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**Bioaccessibility of polycyclic aromatic compounds (PAHs, PCBs) and trace elements:  
influencing factors and determination in a river sediment core**

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## **Abstract**

Organic matter (OM), clays, sand or time are factors possibly influencing the bioaccessibility of polycyclic aromatic hydrocarbons (PAHs) and polychlorobiphenyls (PCBs) from sediments. **An experimental design was performed to monitor and quantify** this process. The bioaccessible fraction, linked to the rapidly-desorbing fraction ( $F_{rap}$ ) of contaminants, was assessed through a non-exhaustive extraction using a carboxymethyl- $\beta$ -cyclodextrin polymer. OM content was the most influential factor as regards  $F_{rap}$ . Clay percentage was a slightly influential factor for PAHs while the interaction sand $\times$ OM was a slightly influential factor for PCBs.  $F_{rap}$  was also determined in a sediment core collected from Martot's Pond (France). **The higher** the PAH/PCB concentration in **this** sediment, the **higher** the **bioaccessible** fraction. The relationship between a lower bioaccessibility and a higher number of PAHs cycles or PCB chlorines was linear. OM content impacted on  $F_{rap}$  only for PAHs. Sequential extractions of some trace elements were also performed to evaluate their mobility. Cu, Cr, Pb, Ni were the less bioaccessible. A great part of As, Cd and Zn was found in the most bioaccessible sediment fractions. The 40-65 cm section might be considered as the most negatively impacting on the aquatic fauna, due to Cd and Zn high bioaccessible concentrations.

## **Key words**

Bioaccessibility, Organic polyaromatic compounds, Inorganic trace elements, Sediments, Carboxymethyl-cyclodextrin polymer

## 1. Introduction

Soils and sediments are important reservoirs for metal, metalloids and persistent organic lipophilic contaminants that can lead to various toxic reactions for living organisms. It is particularly the case for non-essential metals/metalloids which have adverse health effects even at very low concentrations [1]. Among persistent organic pollutants, polycyclic aromatic hydrocarbons (PAHs) are composed of at least two fused aromatic rings and can be released in environment through natural processes, but **mainly** through anthropogenic activities where incomplete combustion is involved. Due to their diffuse sources, large quantities of soils or sediments are contaminated with PAHs which are known for their toxicity or their possible carcinogenicity and mutagenicity [2]. Polychlorinated biphenyls (PCBs) are also polyaromatic compounds composed with one to ten chlorine substitutions on a biphenyl group. Due to their thermal stability and dielectric properties, they have been synthesized for industrial applications and their massive use was followed by important release into environment. PCBs **have been** known for their teratogenicity, carcinogenicity and as endocrine disruptors, leading to their prohibition in most countries since **the** 1980's [3].

It is now **acknowledged** that contaminant bioavailability is a more significant key parameter than the total concentration in soils/sediments to evaluate organism's exposure in risk assessment [4]. **In bioavailability processes**, bioaccessibility is linked to the **reversibly- and** rapidly-desorbing fraction of contaminants from particulate matter, already dissolved into water or easily mobilisable from the geosorbents and likely to be in contact with organisms [5, 6]. Lots of studies and results have been achieved for estimating **bioaccessibility** of trace elements TEs (metals, metalloids) in soils/sediments, but there is still no scientific consensus on the methodologies for assessing them [7]. The term bioaccessibility can be used to define the mobile TE fraction that can be found outside a cell membrane, which can be measured by various single aqueous extraction methods [8]. TEs can be also fractionated through

sequential extractions into different phases which represent decreasing degrees of metal mobility [9-10].

Compared to researches on **TE bioaccessibility**, there is still more work to be done for organic contaminants, particularly for clarifying the relationship between the various soil/sediment physico-chemical properties, the effects of source materials, the duration of soil-contaminant contact [3, 11-12]. From a biological viewpoint, a number of in-vitro bioaccessibility tests have been developed which can determine the possible transfer of organic contaminants into the gut fluid, in order to assess human health impacts [13-14]. But from the chemical viewpoint, a number of procedures have also been developed to assess the fraction of organics potentially accessible to organisms. They mainly consist in extracting the **easiest** to desorb fraction of contaminants from soils/sediments through non-exhaustive extraction methods, using organic solvents, aqueous-based media containing sorbents or hydroxypropyl- $\beta$ -cyclodextrin (HPCD) [6, 15-16]. The rapidly-desorbing fraction ( $F_{rap}$ ), **which corresponds to the loosely and reversibly bound residues**, generally correlates well with the bioaccessible pool of PAHs or PCBs [17].

