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

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Abstract

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

Key words:

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

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,

clean-up and filtration in a single step and reduces drastically the analysis time and the consumption of toxic solvents. MSPD has been developed to extract toxic persistent contaminants such as PAHs, PCBs, organochlorine or organophosphorous compounds more particularly from solid or semi-solid biological samples or fatty foods [12, 14-17]. But methodologies have been also developed for environmental matrices such as soils, sediments or sewage sludges, which are known to accumulate these persistent lipophilic contaminants [10, 11, 18]. MSPD involves the grinding of the solid matrix with dispersing agents, which could be liquids in its original conception but now, solid abrasive particles are used that play two roles [19]. Particles are added to disrupt the sample structure and favour desorption of the lipophilic contaminants from the sample organic matter and re-adsorption on the attracting particles surface; thereafter the lipophilic contaminants are better eluted with appropriate solvent mixtures. Other particles are added to favour adsorption of the polar interfering compounds and prevent their elution, which constitute the purifying step. In general, the most used sorbents for PAHs and PCBs are C₁₈ bonded particles [10, 11, 20, 21] and cleaning sorbents are silica or Florisil particles [18].

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

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

2. Materials and methods

2.1 Chemicals and samples

Hexane, toluene, dichloromethane, acetone, all of HPLC grade, were provided by VWR (Fontenay sous Bois, France). Octan-1-ol (HPLC grade), sodium sulfate (purity >99%), 3-chloropropyl functionalized silica (37-62 μm particulate diameter (d_p), 6 nm pore diameter) and 4-benzylchloride functionalized silica (d_p = 37-74 μm , 6 nm pores) were provided by Sigma-Aldrich (Saint-Quentin-Fallavier, France). Septra Florisil (d_p =180 μm , 8.5 nm pores), Septra silica gel (d_p =50 μm , 6.5 nm pores) and Septra C₁₈ bonded silica (d_p =50 μm , 6.5 nm pores) were furnished by Phenomenex (Le Peck, France).

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

A model sediment was prepared by mixing 73 g silt (collected from surface formations covering the chalk plateau in Normandy, France), 5 g sand (SIKA, Hostun, France), 19.5 g 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 $\mu\text{g g}^{-1}$ dry weight (dw) each PAH) and 5 mL of the solution containing the 7 PCBs (0.5 $\mu\text{g g}^{-1}$ (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

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

2.2.2 Microwave assisted extractions

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

2.3 GC-MS analysis

For GC-MS analyses, 10 μ L of the two IS were added to 990 μ L of the MAE or MSPD extracts. PhenD10 was the IS for PAHs from naphthalene to chrysene and for PCBs, while PerD12 was used for higher molecular weight PAHs. Then 1 μ L of the sample was injected in the splitless mode at 285°C and separated with the column Zebron ZB-SemiVolatiles (60 m length $\times$ 0.25 mm i.d. $\times$ 0.25 μ m film thickness) from Phenomenex. The oven program started at 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 finally to 305°C (at 6°C min⁻¹) during 12 min, under a constant carrier gas flow of 1.4 mL min⁻¹. The temperature of the transfer line was set at 300°C and the detection was conducted

in full SCAN for identification and in selected ion monitoring (SIM) for better sensitivity (Table S1). Calibration curves were established using 6-7 levels of concentrations, from 0.05 to 3 mg L⁻¹, using the internal calibration methodology, and all the correlation coefficients were >0.990. The limits of detection (LOD), calculated as three times the signal-to-noise ratio (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). The limits of quantification (LOQ) calculated as ten times the signal-to-noise ratio (S/N=10) 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 determining matrix effects in GC-MS, the CNS391 certified sediment was spiked with PAHs and PCBs solutions from 0.2 to 3 mg L⁻¹ and extracted by MAE and MSPD (sections 2.2.1 and 2.2.2).

