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

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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^{-1} and 0.3-1.1 ng g^{-1} 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

1. Introduction

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

Nowadays, faster, low cost, less complicated processes and among all, multi-residual sample treatment methods are required to increase analytical throughputs. So matrix solid phase dispersive (MSPD) extraction has been regarded for the past few years as an interesting 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_{18} 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

4

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 µm particulate diameter (d_p), 6 nm pore diameter)

106   and 4-benzylchloride functionalized silica (d_p= 37-74 µm, 6 nm pores) were provided by

107   Sigma-Aldrich (Saint-Quentin-Fallavier, France). Sepra Florisil (d_P=180 µm, 8.5 nm pores),

108   Sepra silica gel (d_p=50 µm, 6.5 nm pores) and Sepra C_{18} bonded silica (d_p=50 µm, 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^{-1} in acetone. A solution containing the 16 priority PAHs (defined by US-

117   EPA, Table S1 in supplementary materials) at 2000 mg L^{-1} and a solution of 7 PCBs (PCB28,

118   PCB52, PCB101, PCB138, PCB153, PCB180, PCB209) at 10 mg L^{-1}, 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

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

2.2 Extraction procedures

2.2.1 Matrix solid phase dispersive extraction

Dry sediment (0.5 g) was spiked with 15 µL of the three SS (at 100 mg L^{-1}) and 1 g sodium sulfate was added. 1 g Florisil and 0.5 g of the best dispersing agent (3-chloropropyl-bonded silica particles) were added and the mixture was ground with a pestle for 10 min. A co-column containing 1 g Florisil was introduced at the bottom of a 12 mL polypropylene SPE tube with a polyethylene frit (20 µm) (Phenomenex) and the solid mixture, blended previously, was put 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 µL 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 µL of the three

157   SS (at 100 mg L^{-1}) 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 µm) from Fisher Scientific (Illkirch,

160   France). Thereafter, the extracts were evaporated to dryness (after adding 60 µL 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 µL of the two IS were added to 990 µL 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 µL 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×0.25 mm i.d.×0.25 µm film thickness) from Phenomenex. The oven program started at

170   60°C (1.2 min) to 190°C (at 40°C min^{-1}) followed by an increase to 240°C (at 4°C min^{-1}) and

171   finally to 305°C (at 6°C min^{-1}) during 12 min, under a constant carrier gas flow of 1.4 mL

172   min^{-1}. 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^{-1}, 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^{-1} for PAHs and 0.4-0.8 µg L^{-1} 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^{-1} for PAHs and 1.3-2.6 µg L^{-1} 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^{-1} 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_{18} 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 π/π 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_{18} grafts. Fig. 1 shows the

225 mean recovery yields (n=3) obtained for the sum of the 7 PAHs (Σ_7PAHs) and the 7 PCBs

226 (Σ_7PCBs) extracted from the spiked model sediment, comparing the effects of Florisil alone,

227 or in combination with C_{18}-, 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 Σ_7PAHs and

230 from 79±1% to 87±4% for the Σ_7PCBs (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_{18} 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_{18}-bonded silica particles was significant for the Σ_7PAHs (62±4% *vs* 55±2%, p=0.044) while

238 it was not significant for the Σ_7PCBs (87±4% *vs* 86±5%, p>0.05). Individually, adding 3-

239 ClPr-functionalized particles to Florisil rather than C_{18} 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±2% and 39±2% for the Σ_7PAHs,

252   respectively, and 59±2% and 72±3% for the Σ_7PCBs, respectively. Pure dichloromethane was

253   appropriate for eluting PCBs (83±1%) but not for PAHs (46±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±2%

269   could be reached for the Σ_7PAH and 109±2% for the Σ_7PCBs. 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 Σ_7PAHs and Σ_7PCBs, 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 Σ_7PAHs and Σ_7PCBs 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±2% for FltD10,

287 97±3% for BaPyrD12 and 105±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^{-1} (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^{-1} (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±3% (instead of 67±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 Σ_{15}PAHs (3415 ng g^{-1}) obtained from MSPD was lower than that mentioned on the CNS391 sediment certificate (3985 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±4% and 88±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 Σ_{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±4% and 92±8% recoveries for FltD10 and BaPyrD12, respectively. The

14

348   total amount of the Σ_{15}PAHs (3063 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 Σ_{15}PAHs using MAE (77%) was less satisfactory

355   than MSPD (86%).