The aim of this present study was, first, to evaluate the importance of some of the main constituents of sediments (sands, silts, clays, organic matter) on the rapidly-desorbing fraction of a mixture of PAHs and PCBs, **which are among the main regulated contaminants in sediments. Indeed, most of studies deal with soils and not with sediments. Moreover, PAHs and PCBs are rarely studied together, leaving aside the possible synergistic effects. In a rather uncommon way, the factors influencing PAHs/PCBs desorption capacity (also including aging) were assessed through an experimental design, to understand the possible interactions between factors.**  $F_{rap}$ , representing the bioaccessible fraction of PAHs/PCBs, was assessed through a recently developed methodology consisting of a non-exhaustive extraction using an aqueous solution of carboxymethyl- $\beta$ -cyclodextrin (pCMCD) polymer [18]. Second, the

methodology was applied **for the first time** to a sediment core in order to determine the bioaccessible concentrations of PAHs/PCBs in relation to the depth, as compared to their total concentration. **Facing the risk of this sediment release in the water body due to a dam removal and a major disturbance in the accumulation area, the easily desorbing fraction  $F_{rap}$  was mainly assessed, considering it as the major hazardous fraction.** Third, sequential extractions of some TEs (Cd, Cr, Cu, Ni, Pb, Zn, As) were **also** performed to evaluate the degrees of metal mobility in relation to the mineralogical speciation and the sediment depth, **in order to have a wider estimation of the risk involving also regulated inorganic pollutants.**

## 2. Materials and methods

### 2.1 Chemicals and sediment materials

Toluene, dichloromethane and acetone (HPLC grade), nitric acid (65%) and hydrochloric acid (37%), were provided by Fisher Scientific (Illkirch, France). Acetic acid, hydroxylammonium chloride, hydrogen peroxide, ammonium acetate were obtained from VWR (Fontenay-sous-Bois, France).

The polymer of carboxymethyl- $\beta$ -cyclodextrin pCMCD was purchased from Cyclolab (Budapest, Hungary).  $\text{NaN}_3$  was furnished by Sigma-Aldrich (Saint-Quentin-Fallavier, France). A multi-element stock solution containing TEs (As, Cd, Cr, Cu, Ni, Pb, Zn) was prepared in pure water and nitric acid (1%) from nitrate salts provided by Fischer Scientific or VWR.

Perdeuterated phenanthrene and perylene (internal standards (IS) for GC-MS), and perdeuterated fluoranthene and benzo[*a*]pyrene, and PCB156 (surrogate standards (SS)) were provided by Sigma-Aldrich. A solution containing the 16 priority PAHs, defined by US-EPA (2000 mg L<sup>-1</sup>) and a solution of 7 PCBs (PCB28, PCB52, PCB101, PCB138, PCB153, PCB180, PCB209) (10 mg L<sup>-1</sup>) were furnished by Sigma-Aldrich. Another solution of 7

PAHs (phenanthrene, fluoranthene, pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, furnished by Sigma-Aldrich), was prepared in acetone (100 mg L<sup>-1</sup>).

With different characteristics, a series of 32 spiked model sediments was prepared by mixing silt (28-92%) collected from the chalk plateau in Normandy (France), sand (5-45%) (SIKA, Hostun, France), kaolinite (2-18%) (IMERYYS, Poigny, France) and organic matter (OM) (1-9%) (VEOLIA, France). The total of silt+sand+clay+OM gave the composition of model sediments. The mineral and the organic composition of the 32 studied model sediments are given in Table 1. One gram of each sediment mixture was mixed with 0.02 g NaN<sub>3</sub> (bactericide), and spiked with 20 µL of the solution of 7 PAHs at 100 mg L<sup>-1</sup> (i.e. 2 mg kg<sup>-1</sup> each) and 50 µL of the solution of 7 PCBs at 10 mg L<sup>-1</sup> (i.e. 0.5 mg kg<sup>-1</sup> each). Sediments were stirred one night in a fume hood for solvent evaporation. Thereafter they were closed and let in the dark, at constant temperature (20±1°C) for 1 to 117 days. We assumed that biodegradation was negligible as sediments were dried and because NaN<sub>2</sub> was added to kill microorganisms.

A sediment core was collected in 2017 from Martot's Pond (49°17'49.5982" N - 1°3'4.4003" E) in Normandy, France, using a gravity corer purchased from UWITEC (Mondsee, Austria). The sediment core (87 cm length) was opened in two parts lengthwise and sliced every 3 cm. Each cut portion was freeze-dried, crushed and stored at -25°C. The sediment was mainly composed of mud (clay+silt) (71.1%, of which 2% clay) and of sand. The grain size distribution was homogeneous along the sediment core with a median grain size equal to 31.2±8.4 µm (Fig. S1A, supplementary materials). The Martot sediment contained 1.4-8.3% total organic carbon (mean value: 3.6%), depending on the sediment depth. It represented approximately a range of 2.5-14.2% OM (mean value: 6.2%) (Fig. S1B).

Certified reference sediments were obtained from Sigma-Aldrich: CNS391 was certified for the 16 priority PAHs and the 7 PCBs indicators (defined by the European Commission BCR) and CNS301 freshwater sediment was certified for 20 TEs.

