<2  $\mu\text{m}$ ),  
408 organic carbon and salts are known to be harder to extract than non-carbonaceous sandy  
409 matrices.

410 Table 4 shows the results obtained for PCBs for BCR-536. As for CNS391 material, PCBs  
411 were better extracted using the MSPD extraction methodology (with an overall increase of  
412 27.7%). The recovery of the spiked PCB156 SS was  $115\pm 11\%$  ( $n=5$ ). Although PCBs were  
413 better extracted through MSPD, they were in the same order of magnitude than the results  
414 delivered by the certificate. Concerning the Wepal-SETOC-717 material, Table 4 shows that  
415 MSPD displayed excellent recoveries for the PAHs, with an overall increase of 14%  
416 compared to the certificate. PCBs were markedly better extracted through MSPD extraction  
417 (+112.7%); the high discrepancy could be explained because PCB levels were very low and  
418 close to quantification limits (Table 1), which was also probably the case for the results from  
419 the certificate. The recoveries of the spiked SS were  $96\pm 7\%$ ,  $115\pm 5\%$  and  $91\pm 6\%$  ( $n=5$ ) for  
420 FltD10, PCB156 and BaPyrD12, respectively.

421 Lastly, to confirm the capacity of the MSPD method to better extract PAHs and PCBs than  
422 MAE from a naturally contaminated sediment, the two extraction processes were applied on a

423 dredged marine harbour sediment collected at Tancarville (France). This sediment was  
424 composed of high contents of fine particles (<63  $\mu\text{m}$ ) (5.9% clays, 75.1% silts) and organic  
425 matter (11%). Table 4 shows the results obtained for the PAHs and PCBs. MSPD extracted  
426 significantly more PAHs and PCBs than MAE ( $p < 0.001$  and  $p = 0.009$ , respectively). All the  
427 PAHs were systematically better extracted through MSPD, even the heavier ones, and low  
428 molecular weight PAHs and PCBs were easily determined because of the reduced print of  
429 interfering compounds in the first 16 min of the chromatogram.

430

### 431 **Concluding remarks**

432 3-Chloropropyl functionalized silica particles were mixed for the first time with the cleaning  
433 sorbent Florisil, improving significantly the simultaneous MSPD extraction of PAHs and  
434 PCBs from various sediment matrices. A compromise could be found for eluting  
435 quantitatively both PAHs and PCBs from the sediment, using a small volume of a mixture of  
436 hexane/acetone. In such conditions, low procedural LOD and LOQ allowed quantifying PAHs  
437 and PCBs at trace levels in sediments. Mean extraction recoveries were good both for PAHs  
438 and PCBs, with good precision. The high recoveries obtained for PCBs in the certified  
439 CNS391 sediment could be reached in comparison with former extraction methodologies  
440 using ultra-sound assisted and Soxhlet extractions. MSPD extraction results could be also  
441 better than those obtained with the most recent MAE extraction methodology, offering in  
442 addition simplicity and significant decrease of sample amount to be analysed, of solvent  
443 consumption and of instrumental cost. The robustness of the MSPD methodology could be  
444 demonstrated extracting quantitatively aged sediments from different sources and with  
445 different mineralogical characteristics. At last, MSPD allowed cleaning of the sediment  
446 matrix, removing interfering compounds without an additional purification step, which  
447 improved the selectivity of the PAHs and PCBs extraction and decreased matrix effects. All

448 the advantages of the faster and economic developed MSPD method may directly benefit the  
449 high throughput routine control of sediments.

450

#### 451 **Supplementary materials**

452 Three tables (Tables S1, S2, S3) and two figures (Fig. S1 and S2) are included in the  
453 supplementary materials.

454

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460

#### 461 **Declarations of interest**

462 None

463

#### 464 **References**

465 [1] ISO 13859, Soil quality - Determination of polycyclic aromatic hydrocarbons (PAH) by  
466 gas chromatography (GC) and high performance liquid chromatography (HPLC), 2014.

467 [2] ISO 13876, Soil quality - Determination of polychlorinated biphenyls (PCB) by gas  
468 chromatography with mass selective detection (GC-MS) and gas chromatography with  
469 electron-capture detection (GC-ECD), 2013.

470 [3] P. Lehnik-Habrink, S. Hein, T. Win, W. Bremser, I. Nehls, Multi-residue analysis of PAH,  
471 PCB, and OCP optimized for organic matter of forest soil, J. Soils Sediments 10 (2010) 1487-  
472 1498.

473 [4] M.C. Bruzzoniti, R. Maina, V. Tumiatti, C. Sarzanini, L. Rivoira, R.M. De Carlo, Fast  
474 low-pressure microwave assisted extraction and gas chromatographic determination of  
475 polychlorinated biphenyls in soil samples, *J. Chromatogr. A* 1265 (2012) 31-38.

476 [5] F. Portet-Koltalo, K. Oukebdane, F. Dionnet, P.L. Desbène, Optimisation of supercritical  
477 fluid extraction of polycyclic aromatic hydrocarbons and their nitrated derivatives adsorbed  
478 on highly sorptive diesel particulate matter, *Anal. Chim. Acta* 651 (2009) 48-56.

479 [6] A.L. Capriotti, C. Cavaliere, P. Foglia, R. Samperi, S. Stampachiacchiere, S. Ventura, A.  
480 Lagana, Recent advances and developments in matrix solid-phase dispersion, *Trends Anal.*  
481 *Chem.* 71 (2015) 186-193.

482 [7] M.R. Burkhardt, S.D. Zaugg, T.L. Burbank, M.C. Olson, J.L. Iverson, Pressurized Liquid  
483 Extraction using water/isopropanol coupled with Solid-Phase Extraction cleanup for  
484 semivolatile organic compounds, Polycyclic Aromatic Hydrocarbons (PAH), and alkylated  
485 PAH homolog groups in sediment, *Anal. Chim. Acta* 549 (2005) 104-116.

486 [8] Z. Zhang, E. Ohiozebau, S.M. Rhind, Simultaneous extraction and clean-up of  
487 polybrominated diphenyl ethers and polychlorinated biphenyls from sheep liver tissue by  
488 selective pressurized liquid extraction and analysis by gas chromatography-mass  
489 spectrometry, *J. Chromatogr. A* 1218 (2011) 1203-1209.