2.3 Statistical analysis

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

3. Results and discussion

3.1 Optimisation of conditions for MSPD extraction from a model sediment

3.1.1 Influence of the nature of dispersing agents

The first step in the optimisation of the MSPD methodology was to find the best combination of additives and dispersing agents introduced in a model sediment spiked with a mixture of 7 PAHs and 7 PCBs. The model sediment, which was of the same mineralogical composition than a real sediment from Tancarville (France) (section 2.1) was used because it could be 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” C₁₈ 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

rings, forces that could increase the attraction between the adsorbate and the adsorbent compared to the London dispersion forces alone developed by the C₁₈ grafts. Fig. 1 shows the mean recovery yields (n=3) obtained for the sum of the 7 PAHs (Σ_7 PAHs) and the 7 PCBs (Σ_7 PCBs) extracted from the spiked model sediment, comparing the effects of Florisil alone, or in combination with C₁₈-, 4-BCl- or 3-ClPr- bonded silica particles. Comparing the use of Florisil alone and the addition of 3-ClPr-functionalized silica, the mean recoveries were significantly increased (p-value=0.044 < 0.05), from 55±2% to 62±4% for the Σ_7 PAHs and from 79±1% to 87±4% for the Σ_7 PCBs (p=0.037). Individually, adding 3-ClPr-functionalized particles to Florisil (compared to Florisil alone) allowed increasing significantly the recoveries of Flt, Pyr, BbFlt, BkFlt, BPer, PCB52, PCB101 and PCB138 (p-values<0.05). Adding C₁₈ bonded particles to Florisil did not significantly favoured the mean extractions of PAHs and PCBs (55±2% and 86±5%, respectively) (p>0.05). Adding 4-BCl-bonded particles to Florisil slightly favoured the mean extractions of PAHs and PCBs (57±1% and 79±2%, respectively), but not significantly (p>0.05). Moreover, the improving effect of 3-ClPr- over C₁₈-bonded silica particles was significant for the Σ_7 PAHs (62±4% vs 55±2%, p=0.044) while it was not significant for the Σ_7 PCBs (87±4% vs 86±5%, p>0.05). Individually, adding 3-ClPr-functionalized particles to Florisil rather than C₁₈ particles allowed increasing significantly the recoveries of Phe, Pyr and BPer (p-values<0.05). Consequently, 3-ClPr-functionalized silica was added to the cleaning sorbent Florisil to improve the simultaneous MSPD extraction of PAHs and PCBs from the sediment matrix.

3.1.2 Influence of the eluting solvent and grinding time

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

analysis, the best solvent had to be found for eluting quantitatively both PAHs and PCBs. Fig 2 shows various tested solvents or solvent mixtures: pure hexane and the mixture hexane/dichloromethane 50/50 (v/v) were the worst solvents for eluting both PAHs and PCBs from the model sediment, with mean recoveries of $12\pm2\%$ and $39\pm2\%$ for the Σ_7 PAHs, respectively, and $59\pm2\%$ and $72\pm3\%$ for the Σ_7 PCBs, respectively. Pure dichloromethane was appropriate for eluting PCBs ($83\pm1\%$) but not for PAHs ($46\pm2\%$). The mixtures containing hexane/acetone 50/50 or 25/75 (v/v) were the best for eluting the two families of compounds, with not significantly different mean recoveries ($p>0.05$). The mixture containing less acetone was chosen in order to limit the elution of polar interfering compounds. The influence of the elution volume on the mean recoveries was also evaluated. Recoveries tended to slightly decrease with the elution volume increase, in the 5-15 mL range (Fig. S1a). Elution with 5 mL of the best solvent mixture was significantly better for PAHs ($p=0.011$) than using 15 mL, or than using 10 mL for PCBs ($p=0.006$).

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

In the optimised conditions with 10 min grinding (section 2.2.1), mean recoveries of $67\pm2\%$ could be reached for the Σ_7 PAH and $109\pm2\%$ for the Σ_7 PCBs. Unlike PCBs, the mean recovery of total PAHs could not be considered quantitative even after the optimisation of MSPD extraction. Indeed a specific degradation of BaPyr after spiking was noted after several weeks of sediment/contaminants equilibration (section 2.1), which was not the case for PCBs.

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

3.2 Performances of the MSPD procedure and comparison with MAE

3.2.1 Performances of the optimised MSPD method

In the optimal conditions, mean recoveries, repeatability (or intra-day precision) and reproducibility (or inter-day precision) of the MSPD method were evaluated by analysing spiked model sediments (n=5). Considering the intra-day study, the mean relative standard deviations (RSD) were 4% and 3% for the Σ_7 PAHs and Σ_7 PCBs, respectively. RSDs were ranging from 2% for BkFlt to 5% for BaPyr and from 2% for PCB28 to 4% for PCB138. Considering the inter-day study (Table 1), the mean RSDs for the Σ_7 PAHs and Σ_7 PCBs were both 7%. RSDs were ranging from 6% for BaPyr to 9% for Flt and from 4% for PCB209 to 10% for PCB138. Mean recoveries of the surrogate standards were $100\pm 2\%$ for FltD10, $97\pm 3\%$ for BaPyrD12 and $105\pm 4\%$ for PCB156 (n=5), that showed that PAHs were better recovered when they were freshly spiked rather than spiked for several weeks.