## 2.2 Exhaustive, non-exhaustive and sequential extractions

Exhaustive extractions of PAHs/PCBs were performed using microwave-assisted extraction (MarsX, CEM Corporation, USA). Approximately 4-g (×2) sub-samples were taken from each dried sliced portion of the Martot sediment core and spiked with 15 µL of the 3 SS (100 mg L<sup>-1</sup>). Each sub-sample was extracted in duplicate with 40 mL of a toluene:acetone 1:1 (v:v) mixture at 130°C for 30 min (1,200 W). The extracts were filtered through 0.2-µm PTFE filters (Phenomenex, le Pecq, France). After addition of a solvent keeper (octanol), extracts were evaporated with a MiVac duo concentrator (Genevac, Ipswich, UK) and reconstituted in 1.5 mL toluene. The same MAE extraction process was performed on 5 sub-samples of the spiked model sediment, of the same composition than experiments no.17 to no.24 with 59 days ageing (Table 1). MAE extraction method was validated using a certified reference sediment (CNS391). Mean recoveries (n=5) were in the 86.3-125.8% range for 15 priority PAHs (an exception was for the most volatile naphthalene whose recovery was 56.4%) and in the 81.9-113.6% range for the 7 studied PCBs.

Non exhaustive extractions of PAHs and PCBs were performed using a methodology developed and adapted from Crampon et al. [18]. Approximately 1-g sub-sample was taken from each dried portion of the Martot sediment core or from the spiked model sediments, and was mixed with 15 mL pure water containing 0.15 g pCMCD. The mixture was shaken for 24 h at 300 rpm, centrifuged (20 min, 5000 rpm) and the supernatant was recovered. Liquid-liquid extraction (LLE) consisted in adding 25 mL dichloromethane into the aqueous supernatant, the mixture being shaken for 30 min and decanted for 20 min. The organic phase

was recovered and the aqueous phase was put in contact 30 min again, under stirring, with 20 mL dichloromethane. After decantation, the two organic phases were combined, 1 g sodium sulfate was added and the mixture was filtered through a 0.2- $\mu\text{m}$  PTFE filter, evaporated and reconstituted in 1 mL toluene. The mean recoveries of PAHs and PCBs after LLE extraction were in the range 92.5%-111.7% (n=5).

Concerning TEs, their pseudo-total extraction from each dried portion of the **Martot** sediment core was performed through microwave-assisted digestion (Ethos 1, Milestone, USA) mixing 0.5-g sub-sample with 3 mL nitric acid and 9 mL hydrochloric acid. The temperature was increased to 150°C in 10 min (800 **W**) followed by a 5-min stage, then to 165°C in 10 min (700 **W**), followed by a 5-min stage and a last rise to 180°C in 5 min (800 **W**), with a 15-min stage. The digestate was diluted in 100 mL water, centrifuged (5 min, 4000 rpm) and the supernatant was analysed. This digestion method was validated using a certified reference sediment (CNS301). Mean recoveries were in the 70.5-120% range for the studied TEs.

Modified BCR (Community Bureau of Reference) sequential extractions of TEs from the **Martot** sediment were performed using the methodology of Pueyo et al [9]. Only the fractions 1-3, 7-9, 13-15, 28-30, 43-45, 52-54, 61-63, 78-80, 85-87-cm were analysed. Briefly, in a first step, exchangeable metals were extracted from 1-g sediment with 40 mL acetic acid (0.11 mol L<sup>-1</sup>), shaken for 16 **h** and centrifuged (15 min, 4000 rpm). In a second step, the reducible fraction from the solid residue was extracted with 40 mL hydroxylammonium chloride (0.5 mol L<sup>-1</sup>) at pH=2, shaken for 16 **h** and centrifuged. In the third step, the oxidisable fraction was obtained mixing the solid residue with 10 **mL** hydrogen peroxide (8.8 mol L<sup>-1</sup>). Digestion was performed in 3 steps at ambient temperature or at 85°C (3×1 **h**). After reduction of the volume to 1 mL, a solution of 40 mL ammonium acetate (1 mol L<sup>-1</sup>), at pH=2, was added, shaken for 16 **h** and centrifuged. The final residue (0.5 g) was digested in the fourth step, as described previously for the pseudo-total extraction.

### 2.3 Quantitative analyses of PAHs, PCBs and trace elements

After the exhaustive and non-exhaustive extractions of PAHs/PCBs, 10  $\mu\text{L}$  of the two IS (100  $\text{mg L}^{-1}$ ) were added to 990  $\mu\text{L}$  of an extract; 1  $\mu\text{L}$  was injected (splitless mode, 285°C) into a gas chromatographer (7890B, Agilent, Santa Clara, USA), coupled with a mass spectrometer (7000C). Separation was performed using a 60 m $\times$ 0.25 mm Rxi-XLB capillary column (0.25  $\mu\text{m}$  film thickness) obtained from Restek (Lisses, France), with helium at 1.4  $\text{mL min}^{-1}$ . The oven temperature was programmed at 60°C (1.2 min), increased to 200°C (40°C  $\text{min}^{-1}$ ), then to 260°C (6°C  $\text{min}^{-1}$ ) and to 305°C (10°C  $\text{min}^{-1}$ ) during 30 min. The MS detector operated at 70 eV. Quantification was based on selected ion monitoring for better sensitivity.