490 [9] J. Zhang, M. Pan, N. Gan, Y. Cao, D. Wu, Employment of a novel magnetically  
491 multifunctional purifying material for determination of toxic highly chlorinated  
492 polychlorinated biphenyls at trace levels in soil samples, *J. Chromatogr. A* 1364 (2014) 36-44.

493 [10] C. Sánchez-Brunete, E. Miguel, J.L. Tadeo, Analysis of 27 polycyclic aromatic  
494 hydrocarbons by matrix solid-phase dispersion and isotope dilution gas chromatography-mass  
495 spectrometry in sewage sludge from the Spanish area of Madrid, *J. Chromatogr. A* 1148  
496 (2007) 219-227.

497 [11] Y. Moliner-Martínez, R.A. González-Fuenzalida, R. Herráez-Hernández, P. Campíns-  
498 Falcó, J. Verdú-Andrés, Cleaning sorbents used in matrix solid-phase dispersion with  
499 sonication: application to the estimation of polycyclic aromatic hydrocarbons at ng/g levels in  
500 marine sediments, *J. Chromatogr. A* 1263 (2012) 43-50.

501 [12] W. Li, D. Liu, J. Li, J. Gao, C. Zhang, P. Wang, Z. Zhou, Matrix Solid-Phase Dispersion  
502 combined with GC-MS/MS for the determination of Organochlorine Pesticides and  
503 Polychlorinated Biphenyls in marketed seafood, *Chromatographia* 80 (2017) 813-824.

504 [13] N.C.L. Vilas, I. García, M. Ignacio, A.M. Moureira, Optimization of a method based on  
505 micro-matrix solid-phase dispersion (micro-MSPD) for the determination of PCBs in mussel  
506 samples, *Anal. Chem. Res.* 11 (2017) 1-8.

507 [14] L. Pensado, M.C. Casais, M.C. Mejuto, R. Cela, Application of matrix solid-phase  
508 dispersion in the analysis of priority polycyclic aromatic hydrocarbons in fish samples, *J.*  
509 *Chromatogr. A* 1077 (2005) 103-109.

510 [15] J.J. Olmos-Espejel, M.P. García de Llasera, M. Velasco-Cruz, Extraction and analysis of  
511 polycyclic aromatic hydrocarbons and benzo[a]pyrene metabolites in microalgae cultures by  
512 off-line/on-line methodology based on matrix solid-phase dispersion, solid-phase extraction  
513 and high-performance liquid chromatography, *J. Chromatogr. A* 1262 (2012) 138-147.

514 [16] H. Ziarrusta, M. Olivares, A. Delgado, O. Posada-Ureta, O. Zuloaga, N. Etxebarria,  
515 Multiscreening determination of organic pollutants in molluscs using matrix solid phase  
516 dispersion, *J. Chromatogr. A.* 1391 (2015) 18-30.

517 [17] V. Castro, R. Montes, J.B. Quintana, R. Rodil, R. Cela, Determination of 18  
518 organophosphorus flame retardants/plasticizers in mussel samples by matrix solid-phase  
519 dispersion combined to liquid chromatography-tandem mass spectrometry, *Talanta* 208 (2020)  
520 120470.

521 [18] M.T. Pena, M.C. Casais, M.C. Mejuto, R. Cela, Optimization of the matrix solid-phase  
522 dispersion sample preparation procedure for analysis of polycyclic aromatic hydrocarbons in  
523 soils: comparison with microwave-assisted extraction, *J. Chromatogr. A* 1165 (2007) 32-38.

524 [19] D. Wianowska, A.L. Dawidowicz, Can matrix solid phase dispersion (MSPD) be more  
525 simplified? Application of solventless MSPD sample preparation method for GC-MS and  
526 GC-FID analysis of plant essential oil components, *Talanta* 151 (2016) 179-182.

527 [20] O.D. Christopoulou, V.A. Sakkas, T.A. Albanis, Evaluation of matrix solid-phase  
528 dispersion extraction for the determination of polycyclic aromatic hydrocarbons in household  
529 dust with the aid of experimental design and response surface methodology, *J. Sep. Sci.* 35  
530 (2012) 3554-60.

531 [21] F. De Nicola, E. Concha Graña, J.R. Aboal, A. Carballeira, J.Á. Fernández, P. López  
532 Mahía, D. Prada Rodríguez, S. Muniategui Lorenzo, PAH detection in *Quercus robur* leaves  
533 and *Pinus pinaster* needles: A fast method for biomonitoring purpose, *Talanta* 153 (2016) 130-  
534 137.

535 [22] F. Portet-Koltalo, K. Oukebdane, F. Dionnet, P.L. Desbène, Optimisation of the  
536 extraction of polycyclic aromatic hydrocarbons and their nitrated derivatives from Diesel  
537 particulate matter using microwave-assisted extraction, *Anal. Bioanal. Chem.* 390 (2008) 389-  
538 398.

539 [23] E. Guerra, M. Llompart, C. Garcia-Jares, Miniaturized matrix solid-phase dispersion  
540 followed by liquid chromatography-tandem mass spectrometry for the quantification of  
541 synthetic dyes in cosmetics and foodstuffs used or consumed by children, *J. Chromatogr. A*  
542 1529 (2017) 29-38.

543 [24] M. García-López, P. Canosa, I. Rodríguez, Trends and recent applications of matrix  
544 solid-phase dispersion, *Anal. Bioanal. Chem.* 391 (2008) 963-97.

545 [25] S.A. Barker, Matrix solid phase dispersion (MSPD), *J. Biochem. Biophys. Methods* 70  
546 (2007) 151-162.

547 [26] J.L. Roscales, A. Vicente, L. Ramos, B. Jiménez, Miniaturised sample preparation  
548 method for the multiresidual determination of regulated organohalogenated pollutants and  
549 related compounds in wild bird eggs, *Anal. Bioanal. Chem.* 409 (2017) 4905-4913.