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

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

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

3.2.3 Comparison of MSPD and MAE extraction methodologies

The optimised MSPD extraction was compared with microwave-assisted extraction (MAE), which has been validated with a certified reference sediment (CRM104) for the extraction of PAHs. Excepting naphthalene, all the PAHs were quantitatively extracted (78-132%) using MAE (Table S3), with a mean recovery of the 16 priority PAHs of 101% compared to the certified values (recently revised in a certificate dated 2017). It can be noted that even if MAE gave excellent results for extracting PAHs from the naturally contaminated CRM104 sediment, it gave significantly lower results ($p=0.01$) than MSPD for extracting the spiked model sediment, with a mean extraction recovery of $59\pm3\%$ (instead of $67\pm2\%$ for MSPD) and recoveries ranging between 45-68% for individual PAHs. As mentioned previously, PAHs were measured 3-5 weeks after they were spiked on the model sediment and they were probably subject to slight biodegradation, and more particularly BaPyr which recovery was the lowest.

The MSPD methodology was then tested on a real sediment, initially the CNS391 reference material. Table 2 gives the recoveries obtained from the MSPD and MAE extraction 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 $100\pm4\%$ and $88\pm9\%$ 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 $99\pm4\%$ and $92\pm8\%$ recoveries for FltD10 and BaPyrD12, respectively. The

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

Table 2 shows that the total amount of the Σ_6 PCBs (PCB209 was not considered here, because it is generally missing from naturally contaminated sediments), extracted by MSPD (377 ng g⁻¹), was much higher than the total amount listed in the certificate (295 ng g⁻¹). The extraction of the PCBs was higher using the MSPD method whatever the PCB, from the less chlorinated (3 Cl) to the more chlorinated (7 Cl), with a mean extraction gain of 28.1% compared to the certified values. The spiked SS PCB156 was quantitatively extracted, with 112±10% recovery. Only one value of PCB (PCB180) did not enter in the interval of prediction of the certified sediment. The results achieved from the extraction of PCBs were compared with the MAE extraction of the reference material, performed in the same conditions than those applied for PAHs. Table 2 shows that results obtained using MAE were higher than those listed in the certificate, with a mean gain of 8.6%. The spiked SS PCB156 was quantitatively extracted, with 100±8% recovery. Compared to the values of the certificate, the mean extraction level of the Σ_6 PCBs using MAE (109%) was less satisfactory than MSPD (128%).

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

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

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

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

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

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

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

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

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

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

Concluding remarks

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

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

Supplementary materials

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

Acknowledgments

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Declarations of interest

None

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566

Figure captions

Figure 1: Influence of the nature of the dispersing agents (Florisil alone, Florisil + C₁₈ bonded silica, Florisil + 4-benzylchloride bonded silica, Florisil + 3-chloropropyl bonded silica) on the mean recovery yields (n=3) of the Σ_7 PAHs and Σ_7 PCBs spiked on the model sediment (m=0.5 g sediment, m= 1 g Florisil, m= 0.5 g sorbents, volume of hexane/acetone 50/50 (v/v) = 10 mL, time of grinding = 5 min).

Figure 2: Influence of the nature of eluting solvent on the mean recovery yields (n=3) of the Σ_7 PAHs and Σ_7 PCBs spiked on the model sediment, with V=10 mL (Hex: hexane, DCM: dichloromethane, Ace: acetone) (m=0.5 g sediment, m= 1 g Florisil, m= 0.5 g 3-chloropropyl bonded silica, time of grinding = 5 min).