356   Table 2 shows that the total amount of the Σ_6PCBs (PCB209 was not considered here, because

357   it is generally missing from naturally contaminated sediments), extracted by MSPD (377 ng g^{-1}

358     $^{-1}$), was much higher than the total amount listed in the certificate (295 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±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±8% recovery. Compared to the values of the certificate, the mean

368   extraction level of the Σ_6PCBs 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 v*s*

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 µm),

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±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±7%, 115±5% and 91±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 µm) (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

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. Mouteira, 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. Kruve, 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_{18} bonded

569 silica, Florisil + 4-benzylchloride bonded silica, Florisil + 3-chloropropyl bonded silica) on

570 the mean recovery yields (n=3) of the Σ_7PAHs and Σ_7PCBs 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 Σ_7PAHs and Σ_7PCBs 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.
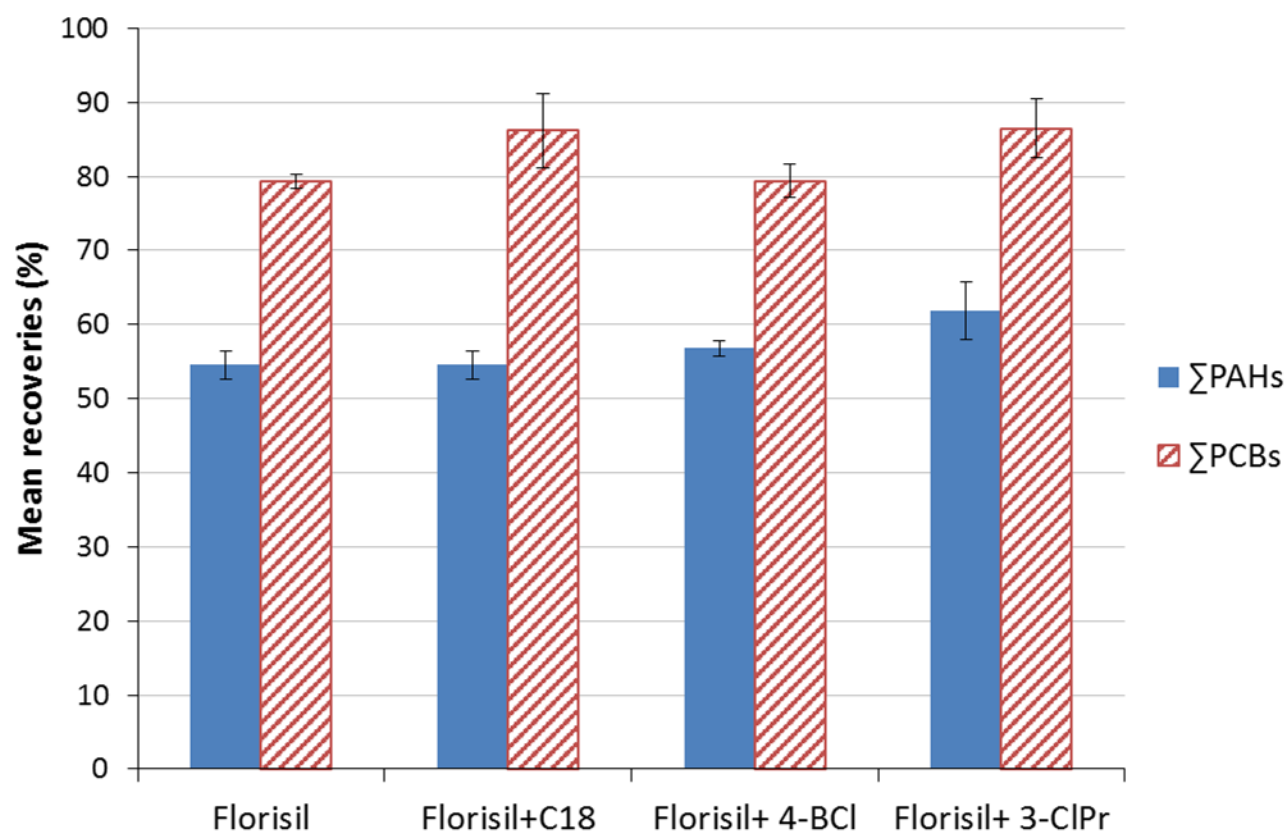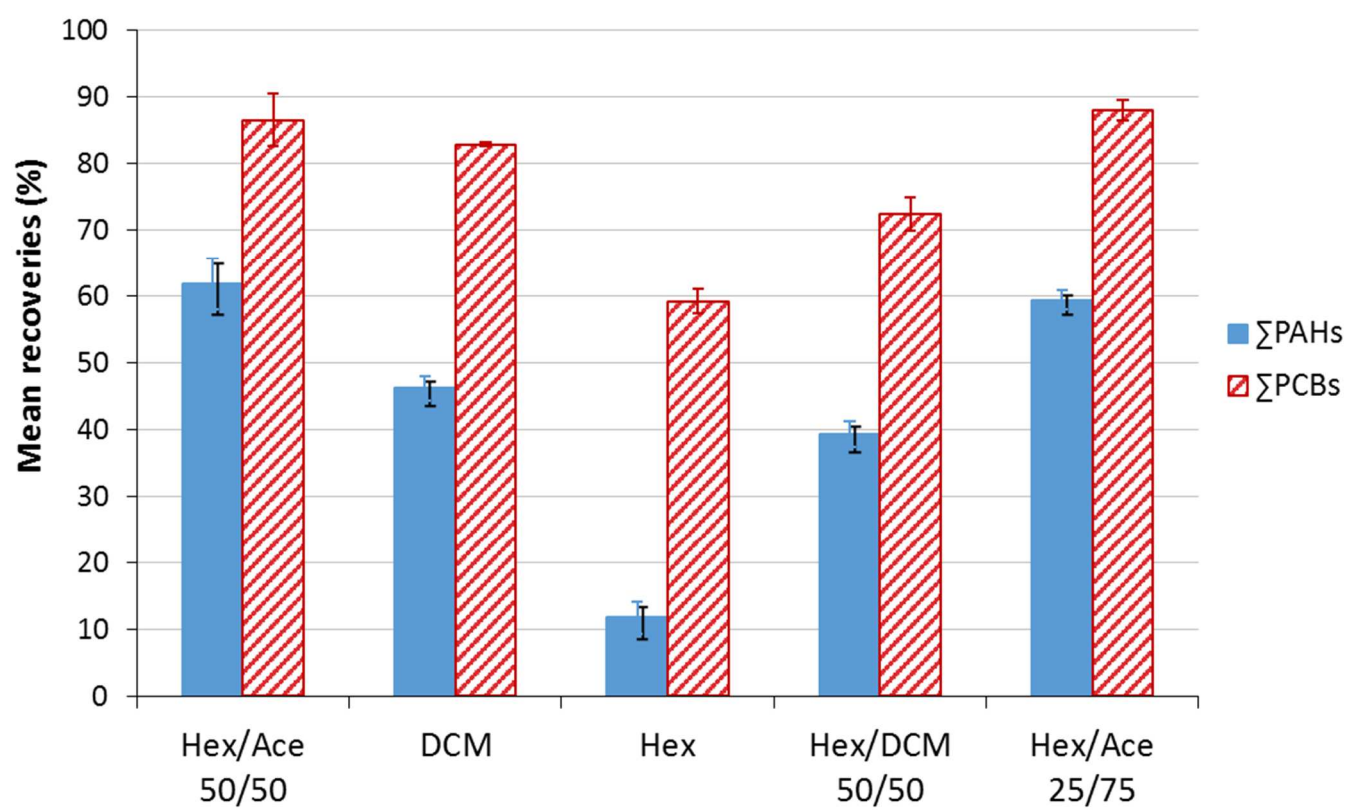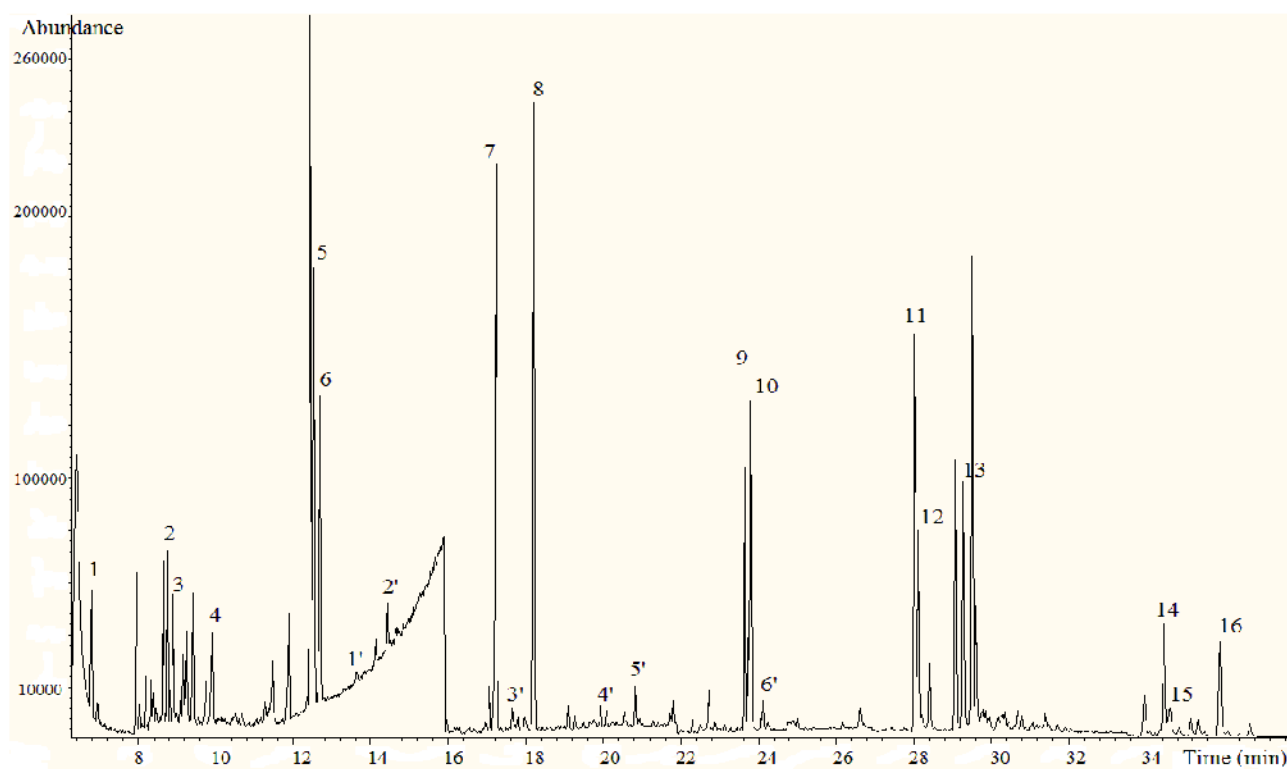
582