550 [27] M.T. Pena, M.C. Casais, M.C. Mejuto, R. Cela, Development of a matrix solid-phase  
551 dispersion method for the determination of polycyclic aromatic hydrocarbons in sewage  
552 sludge samples, *Anal. Chim. Acta* 626 (2008) 626, 155-65.

553 [28] G.N. Rallis, V.A. Sakkas, V.A. Boumba, T. Vougiouklakis, T.A. Albanis, Determination  
554 of organochlorine pesticides and polychlorinated biphenyls in post-mortem human lung by  
555 matrix solid-phase dispersion with the aid of response surface methodology and desirability  
556 function, *J. Chromatogr. A* 1227 (2012) 1-9.

557 [29] J. Zhan, J. Li, D. Liu, C. Liu, P. Wang, A simple method for the determination of  
558 organochlorine pollutants and the enantiomers in oil seeds based on matrix solid-phase  
559 dispersion, *Food Chem.* 194 (2016) 319-324.

560 [30] M. Crampon, F. Bureau, M. Akpa-Vinceslas, J. Bodilis, N. Machour, F. Le Derf, F.  
561 Portet-Koltalo, Correlations between PAH bioavailability, degrading bacteria and soil  
562 characteristics during PAH biodegradation in five diffusely contaminated dissimilar soils,  
563 *Environ. Sci. Poll. Res.* 21 (2014) 8133-8145.

564 [31] A. Krueve, A. Künnapas, K. Herodes, I. Leito, Matrix effects in pesticide multi-residue  
565 analysis by liquid chromatography–mass spectrometry, *J. Chromatogr. A* 1187 (2008) 58-66.

566

567 **Figure captions**

568 Figure 1: Influence of the nature of the dispersing agents (Florisil alone, Florisil + C<sub>18</sub> bonded  
569 silica, Florisil + 4-benzylchloride bonded silica, Florisil + 3-chloropropyl bonded silica) on  
570 the mean recovery yields (n=3) of the  $\Sigma_7$ PAHs and  $\Sigma_7$ PCBs spiked on the model sediment  
571 (m=0.5 g sediment, m= 1 g Florisil, m= 0.5 g sorbents, volume of hexane/acetone 50/50 (v/v)  
572 = 10 mL, time of grinding = 5 min).

573

574 Figure 2: Influence of the nature of eluting solvent on the mean recovery yields (n=3) of the  
575  $\Sigma_7$ PAHs and  $\Sigma_7$ PCBs spiked on the model sediment, with V=10 mL (Hex: hexane, DCM:  
576 dichloromethane, Ace: acetone) (m=0.5 g sediment, m= 1 g Florisil, m= 0.5 g 3-chloropropyl  
577 bonded silica, time of grinding = 5 min).

578

579 Figure 3: GC-MS analysis (SIM mode) of PAHs and PCBs extracted from the certified  
580 sediment CNS391 a/ by MAE b/ by MSPD. Numbers make reference to PAHs and PCBs  
581 listed in Table S1 (supplementary materials) or Tables 1, 2, 3, 4.