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

Fig. 1

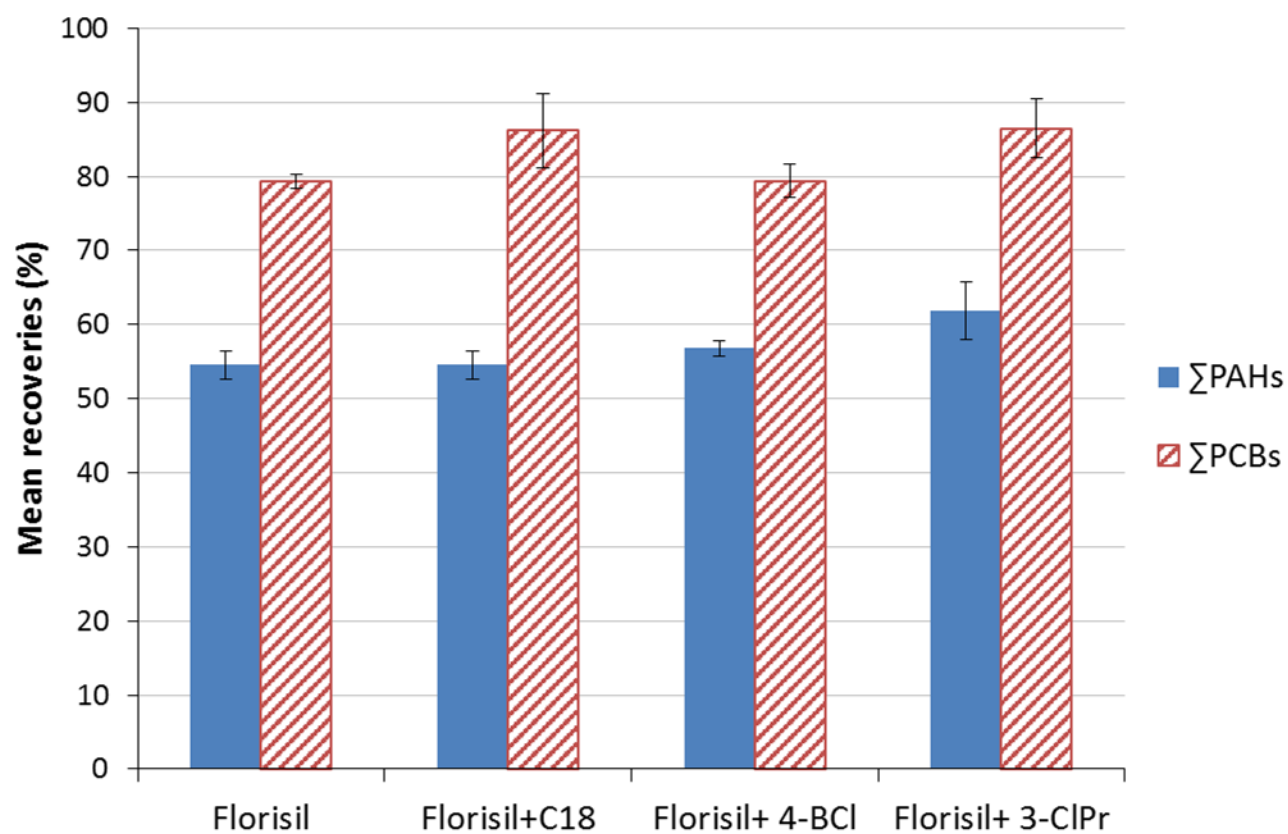