TE concentrations were analysed using an ICP-AES system (ICAP6300, ThermoFisher Scientific, USA), at 189.0 nm for As, 214.4 nm for Cd, 267.7 nm for Cr, 204.3 nm for Cu, 231.6 nm for Ni, 283.3 nm for Pb, and 472.2 nm for Zn.

### 2.4 Statistical analyses

PAHs/PCBs recoveries obtained from pCMCD non-exhaustive extractions from the spiked model sediments were treated with JMP13 software (SAS institute, Cary, USA) for statistical calculations and modeling. It allowed giving (i) the coefficient of determination of the model ( $r^2$ ), (ii) the adjusted coefficient of determination ( $r^2_{\text{adj}}$ ), (iii) the p-value (95% confidence level) corresponding to the analysis of variance (ANOVA) used for testing the significance of the model, (iv) the p-value (95% confidence level) obtained from the lack-of-fit (LOF) test. The idea of this test is to compare the pure error (measured for exact replicates) to the residual error of the model. Moreover, taking into account the results from these statistical tests, the most influential factors and interactions (p-values $<$ 0.05) were reported, ranking from the most to the less influential ones (with increasing p-values).

### 3. Results and discussion

#### 3.1. Factors influencing the bioaccessibility of PAHs/PCBs in sediments

Several factors can influence the way in which lipophilic organic compounds can sorb-desorb more or less quickly from sediment. Among the physicochemical factors, sediment characteristics (particle size, nature of clays, OM percentage and nature, pH, water content...), compound properties (aqueous solubility, polarizability...) and transformation processes (aging...), are responsible for more or less strong interactions between particles and contaminants which lead to different degrees of desorption. The fraction that desorbs rapidly and reversibly ( $F_{rap}$ ) is generally believed to represent the bioaccessible fraction [19].

Central composite designs (CCD) can be applied to explain the influence of each factor on  $F_{rap}$  but also their interactions (which cannot be done with univariate experiments), and also to develop response models with a few number of experiments. Among all the factors that can affect  $F_{rap}$ , four of them were selected: the percentages of clay ( $F_1$  factor), of sand ( $F_2$ ), of OM ( $F_3$ ) constituting the model sediments, and aging ( $F_4$ ) (contact time between the sediment and the spiked PAHs/PCBs). OM, clay, ageing were selected because they were pointed out as markedly influencing bioaccessibility of PAHs/PCBs on soils [3, 18] and sand because its influence has hardly been reported in literature.

$F_{rap}$  was assessed in this study through a chemical non-exhaustive extraction using a methodology developed and already described in Crampon et al. [18], with a polymer of carboxymethyl- $\beta$ -cyclodextrin (pCMCD) as an extracting additive in aqueous phase. In previous studies, PAH bioaccessibility was first assessed through the typical non-exhaustive extraction using HPCD [20], but it was demonstrated that pCMCD was better to estimate the mass transfer between soil particles and the soil solution, but also more economical than

HPCD [18]. This methodology, using pCMCD, was also performed for PCBs in this study, knowing that it was previously demonstrated that HPCD extractions could also predict PCBs  $F_{rap}$  and so bioaccessibility [3]. In the case of PCBs, Wong and Bidleman [21] actually demonstrated that the extractability of high molecular weight (HMW) PCBs was not influenced by the size of the  $\beta$ -cyclodextrin cavity but mainly by their sorption to the soil. **So it could be assumed** that pCMCD could be also efficiently used to softly extract PCBs and predict  $F_{rap}$ .

The CCD is shown in Table 1. It is composed of (i) a full design, where the factor levels are coded to a low (-1) and a high (+1) value; (ii) center points (0) that are replicated to estimate the experimental error variance; (iii) axial points at the distance  $\alpha$  ( $\pm 2$ ) from the center that can be used to develop second-order response modeling. The studied response was PAH or PCB extractability (%) through pCMCD mild extraction, relative to their total extraction through MAE **(estimated from 5 sub-samples of the same composition as the one of center points)**. PAH/PCB extractability **gave** the percentage of the rapidly-desorbing fraction ( $F_{rap}$ ) from the sediment and so the percentage of bioaccessible contaminants. Table S1 (supplementary materials) gives the overall **raw** results. The effects and the interactions of the factors on the extractability were estimated using **linear or quadratic models** and it appeared **from the best values of  $r^2$  and  $r^2_{adj}$**  that the quadratic modeling fitted better between the model and the experimental values for a majority of the compounds studied. **It can be noted from Table 2** that the **lowest** molecular weight (LMW) PAHs (fluorene and phenanthrene)  $F_{rap}$  **values** could not be modeled considering only the 4 factors studied, with poor values for  $r^2$  and  $r^2_{adj}$ . **ANOVA that was used to test the model by comparing the model mean square to the error (residual) mean square led to p-values > 0.05. Thus, the significance of the model was not proved and no influential factor could be highlighted. It can be supposed** that other factors, not considered in this study, were responsible of the variability of the results. LMW PAHs are

quite volatile **which** possibly led to variable but significant losses for many of them. Also, although a bactericide was added to the model sediments, **it can be supposed** that LMW PAHs could be **anyway partially** biodegraded **even in dry sediments**. Biodegradation was negligible after 59 days ageing since PAHs recoveries were all exceeding 84%. Nevertheless, **microorganisms could degrade the LMW PAHs after 59 days anyway**. This could affect the results concerning these compounds but not those related to HMW PAHs. The easier degradation of LMW PAHs by microorganisms compared to HMW PAHs was actually **demonstrated in soils and in sediments [22, 23]**.