582

Fig. 1

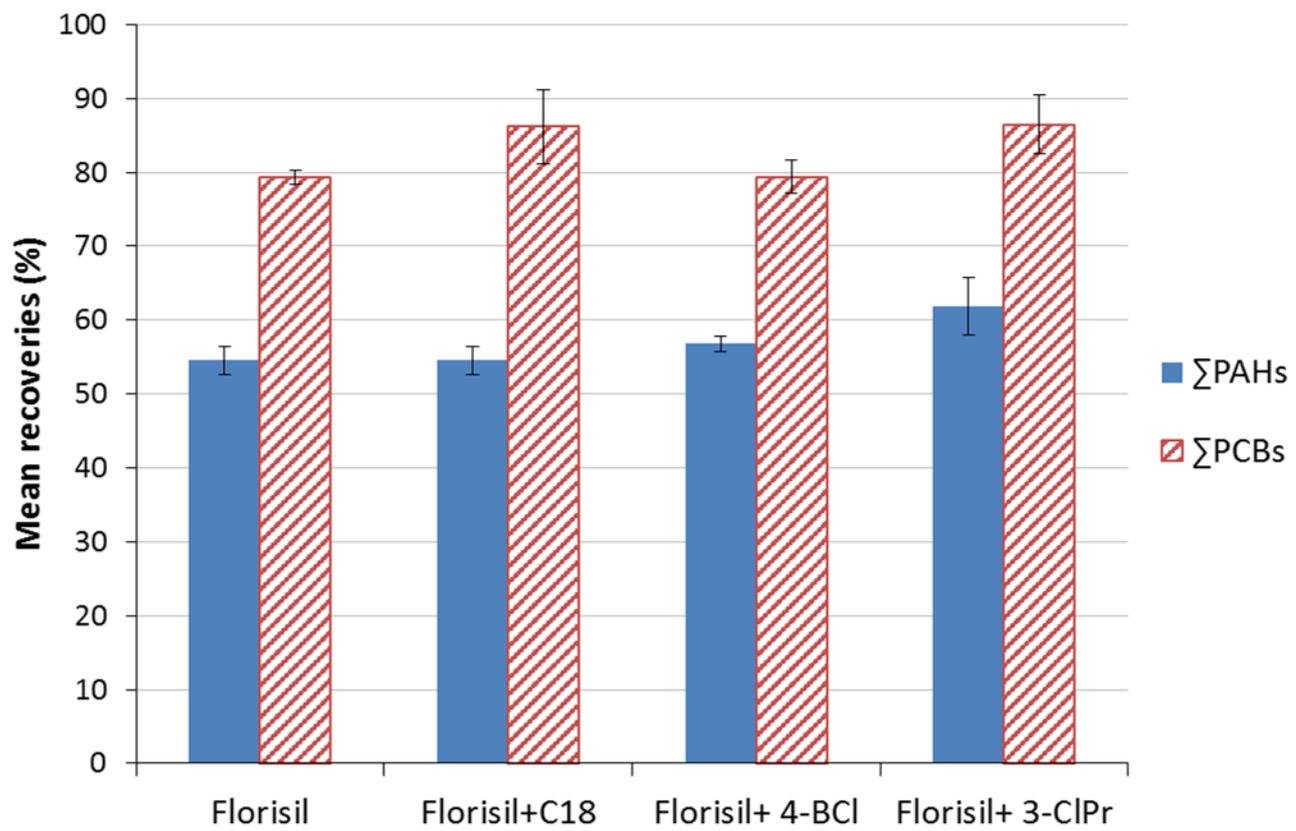


Fig 2

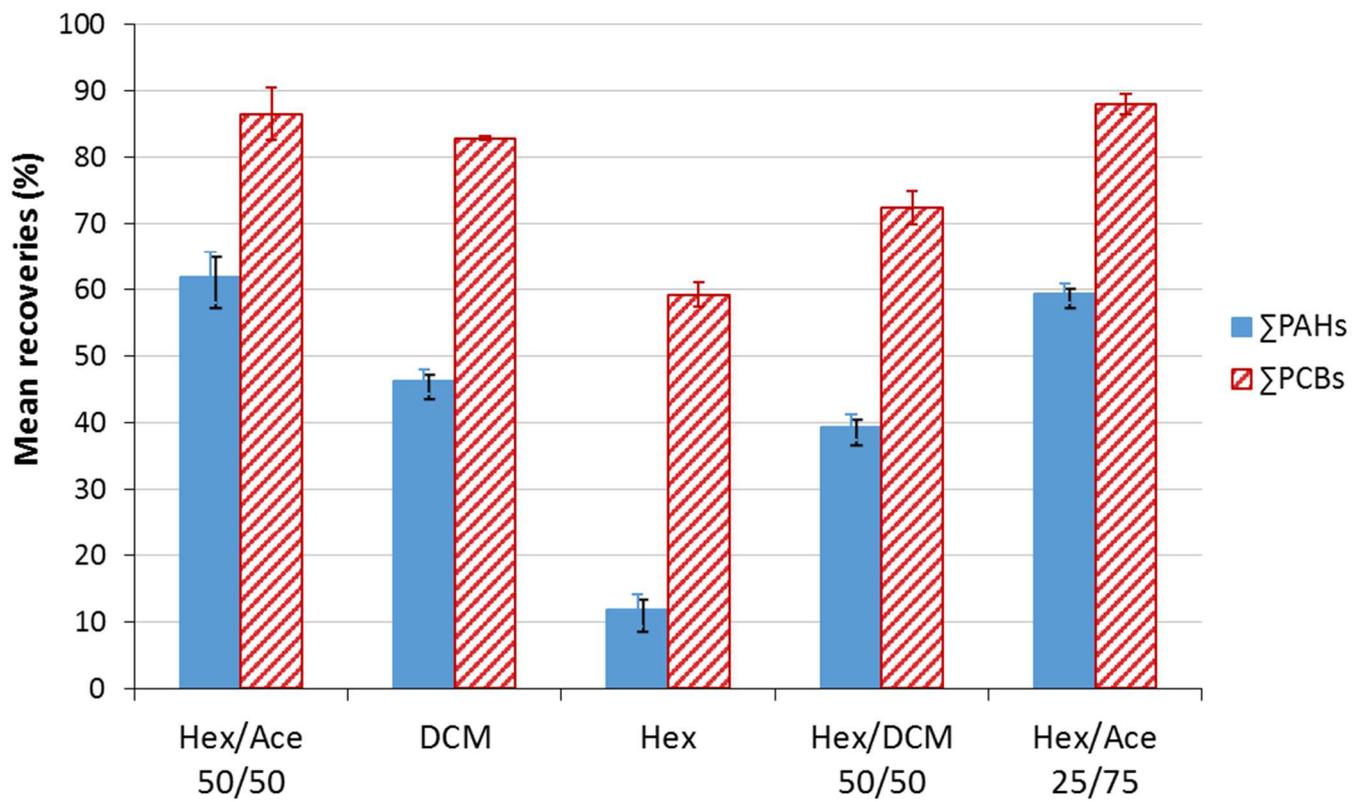
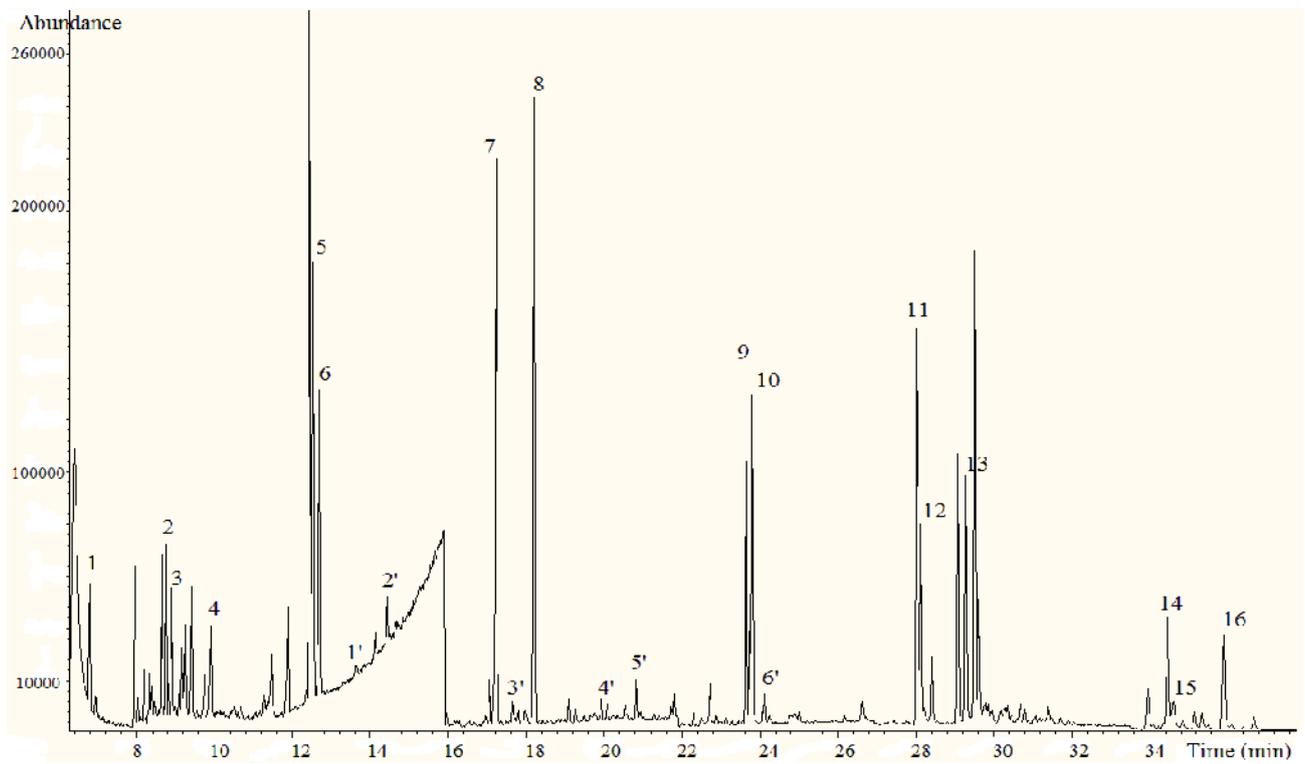