Fig 2

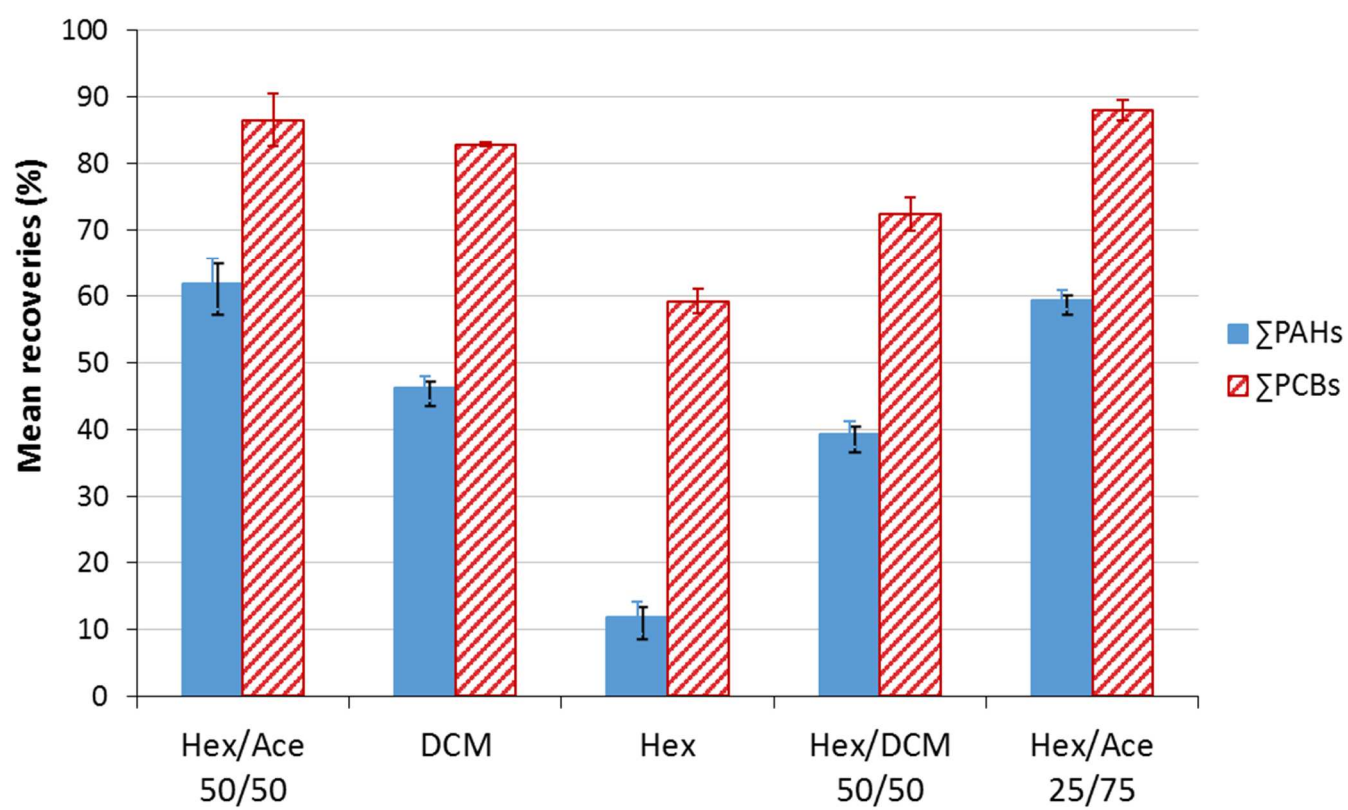
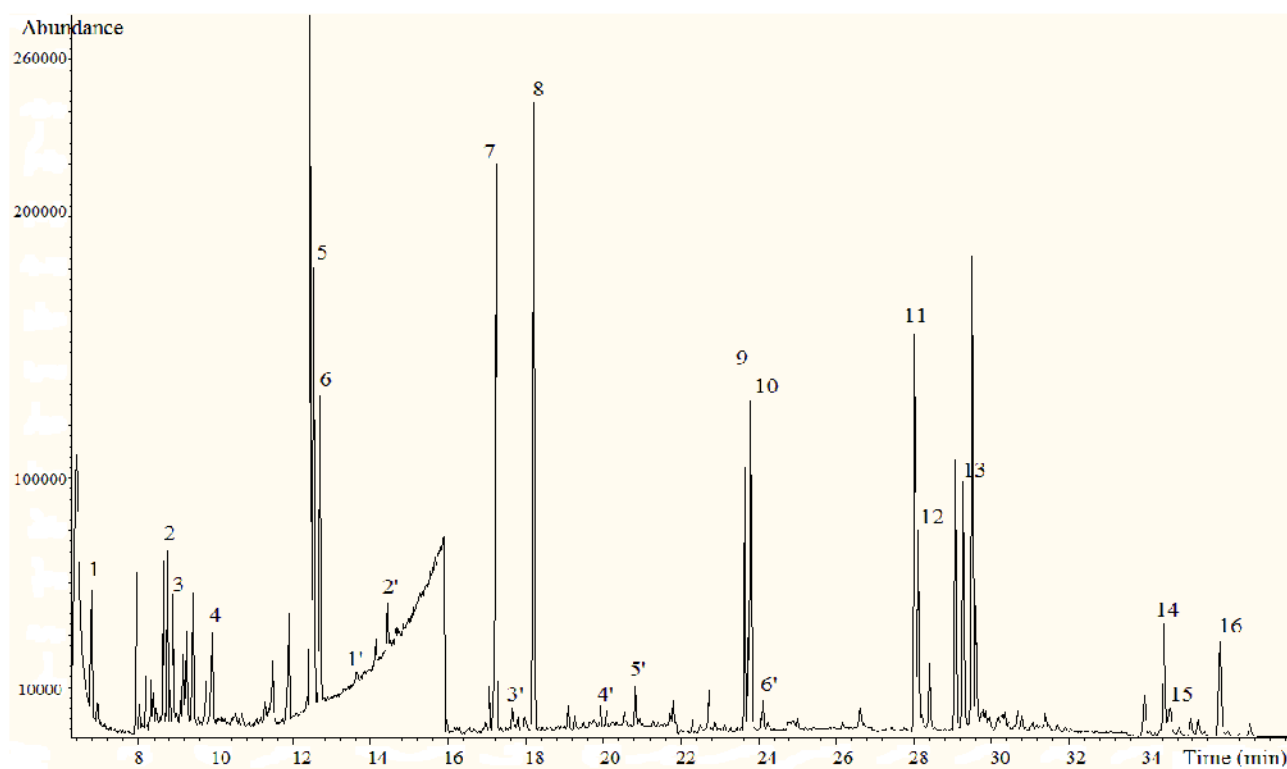