In contrast, the other PAHs/PCBs showed a good fitting between the model and the experimental values, with p-values < 0.05 for ANOVA tests (Table 2). **In their case, the independent variables of the quadratic model were highly significant parameters**. Also, in the majority of cases, p-values > 0.05 were obtained for the lack-of-fit tests that shows the models were **adequate** (Table 2). Fig. 1 shows **examples of** cube plot representations obtained from the modeling software program, representing the extractability ( $F_{rap}$ ) of Fluoranthene and PCB153 as a function of two of their most influential factors.

For PAHs/PCBs for which rapid extractability could be modeled, the percentage of OM in the sediments was the most influential factor (Table 2). OM had systematically negative coefficients in modeling equations which indicated that increasing its level would decrease PAH/PCB  $F_{rap}$ , and so their bioaccessibility. **As shown** in Fig. 1A and 1B, this decrease was non-linear for PAHs and PCBs. Ti et al. [3] also observed a non-linear relationship between the decline in PCBs bioaccessibility and the increment of OM in soils. It was also observed that the quality of OM could be important and particularly, aromaticity of OM increased the sorption/desorption non-linearity for PAHs [12].

In the case of PAHs, clay percentage appeared also influential **but less than OM** (Table 2), and only for the LMW fluoranthene and pyrene (4 cycles), with a negative coefficient and so

a decreasing extractability when clay percentage increases. The decrease in PAH bioaccessibility associated to the higher presence of the finest particles has been also observed in other studies [18, 24]. Concerning PAHs, aging effect was influential only for the HMW benzo[*a*]pyrene and benzo[*ghi*]perylene and was non-linear, with a high decrease of extractability in the first 60 days followed by a slow decrease until 117 d. It has been already observed that the effects of aging on spiked PAH accessibility in soils is mainly concentrated in the initial stage of the process and weakens in the later aging time [25].

In the case of PCBs, the two-factor interaction sand×OM surprisingly appeared influential (Table 2) and its influence was negative. The role of sand fraction on PCB extractability/bioaccessibility has not yet been reported, but Adeyinka and Moodley [26] noted a small adsorption increase of PCBs with the soil grain size increase, attributed to a higher soil porosity allowing PCBs to enter the pore space. So it appears that associating OM with high porosity materials such as sand could contribute to increase PCB sorption, which could decrease their bioaccessibility. It can be also underlined that PCBs, unlike PAHs, have dipole moments and so may have a greater affinity for polar silica surfaces. Aging was also often an influential factor for PCBs (but much less than OM), with a negative influence on  $F_{rap}$ . Wong and Bidleman [21] showed that the effect of aging on HPCD PCB extractability was very weak on 550 d, the largest decrease being between 2-10 days, with no significant decrease afterwards. In our study, restricted PCB extractability due to aging was observed throughout the 177 d but was of low impact and was quite linear, unlike PAHs.

Table 2 gives the median values of extractabilities for the 14 studied compounds, obtained from the 32 CCD experiments. As expected, 3-fused cycle PAHs were easier to rapidly desorb than 5-6 cycles PAHs. In the same way, 3-chlorinated PCBs were easier to desorb than 7-10 chlorinated PCBs. Fig. S2A shows that PAHs median extractability decreases linearly with the number of fused cycles ( $r^2=0.83$ ). Fig S2B also shows the linear decrease of the

PCBs median extractability with their degree of chlorination ( $r^2=0.80$ ). It suggested the strong dependence of bioaccessibility on molecular structures, linked to their hydrophobicity. Indeed PAH extractability was also strongly linked ( $r^2=0.79$ ) to the octanol/water partition coefficient **Kow** through the relation: PAH median extractability (%) =  $-11.9 \times (\log \text{Kow}) + 82.6$ . It was also the case for PCBs: PCB median extractability (%) =  $-7.2 \times (\log \text{Kow}) + 57.4$  ( $r^2= 0.89$ ) (log **Kow** values are referenced in Table 2).