Fig. 3

a



b

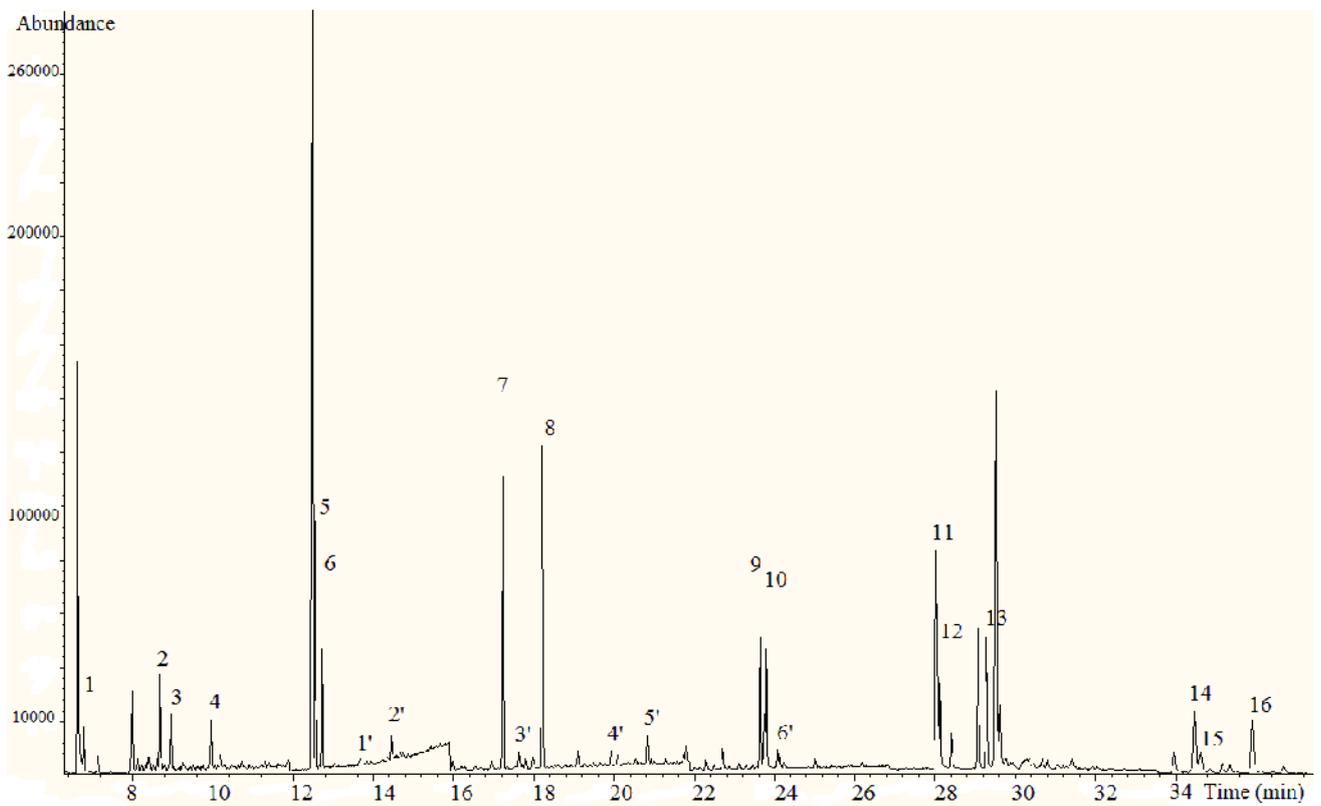


Table 1: Mean recoveries obtained from the MSPD optimized extraction of the spiked model sediment, procedural limits of detection (LOD) compared to literature data, limits of quantification (LOQ) and mean concentrations measured in the non-spiked model sediment (procedural blank).