Fig. 3

a



b

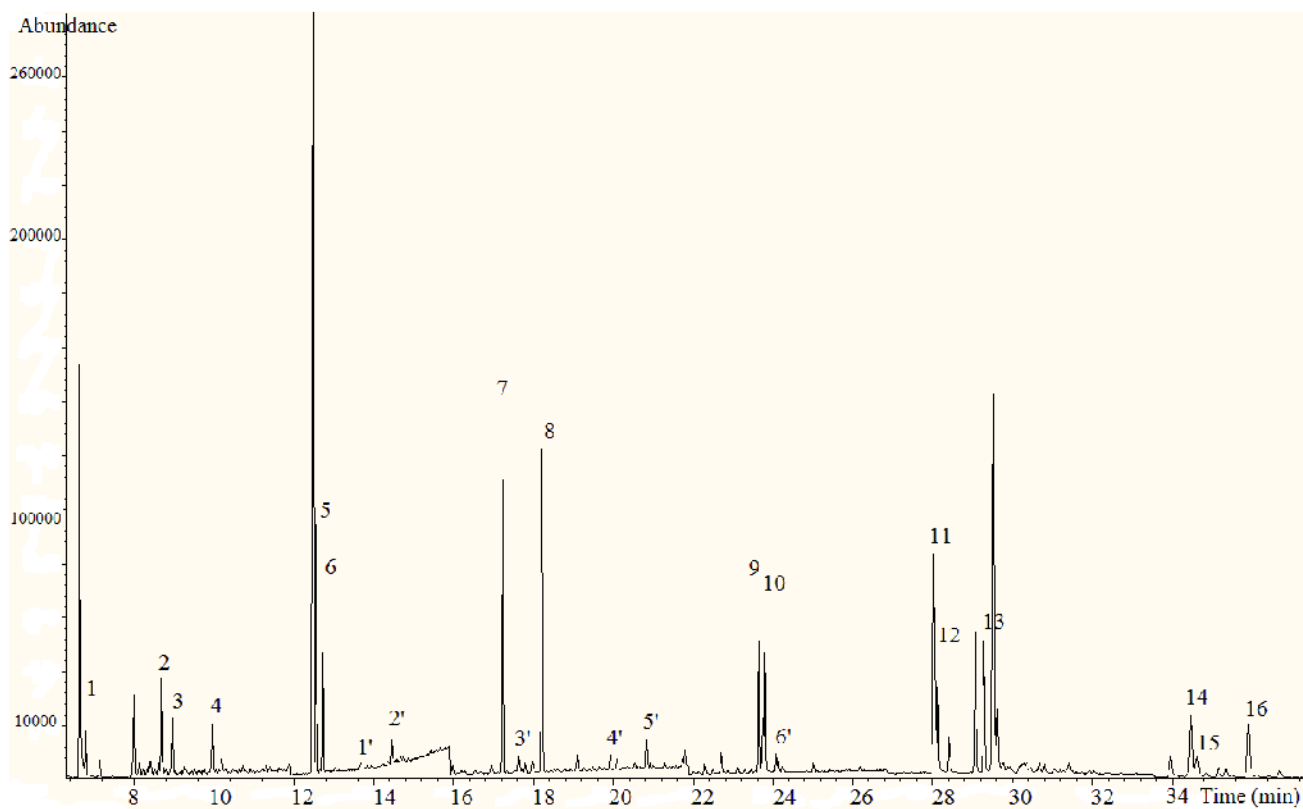


Table 1: Mean recoveries obtained from the MSPD optimized extraction of the spiked model sediment, procedural limits of detection (LOD) compared to literature data, limits of quantification (LOQ) and mean concentrations measured in the non-spiked model sediment (procedural blank).