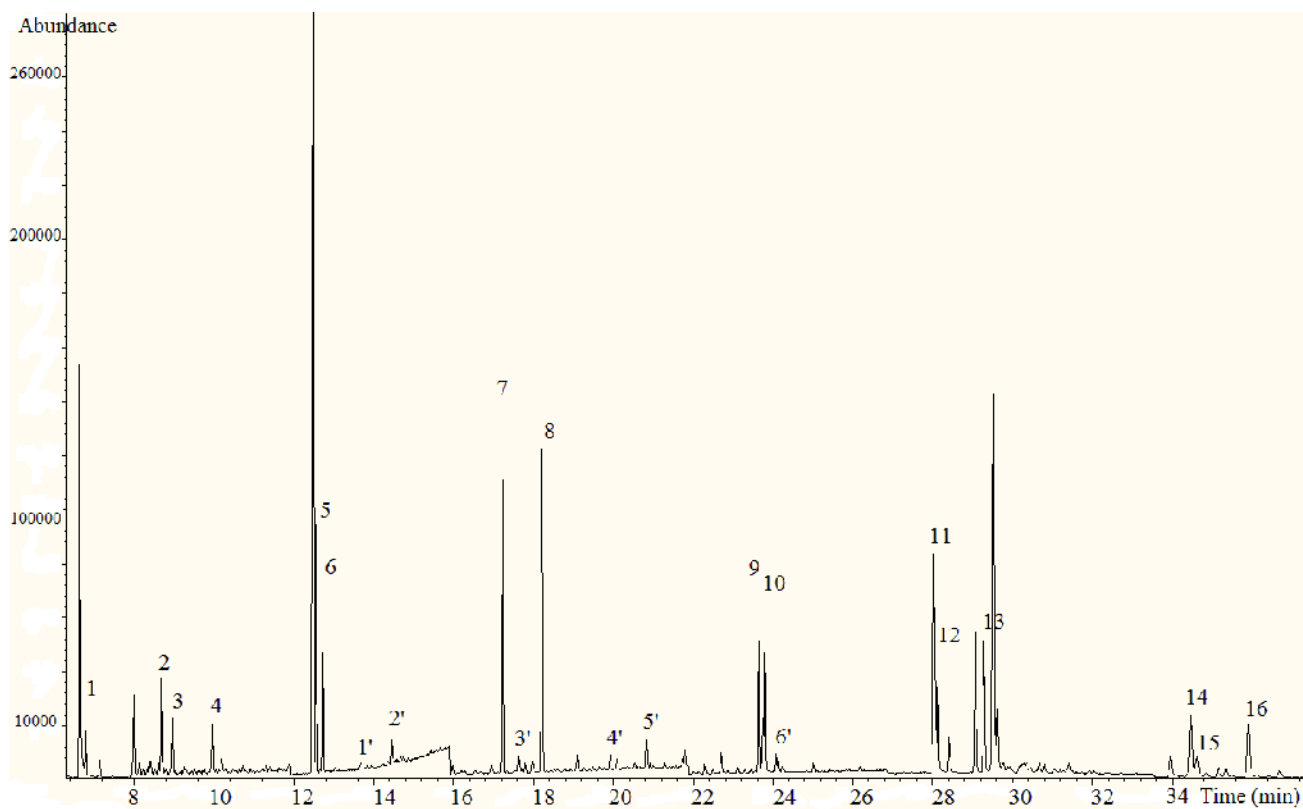Fig. 1

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

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

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

Table 3: Slopes of the internal calibration curves and matrix effects ME (%) after MSPD or MAE extractions of spiked CNS391 certified sediment.
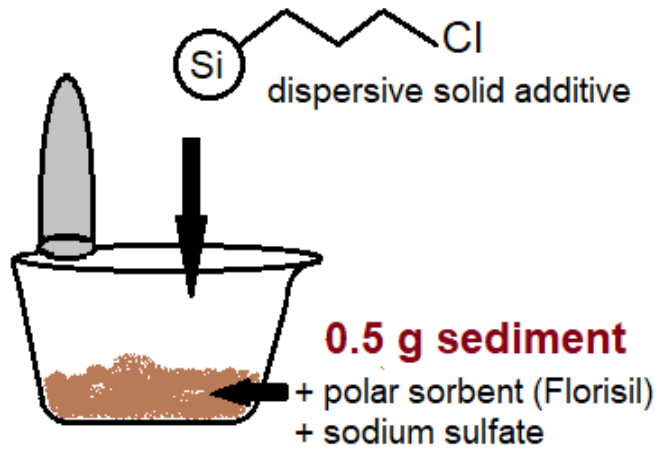
Compounds (numbered)	Slopes for standard solutions	Slopes for spiked CNS391 and ME% (MSPD extraction)	Slopes for spiked CNS391 and ME% (MAE extraction)
Naph (n°1)	0.804	0.644 (-20.0%)	0.421 (-47.7%)
Ace (n°2)	1.371	1.239 (-9.6%)	1.187 (-13.4%)
Acy (n°3)	1.107	0.898 (-18.9%)	0.843 (-23.8%)
Fluo (n°4)	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%)
Mean ME (16 PAHs)		**-20.9%**	**-26.1%**
Mean ME (7 PCBs)		**-17.0%**	**-22.4%**