Compounds (numbered)	Mean recoveries $\pm$ SD (n=5, inter-day studies) (%)	LOD <sup>(a)</sup> (ng g <sup>-1</sup> ) (n=3)	LOD (ng g <sup>-1</sup> ) in literature data	LOQ <sup>(a)</sup> (ng g <sup>-1</sup> ) (n=3)	Mean concentration in model sediment (ng g <sup>-1</sup> ) (n=3)
Naph (n°1)					0.92 $\pm$ 0.07
Ace (n°2)					0.32 $\pm$ 0.03
Acy (n°3)					<i>nd</i> <sup>(b)</sup>
Fluo (n°4)					0.23 $\pm$ 0.08
Phe (n°5)	75 $\pm$ 5	0.08 $\pm$ 0.03	0.05 (c) ; 0.07 (d) ; 0.3 (e)	0.26 $\pm$ 0.08	0.28 $\pm$ 0.48
Ant (n°6)					0.14 $\pm$ 0.06
PCB28 (n°1')	89 $\pm$ 6	0.30 $\pm$ 0.10	8.2 (f) ; 0.031 (g)	0.90 $\pm$ 0.20	<i>nd</i>
PCB52 (n°2')	92 $\pm$ 9	0.50 $\pm$ 0.10	7.9 (f) ; 0.026 (g)	1.50 $\pm$ 0.40	<i>nd</i>
Flt (n°7)	68 $\pm$ 6	0.06 $\pm$ 0.02	0.1 (c) ; 0.6 (d) ; 0.3 (e)	0.19 $\pm$ 0.06	0.34 $\pm$ 0.15
PCB101 (n°3')	93 $\pm$ 7	0.30 $\pm$ 0.10	6.9 (f) ; 0.008 (g)	1.00 $\pm$ 0.20	<i>nd</i>
Pyr (n°8)	66 $\pm$ 6	0.06 $\pm$ 0.02	0.04 (c) ; 0.07 (d) ; 0.2 (e)	0.18 $\pm$ 0.06	<i>nd</i>
PCB153 (n°4')	98 $\pm$ 4	0.40 $\pm$ 0.10	4.5 (f) ; 0.006 (g)	1.30 $\pm$ 0.30	<i>nd</i>
PCB138 (n°5')	121 $\pm$ 12	0.40 $\pm$ 0.10	5.0 (f) ; 0.008 (g)	1.40 $\pm$ 0.30	<i>nd</i>
BaAnt (n°9)					0.21 $\pm$ 0.16
Chry (n°10)					0.16 $\pm$ 0.11
PCB180 (n°6')	106 $\pm$ 10	0.50 $\pm$ 0.20	1.1 (f) ; 0.01 (g)	1.60 $\pm$ 0.50	<i>nd</i>
BbFlt (n°11)	71 $\pm$ 5				0.41 $\pm$ 0.30
BkFlt (n°12)	72 $\pm$ 6	0.18 $\pm$ 0.06	0.004 (c) ; 0.03 (d) ; 0.3 (e)	0.61 $\pm$ 0.20	0.18 $\pm$ 0.10
PCB209 (n°7')	112 $\pm$ 4	1.1 $\pm$ 0.40		3.60 $\pm$ 1.20	<i>nd</i>
BaPyr (n°13)	52 $\pm$ 3	0.22 $\pm$ 0.08	0.007 (c) ; 0.05 (d) ; 0.2 (e)	0.73 $\pm$ 0.24	<i>nd</i>
IPyr (n°14)					<i>nd</i>
DbAnt (n°15)					<i>nd</i>
BPer (n°16)	64 $\pm$ 4				<i>nd</i>

(a) LOD and LOD determined when spiking the model sediment with only 5 PAHs and 7 PCBs.

- (b) *nd*: not detected
- (c) PAHs in soils (HPLC-FLD) [18]
- (d) PAHs in sewage sludge (HPLC-FLD) [27]
- (e) PAHs in dust (GC-MS) [20]
- (f) PCBs in molluscs (GC-MS) [16]
- (g) PCBs in eggs (GC-MS) [26]

Table 2: Mean amounts of 15 PAHs and 6 PCBs in CNS391 certificate and obtained from MSPD and MAE extractions; Deviations compared to the values of the certificate and inter-comparisons between MSPD and MAE extractions.

Compounds (numbered)	CNS391 mean certified values (Prediction interval) (ng g <sup>-1</sup> )	Mean amounts from MSPD (n=5) (ng g <sup>-1</sup> )	Mean amounts from MAE (n=5) (ng g <sup>-1</sup> )	Deviation MSPD vs certified values (%)	Deviation MAE vs certified values (%)	<b>Deviation MSPD vs MAE (%)</b>
Ace (n°2)	29.9 (3.16-56.7)	49.9±5.5	13.6±2.6	+66.9	-54.5	<b>+267</b>
Acy (n°3)	53.4 (8.35-98.4)	73.7±14.5	68.1±6.4	+38.0	+27.5	<b>+8.2</b>
Fluo (n°4)	409.0 (248-568)	229.7±20.3	116.4±6.8	-43.8	-71.5	<b>+97.3</b>
Phe (n°5)	660.0 (529-791)	830.5±81.2	648.4±19.6	+25.8	-1.8	<b>+21.9</b>
Ant (n°6)	15.0 (1.02-29.0)	33.3±2.4	31.9±2.2	+122	+112.7	<b>+4.2</b>
PCB28 (n°1')	44.9 (31.1-58.7)	52.1±1.1	47.8±1.9	+16.0	+6.5	<b>+8.3</b>
PCB52 (n°2')	64.6 (47.0-82.2)	78.4±6.8	77.8±4.0	+21.4	+20.4	<b>+0.8</b>
Flt (n°7)	557.0 (443-671)	581.5±19.1	526.7±15.8	+4.4	-5.4	<b>+9.4</b>
PCB101 (n°3')	45.7 (32.7-58.7)	58.6±4.1	49.4±4.0	+28.2	+8.1	<b>+15.7</b>
Pyr (n°8)	331.0 (211-451)	132.5±6.2	139.4±7.3	-60.0	-57.9	<b>-5.2</b>
PCB153 (n°4')	50.1 (34.8-65.4)	63.2±10.1	54.6±2.3	+26.1	+9.0	<b>+13.6</b>
PCB138 (n°5')	34.6 (18.8-50.4)	46.2±4.5	42.0±3.5	+33.5	+21.4	<b>+9.1</b>

BaAnt (n°9)	338.0 (237-439)	169.0±5.0	167.4±7.5	-50.0	-50.5	<b>+1.0</b>
Chry (n°10)	376.0 (326-426)	355.1±11.2	358.8±14.7	-5.5	-4.6	<b>-1.0</b>
PCB180 (n°6')	54.7 (42.2-67.2)	78.8±8.5	48.2±1.6	+44.0	-11.9	<b>+63.5</b>
BbFlt (n°11)	210.0 (114-353)	182.7±7.9	192.2±8.2	-13.0	-8.5	<b>-4.9</b>
BkFlt (n°12)	300.0 (256-344)	307.0±12.8	298.8±14.0	+2.3	-0.4	<b>+2.7</b>
BaPyr (n°13)	38.2 (0-80.8)	53.1±7.1	13.6±6.5	+39.0	-64.4	<b>+74.4</b>
IPyr (n°14)	235.0 (189-281)	154.6±9.6	179.9±5.6	-34.2	-23.4	<b>-14.1</b>
DbAnt (n°15)	294.0 (248-340)	207.5±12.9	256.9±12.4	-29.4	-12.6	<b>-19.2</b>
BPer (n°16)	139.0 (101-177)	54.4±3.2	51.3±3.3	-60.8	-63.1	<b>+5.7</b>
<b>Σ<sub>15</sub> PAHs</b>	<b>3985</b>	<b>3415 ± 205</b>	<b>3063 ± 158</b>	<b>-14.3</b>	<b>-23.1</b>	<b>+10.3</b>
<b>Σ<sub>6</sub> PCBs</b>	<b>295</b>	<b>377 ± 29</b>	<b>320 ± 17</b>	<b>+28.1</b>	<b>+8.6</b>	<b>+15.2</b>