### 3.2. Evaluation of the bioaccessibility of PAHs/PCBs in the Martot sediment core

The contaminated sediment collected from Martot's Pond **has accumulated** since 1940 in this area because of the presence of a dam on the Eure river (Normandy, France) which **was** dismantled in October 2017. This destruction is likely to disturb the pond area and sediment release in the Eure river is expected and currently studied. **The Martot** sediment core was first analysed considering the total concentrations (**evaluated by MAE**) for the 16 priority PAHs and 6 (PCB28, 52, 101, 138, 153, 180) of the 7 PCBs **indicators**. Second, each sediment fraction was also extracted with pCMCD, and the rapidly-desorbing concentrations of the 16 PAHs and the 6 PCBs were evaluated as a function of the sediment depth. Fig. 2 shows the results of exhaustive and non-exhaustive extractions for the PAHs/PCBs. It must be noted that a decree dated 9 August 2006 by decision of the French Minister of Ecology and Sustainable Development considers that a river sediment is polluted (and cannot be dredged and deposited again in aquatic environments without damages on aquatic fauna) if critical levels ( $S_1$ ) are exceeded. Concerning the 16 priority PAHs and the 7 PCBs indicators, the  $S_1$  levels are respectively  $22.8 \text{ mg kg}^{-1}$  and  $0.68 \text{ mg kg}^{-1}$ . Fig. 2 shows that only few Martot sediment sections were concerned by a PAH threshold exceeding (67-69 and 75-78 cm depth) but that it is more critical for PCBs (between 52-69 cm depth).

PAHs/PCBs  $F_{rap}$  assessed through pCMCD extractions were markedly lower than the ones obtained from total extracts and systematically under the  $S_1$  critical levels (Fig. 2). Only an average of 5.1% of the 16 priority PAHs was bioaccessible, and an average of 13.7% of the 6 studied PCBs. The results were dissimilar if PAHs/PCBs were considered individually. For example, the mean value of  $F_{rap}$  for the LMW PAH Fluorene was 7.1% (2.8-17.6% range, as a function of depth) while it was only 2.8% for the HMW PAH Benzo[*b*]fluoranthene (0.4-7.4% range).  $F_{rap}$  of PCB52 (4 chlorines) was 19.3% in average (0-57.4% range, as a function of depth) while it was only 2.9% (0-9.8% range) for the PCB138 (6 chlorines). Fig. 3A shows the mean extractabilities obtained through pCMCD extractions for PAHs as a function of their cycle number and Fig 3B for PCBs, as a function of their chlorine number. As shown in part 3.1, LMW PAHs were more easily desorbed and so more bioaccessible than HMW PAHs in long-term contaminated sediments, and low-chlorinated PCBs were more bioaccessible than highly-chlorinated PCBs. As shown for the model sediment, the relationship between rapid extractability and the number of PAHs cycles or PCB chlorines was also linear in the contaminated Martot sediment, with good coefficient of determinations ( $r^2=0.99$  and  $0.95$ , respectively) (Fig. 3).

Fig. S3A shows that the rapidly-desorbing concentrations of the 16 PAHs correlated well with the OM content measured in the different Martot sediment sections, with the power law: rapidly-desorbing concentration =  $4.47 \times (OM)^{1.35}$  ( $r^2=0.68$ ). Considering individual PAHs, the tendency was the same for all of them ( $r^2$  ranging from 0.58 for the LMW acenaphthylene to 0.76 for the HMW benzo[*a*]pyrene). As regards the lowest MW PAHs (naphthalene, fluorene and acenaphthene), no correlation with OM content could be found. It shows that PAH bioaccessibility decreases drastically and non-linearly with an OM-content increase in the Martot sediment, as it was the case for the model sediments (part 3.1) and also for soils [20]. On the contrary, the rapidly-desorbing concentrations of none of the 16 PAHs correlated at all

with median grain sizes measured in each section of the sediment core (Fig. S3B). Concerning PCBs,  $F_{rap}$  for the 6 PCBs did not correlated either with median grain size of the Martot sediment (Fig. S4B). The lack of correlation with grain size could be explained by the very low variability in the composition of inorganic components in the Martot sediment, which could be considered homogeneous all along the core (Fig S1A).

Surprisingly, concerning the 6 PCBs, their rapidly-desorbing concentrations did not correlate either with OM content (Fig. S4A). The link found between OM content and PCB  $F_{rap}$  in model sediments was possibly attenuated because of the lower variability of OM content all along the sediment core ( $5.1 \pm 1.5\%$  from 18 to 87 cm depth) and because of the very low PCB concentration range found in the Martot sediment (50% of the values were under  $0.17 \text{ mg kg}^{-1}$ ).

However, the rapidly-desorbing concentrations of the 16 PAHs and the 6 PCBs correlated well with the total concentrations of the compounds measured through exhaustive extractions, with a linear coefficient of determination  $r^2 = 0.73$  for the sum of PAHs and  $r^2 = 0.91$  for the sum of PCBs (Fig. S3C and Fig. S4C). Individually, the same linear correlation between the contamination level and the bioaccessible fraction was found for all the PAHs and PCBs (with  $r^2$  ranging from 0.54 to 0.98) except for naphthalene and acenaphthene. So in the Martot sediment, the higher the contaminant concentration, the higher its bioaccessible fraction. It was particularly pronounced for PCBs for which low concentration levels in sediment (approximately under  $0.1 \text{ mg kg}^{-1}$ ) led to a null bioaccessible fraction. As OM, which was demonstrated as one of the major factors in the PAHs/PCBs mass transfer process between sediment particles and solution, it seems that the pollutant concentration level is also a particularly significant factor that plays an important role in the bioaccessibility process. But it should be demonstrated that the linear correlation between the PAHs/PCBs concentration

level and  $F_{rap}$  is valid in wider concentration ranges than those studied in the Martot sediment and whatever the OM content.