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 (± SD) (ng g^{-1}) (n=6-14)	Mean amounts from MSPD (± SD) (ng g^{-1}) (n=5)	Mean amounts from certificate (± SD) (ng g^{-1}) (n>39)	Mean amounts from MSPD (± SD) (ng g^{-1}) (n=5)	Mean amounts from MAE (± SD) (ng g^{-1}) (n=5)	Mean amounts from MSPD (± SD) (ng g^{-1}) (n=5)
Naph (n°1)			60.0	30.4±5.8	23.4±0.9	75.2±1.6
Ace (n°2)			20.0±9.3	49.6±16.9	14.6±3.0	34.5±2.4
Acy (n°3)			16.0	51.6±22.2	5.7±0.8	35.6±1.5
Fluo (n°4)			28.5±13.0	34.5±4.5	13.7±1.1	27.8±1.1
Phe (n°5)			131.0±35.7	361.0±28.9	63.2±1.6	191.3±5.2
Ant (n°6)			44.6±16.8	32.1±7.1	49.5±0.5	38.2±1.4
PCB28 (n°1')	44.0±5.0	40.0±4.4	1.8	4.2±1.7	4.4±0.1	7.4±0.7
PCB52 (n°2')	38.0±5.0	65.0±2.7	2.4±1.0	7.7±3.4	5.2±0.5	16.1±1.4
Flt (n°7)			283±65.7	261.8±57.3	109.3±5.4	150.0±8.7
PCB101 (n°3')	44.0±4.0	39.7±4.0	3.6±1.4	6.9±2.1	22.9±3.6	15.5±1.2
Pyr (n°8)			229.0±65.0	157.5±36.4	102.7±5.3	146.9±9.9
PCB153 (n°4')	50.0±4.0	52.5±5.6	5.0±1.6	10.5±5.0	15.8±0.9	36.3±2.4
PCB138 (n°5')	27.0±5.0	27.2±4.0	4.6±1.5	7.4±4.0	18.2±0.5	36.5±1.6
BaAnt (n°9)			128.0±33.02	104.1±32.9	71.8±2.7	91.5±2.0
Chry (n°10)			125.0±42.3	113.5±38.3	56.4±2.6	74.0±0.6
PCB180 (n°6')	22.4±2.1	63.1±11.4	3.0±1.0	8.3±2.7	45.4±2.3	63.2±2.1
BbFlt (n°11)			198.0±55.1	254.0±57.7	106.0±5.3	160.1±3.7
BkFlt (n°12)			90.8±21.0	104.3±21.5	32.2±0.8	48.6±2.4
BaPyr (n°13)			126.0±35.8	204.8±59.2	59.1±6.3	81.0±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
Σ_{16} PAHs	**-**	**-**	**1755**	**2001 ± 382**	**841 ± 40**	**1346 ± 56**
Σ_{6} PCBs	**225**	**288 ± 19**	**20**	**43 ± 8**	**112 ± 4**	**175 ± 4**

5 mL Hexane/Acetone

Si — dispersive solid additive

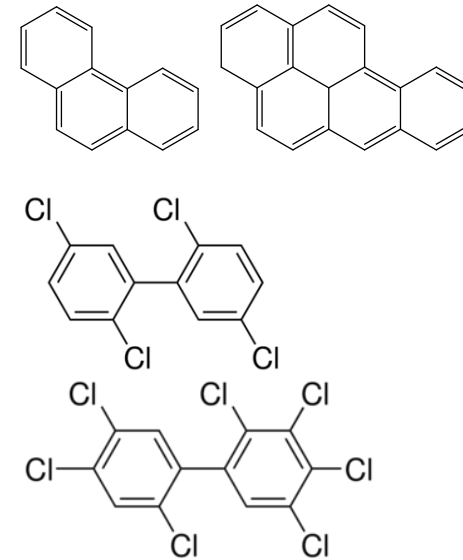0.5 g sediment
+ polar sorbent (Florisil)
+ sodium sulfate

SPE tube
PE Filter
Blended mixture
Florisil
PE Filter

↗ **PCB + PAH extraction**

↗ Purification

↘ Environmental matrix + solvent volumes