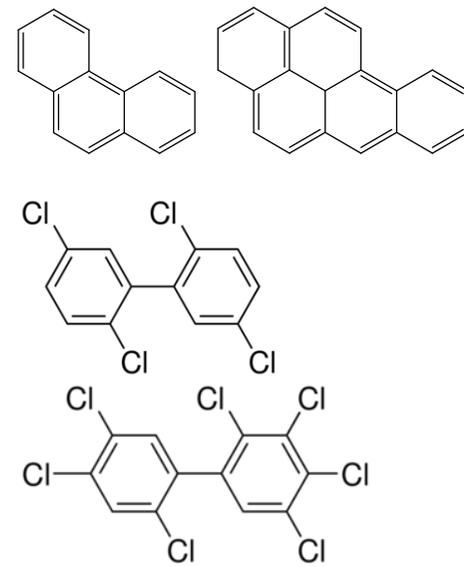
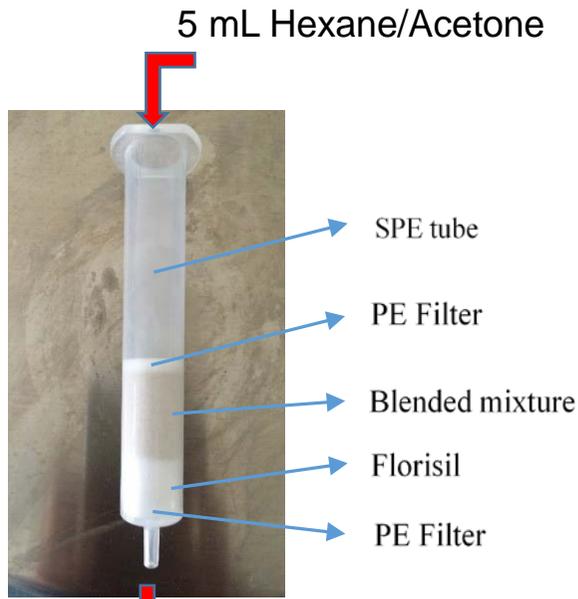
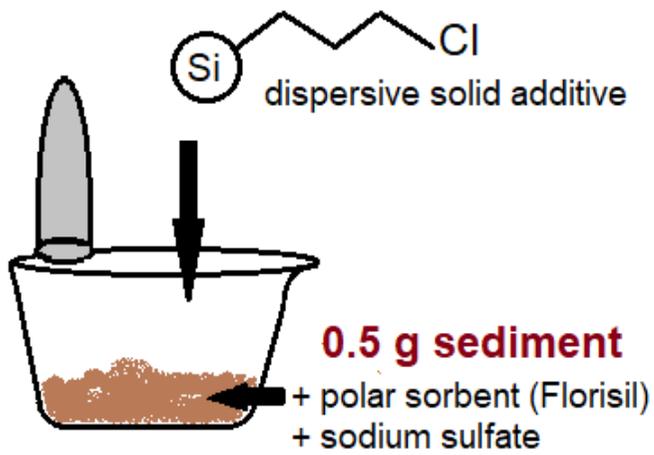
Table 3: Slopes of the internal calibration curves and matrix effects ME (%) after MSPD or MAE extractions of spiked CNS391 certified sediment.

Compounds (numbered)	Slopes for standard solutions	Slopes for spiked CNS391 and ME% (MSPD extraction)	Slopes for spiked CNS391 and ME% (MAE extraction)
Naph (n°1)	0.804	0.644 (-20.0%)	0.421 (-47.7%)
Ace (n°2)	1.371	1.239 (-9.6%)	1.187 (-13.4%)
Acy (n°3)	1.107	0.898 (-18.9%)	0.843 (-23.8%)
Fluo (n°4)	1.288	1.141 (-11.4%)	1.087 (-15.7%)
Phe (n°5)	1.042	0.885 (-15.1%)	0.770 (-26.2%)
Ant (n°6)	1.056	0.793 (-24.9%)	0.833 (-21.1%)
PCB28 (n°1')	0.893	0.712 (-20.3%)	0.655 (-26.7%)
PCB52 (n°2')	0.465	0.401 (-13.9%)	0.360 (-22.7%)
Flt (n°7)	1.330	1.055 (-20.6%)	0.911 (-31.5%)
PCB101 (n°3')	0.610	0.533 (-12.6%)	0.483 (-20.9%)
Pyr (n°8)	1.351	1.149 (-14.9%)	1.042 (-22.9%)
PCB153 (n°4')	0.875	0.776 (-11.3%)	0.743 (-15.1%)
PCB138 (n°5')	0.794	0.709 (-10.8%)	0.598 (-24.8%)
BaAnt (n°9)	1.180	0.971 (-17.7%)	0.912 (-22.7%)
Chry (n°10)	1.068	0.896 (-16.1%)	0.806 (-24.5%)
PCB180 (n°6')	1.547	1.147 (-25.9%)	1.175 (-24.0%)
BbFlt (n°11)	2.935	2.111 (-28.1)	2.085 (-29.0%)
BkFlt (n°12)	2.795	1.991 (-28.8%)	1.878 (-32.8%)
PCB209 (n°7')	2.048	1.554 (-24.1)	1.587 (-22.5%)
BaPyr (n°13)	2.47	1.648 (-33.3)	1.819 (-26.4%)
IPyr (n°14)	2.984	2.183 (-26.8%)	2.083 (-30.2%)
DbAnt (n°15)	2.765	1.982 (-28.3%)	1.883 (-31.9%)
BPer (n°16)	2.828	2.059 (-27.2)	2.175 (-23.1%)
<b>Mean ME (16 PAHs)</b>		<b>-20.9%</b>	<b>-26.1%</b>
<b>Mean ME (7 PCBs)</b>		<b>-17.0%</b>	<b>-22.4%</b>

Table 4: Comparison of the mean amounts of the 16 PAHs and 6 PCBs obtained (i) from MSPD extractions and from the certificates of the two certified materials and (ii) from MSPD and MAE extractions of the Tancarville sediment.