Compounds (numbered)	Mean recoveries $\pm$ SD (n=5, inter-day studies) (%)	LOD ^(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 $\pm$ 0.07
Ace (n°2)					0.32 $\pm$ 0.03
Acy (n°3)					<i>nd</i> ^(b)
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 ⁻¹)	Mean amounts from MSPD (n=5) (ng g ⁻¹)	Mean amounts from MAE (n=5) (ng g ⁻¹)	Deviation MSPD <i>vs</i> certified values (%)	Deviation MAE <i>vs</i> certified values (%)	Deviation MSPD <i>vs</i> 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
Σ₁₅ PAHs	3985	3415 ± 205	3063 ± 158	-14.3	-23.1	+10.3
Σ₆ 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.

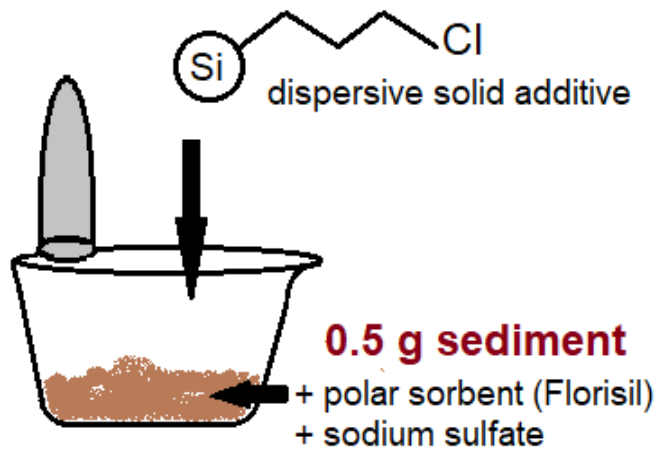
Compounds (numbered)	Slopes for standard solutions	Slopes for spiked CNS391 and ME% (MSPD extraction)	Slopes for spiked CNS391 and ME% (MAE extraction)
Naph (n°1)	0.804	0.644 (-20.0%)	0.421 (-47.7%)
Ace (n°2)	1.371	1.239 (-9.6%)	1.187 (-13.4%)
Acy (n°3)	1.107	0.898 (-18.9%)	0.843 (-23.8%)
Fluo (n°4)	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 ($\pm$ SD) (ng g ⁻¹) (n=6-14)	Mean amounts from MSPD ($\pm$ SD) (ng g ⁻¹) (n=5)	Mean amounts from certificate ($\pm$ SD) (ng g ⁻¹) (n>39)	Mean amounts from MSPD ($\pm$ SD) (ng g ⁻¹) (n=5)	Mean amounts from MAE ($\pm$ SD) (ng g ⁻¹) (n=5)	Mean amounts from MSPD ($\pm$ SD) (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
Σ₁₆ PAHs	-	-	1755	2001 ± 382	841 ± 40	1346 ± 56
Σ₆ PCBs	225	288 ± 19	20	43 ± 8	112 ± 4	175 ± 4

5 mL Hexane/Acetone



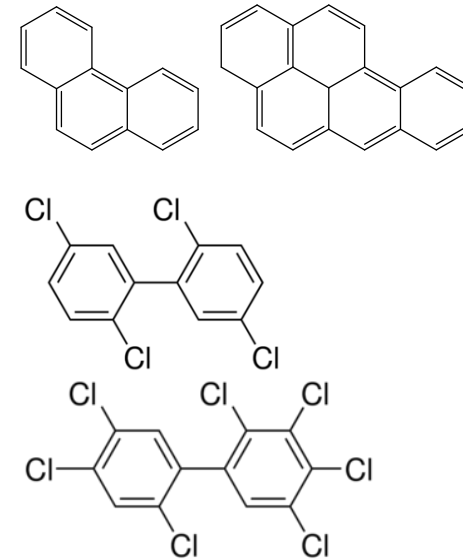
SPE tube

PE Filter

Blended mixture

Florisil

PE Filter



↗ **PCB + PAH extraction**

↗ **Purification**

↘ **Environmental matrix + solvent volumes**