At last, if the deepest sediments from the sediment core are considered to be the oldest, no correlation could be found for PAHs and PCBs between sediment aging and their measured bioaccessible fraction, even for HMW PAHs. It should be recalled that the results of the CCD showed a low influence of ageing on PAHs/PCBs extractability and rather in the first weeks of the contact with sediments particles. Here, preliminary results on an age model (data not shown) showed that every cm of the Martot sediment was approximately 1 year old, so the oldest fraction was possibly more than 80 years old. At this time scale, it was not possible to demonstrate a lower bioaccessibility of PAHs/PCBs with ageing in the Martot sediment.

### 3.3. Evaluation of the mobility of trace metals in the Martot sediment core

Fig. 4 shows the BCR modified sequential extractions for three TEs (As, Pb, Cd) from the Martot sediment core, as a function of the depth. The same sequential extractions were performed for Cu, Cr, Ni and Zn (Fig. S5). For As, concentrations were higher in the depth of the Martot sediment (Fig. 4A). Concerning Pb, it was more concentrated in the fractions near 30 cm depth, corresponding to more recent sediment deposits (Fig. 4B). Concerning the other studied TEs, they were all more concentrated in the fractions near 50-65 cm depth (Fig. 4C and Fig. S5). As mentioned in the part 3.2, the French decree dated 9 August 2006 considers that the river sediment is polluted with TEs if their  $S_1$  level is exceeded.  $S_1$  thresholds are 30, 100, 2, 100, 150, 50 and 300 mg kg<sup>-1</sup> for As, Pb, Cd, Cu, Cr, Ni and Zn, respectively. As shown in Fig. 4, the Martot sediment could not be considered polluted by As, but it could be considered polluted by Pb in the more recently deposited fractions, from 0-45 cm depth, and polluted by Cd from 0-80 cm depth, with particularly high levels of pollution between 35-80 cm depth. Moreover, sediments stored in Martot's Pond could not be considered polluted by

Cr and Ni, but were polluted by Cu in the fractions 40-80 cm depth and by Zn in the fractions 35-80 cm depth (Fig. S5). So the Martot sediment was polluted throughout the 0-80 cm depth by Pb, Cd, Cu and/or Zn.

Table 3 summarizes the mean percentages of extracted metals all along the sediment core through the sequential extractions. The first step allowed measuring the water soluble/exchangeable/bound to carbonates TEs, so the more mobile ones. The second step measured TEs sorbed on the reducible (bound to Fe and Mn oxides) and less mobile sediment fraction; the third step allowed measuring TEs sorbed on the oxidizable fraction (bound to sulphides and OM) and even less mobile sediment fraction; at last, the fourth fraction represented TEs strongly sorbed on refractory minerals, which are immobile [27]. From the first to the fourth step, the degree of mobility was decreasing and only the first and second steps represent the most bioaccessible TEs fractions [10]. Pb, Cr and Ni were more concentrated on the refractory minerals, then on the oxidizable fraction. Only 0.8-15.6% of them was found on the mobile reducible and exchangeable fractions (Table 3). Cd and Zn were more concentrated on the quite mobile reducible fraction, then on the oxidizable fraction, then on the refractory fraction and finally on the most mobile exchangeable fraction. 47.2-47.5% of them were found in the most mobile sediment fractions. Arsenic was concentrated in majority on the refractory fraction, then on the exchangeable and reducible fractions, then on the oxidizable fraction (Table 3). 35.2% of As was found on the most mobile sediment fractions. Cu was also particular, with a higher concentration on the oxidizable fraction, then on the refractory fraction, then on the exchangeable and reducible fractions. Only 1.9% of Cu could be considered bioaccessible. So Cr and Cu were the less bioaccessible TEs contained in the Martot sediment. Pb and Ni were very few bioaccessible. In contrast As, Cd and Zn were the most bioaccessible TEs. The most problematic was certainly Cd, for which the two bioaccessible fractions were above the  $S_1$  threshold in the 40-

65 cm depth. Zn was also concerned by bioaccessible fractions exceeding the S<sub>1</sub> threshold in narrower sediment sections (50-55 cm depth).

#### 4. Conclusions

The CCD allowed showing the main influencing factors on PAHs/PCBs bioaccessibility from model sediments, with (i) a high negative quadratic influence of OM, (ii) a lower negative influence of clay on 4-cycles PAHs and of sand (in association with OM) on 5-6 chlorinated PCBs, (iii) and a low negative influence of ageing on HMW PAHs and PCBs throughout 177 days.

In the case of the long-term contaminated Martot sediment, PAH/PCB bioaccessible concentrations were very low throughout the core. As for model sediments, the bioaccessible fraction was strongly linked to PAHs/PCBs chemical structure and was linearly correlated to their hydrophobicity. OM content impacted negatively on the bioaccessible fraction of PAHs but not of PCBs, possibly because of the very low concentrations of bioaccessible PCBs and the low variability of OM in the Martot sediment. Unlike model sediments, grain size and sediment aging had no influence on PAH/PCB bioaccessibility. In fact, the effects of these low influencing factors were probably masked by another major factor, which appeared to be the concentration level: the higher the PAH/PCB concentration in the Martot sediment, the higher the bioaccessible fraction. Concerning TEs, Cr and Cu were the less bioaccessible in the Martot sediment; Pb and Ni bioaccessible fractions were also very low. However, a great part of As, Cd and Zn was found in the most mobile (exchangeable and reducible) sediment fractions.