Compounds (numbered)	BCR-536		SETOC-717		Tancarville sediment	
	Mean amounts from certificate ( $\pm$ SD) ( $\text{ng g}^{-1}$ ) (n=6-14)	Mean amounts from MSPD ( $\pm$ SD) ( $\text{ng g}^{-1}$ ) (n=5)	Mean amounts from certificate ( $\pm$ SD) ( $\text{ng g}^{-1}$ ) (n>39)	Mean amounts from MSPD ( $\pm$ SD) ( $\text{ng g}^{-1}$ ) (n=5)	Mean amounts from MAE ( $\pm$ SD) ( $\text{ng g}^{-1}$ ) (n=5)	Mean amounts from MSPD ( $\pm$ SD) ( $\text{ng g}^{-1}$ ) (n=5)
Naph (n°1)			60.0	30.4 $\pm$ 5.8	23.4 $\pm$ 0.9	75.2 $\pm$ 1.6
Ace (n°2)			20.0 $\pm$ 9.3	49.6 $\pm$ 16.9	14.6 $\pm$ 3.0	34.5 $\pm$ 2.4
Acy (n°3)			16.0	51.6 $\pm$ 22.2	5.7 $\pm$ 0.8	35.6 $\pm$ 1.5
Fluo (n°4)			28.5 $\pm$ 13.0	34.5 $\pm$ 4.5	13.7 $\pm$ 1.1	27.8 $\pm$ 1.1
Phe (n°5)			131.0 $\pm$ 35.7	361.0 $\pm$ 28.9	63.2 $\pm$ 1.6	191.3 $\pm$ 5.2
Ant (n°6)			44.6 $\pm$ 16.8	32.1 $\pm$ 7.1	49.5 $\pm$ 0.5	38.2 $\pm$ 1.4
PCB28 (n°1')	44.0 $\pm$ 5.0	40.0 $\pm$ 4.4	1.8	4.2 $\pm$ 1.7	4.4 $\pm$ 0.1	7.4 $\pm$ 0.7
PCB52 (n°2')	38.0 $\pm$ 5.0	65.0 $\pm$ 2.7	2.4 $\pm$ 1.0	7.7 $\pm$ 3.4	5.2 $\pm$ 0.5	16.1 $\pm$ 1.4
Flt (n°7)			283 $\pm$ 65.7	261.8 $\pm$ 57.3	109.3 $\pm$ 5.4	150.0 $\pm$ 8.7
PCB101 (n°3')	44.0 $\pm$ 4.0	39.7 $\pm$ 4.0	3.6 $\pm$ 1.4	6.9 $\pm$ 2.1	22.9 $\pm$ 3.6	15.5 $\pm$ 1.2
Pyr (n°8)			229.0 $\pm$ 65.0	157.5 $\pm$ 36.4	102.7 $\pm$ 5.3	146.9 $\pm$ 9.9
PCB153 (n°4')	50.0 $\pm$ 4.0	52.5 $\pm$ 5.6	5.0 $\pm$ 1.6	10.5 $\pm$ 5.0	15.8 $\pm$ 0.9	36.3 $\pm$ 2.4
PCB138 (n°5')	27.0 $\pm$ 5.0	27.2 $\pm$ 4.0	4.6 $\pm$ 1.5	7.4 $\pm$ 4.0	18.2 $\pm$ 0.5	36.5 $\pm$ 1.6
BaAnt (n°9)			128.0 $\pm$ 33.02	104.1 $\pm$ 32.9	71.8 $\pm$ 2.7	91.5 $\pm$ 2.0
Chry (n°10)			125.0 $\pm$ 42.3	113.5 $\pm$ 38.3	56.4 $\pm$ 2.6	74.0 $\pm$ 0.6
PCB180 (n°6')	22.4 $\pm$ 2.1	63.1 $\pm$ 11.4	3.0 $\pm$ 1.0	8.3 $\pm$ 2.7	45.4 $\pm$ 2.3	63.2 $\pm$ 2.1
BbFlt (n°11)			198.0 $\pm$ 55.1	254.0 $\pm$ 57.7	106.0 $\pm$ 5.3	160.1 $\pm$ 3.7
BkFlt (n°12)			90.8 $\pm$ 21.0	104.3 $\pm$ 21.5	32.2 $\pm$ 0.8	48.6 $\pm$ 2.4
BaPyr (n°13)			126.0 $\pm$ 35.8	204.8 $\pm$ 59.2	59.1 $\pm$ 6.3	81.0 $\pm$ 7.7

IPyr (n°14)			131.0±44.2	114.7±33.8	4.2±0.9	5.6±0.4
DbAnt (n°15)			30.0	38.1±9.1	65.9±5.3	94.6±1.5
BPer (n°16)			114.0±31.4	118.1±43.7	63.6±6.0	91.0±4.9
<b>Σ<sub>16</sub> PAHs</b>	-	-	<b>1755</b>	<b>2001 ± 382</b>	<b>841 ± 40</b>	<b>1346 ± 56</b>
<b>Σ<sub>6</sub> PCBs</b>	<b>225</b>	<b>288 ± 19</b>	<b>20</b>	<b>43 ± 8</b>	<b>112 ± 4</b>	<b>175 ± 4</b>



- ↗ **PCB + PAH extraction**
- ↗ **Purification**
- ↘ **Environmental matrix + solvent volumes**