Finally, a few Martot sediment sections were concerned by a PAH S<sub>1</sub> threshold exceeding (for total concentrations) but it was more critical for PCBs. However, if the bioaccessible fractions are only considered, none exceeded the S<sub>1</sub> thresholds throughout the sediment core. It was not

the case for some TEs: Pb, Cd, Zn and Cu exceeded their  $S_1$  thresholds for their total concentrations, but Cd and Zn also exceeded their  $S_1$  level for their bioaccessible fractions in some sections of the sediment core (40-65 cm depth). **Considering** that Martot's Pond area was recently disturbed by a dam removal, leading to continuous sediment release in the water column, the 40-65 cm fraction might be considered as the most negatively impacting sediments as regards the aquatic fauna.

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## References

- [1] M. Jaishankar, T. Tseten, N. Anbalagan, B.B. Mathew, K.N. Beeregowda, Toxicity, mechanism and health effects of some heavy metals, *Interdiscip. Toxicol.* 7 (2014) 60–72.
- [2] K. Misaki, T. Takamura-Enya, H. Ogawa, K. Takamori, M. Yanagida, Tumour-promoting activity of polycyclic aromatic hydrocarbons and their oxygenated or nitrated derivatives, *Mutagenesis* 31 (2016) 205–213.
- [3] Q. Ti, C. Gu, C. Liu, J. Cai, Y. Bian, X. Yang, Y. Song, F. Wang, C. Sun, X. Jiang, Comparative evaluation of influence of aging, soil properties and structural characteristics on bioaccessibility of polychlorinated biphenyls in soil, *Chemosphere* 210 (2018) 941-948.
- [4] J.J. Ortega-Calvo., J. Harmsen, J.R. Parsons, K.T. Semple, M.D. Aitken, C. Ajao, C. Eadsforth, M. Galay-Burgos, R. Naidu, R. Oliver, W.J.G.M. Peijnenburg, J. Römbke, G. Streck, B. Versonnen, From bioavailability science to regulation of organic chemicals, *Environ. Sci. Technol.* 49 (2015) 10255–10264.
- [5] K.T. Semple, K.J. Doick, K.C. Jones, P. Burauel, A. Craven, H. Harms, Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated, *Environ. Sci. Technol.* 38 (2004) 228A-231A.
- [6] M.J. Riding, K.J. Doick, F.L. Martin, K.C. Jones, K.T. Semple, Chemical measures of bioavailability/bioaccessibility of PAHs in soil: Fundamentals to application, *J. Hazard. Mater.* 261 (2013) 687-700.
- [7] J.C. Ng, A. Juhasz, E. Smith, R. Naidu, Assessing the bioavailability and bioaccessibility of metals and metalloids, *Environ. Sci. Pollut. Res.* 22 (2015) 8802–8825.
- [8] J. Kumpiene, L. Giagnoni, B. Marschner, S. Denys, M. Mench, K. Adriaensen, J. Vangronsveld, M. Puschenreiter, G. Renella, Assessment of methods for determining bioavailability of trace elements in soils: a review, *Pedosphere* 27(2017) 389-406.

- [9] M. Pueyo, J. Mateu, A. Rigol, M. Vidal, J.F. Lopez-Sanchez, G. Rauret, Use of the modified BCR three step sequential extraction procedure for the study of trace element dynamics in contaminated soils, *Environ. Pollut.* 152 (2008) 330-341.
- [10] C.M. Alves, C.M.H. Ferreira, H.M.V.M. Soares, Relation between different metal pollution criteria in sediments and its contribution on assessing toxicity, *Chemosphere* 208 (2018) 390-398.
- [11] N. Bartolomé, I. Hilber, D. Sosa, R. Schulin, P. Mayer, T.D. Bucheli, Applying no-depletion equilibrium sampling and full-depletion bioaccessibility extraction to 35 historically polycyclic aromatic hydrocarbon contaminated soils, *Chemosphere* 199 (2018) 409-416.
- [12] L. Yu, L. Duan, R. Naidu, K.T. Semple, Abiotic factors controlling bioavailability and bioaccessibility of polycyclic aromatic hydrocarbons in soil: Putting together a bigger picture, *Sci. Total Environ.* 613–614 (2018) 1140-1153.
- [13] C.D. Collins, M. Craggs, S. Garcia-Alcega, K. Kademoglou, S. Lowe, Towards a unified approach for the determination of the bioaccessibility of organic pollutants, *Environ. Int.* 78 (2015) 24-31.
- [14] S. Zhang, C. Li, Y. Li, R. Zhang, P. Gao, X. Cui, L.Q. Ma, Bioaccessibility of PAHs in contaminated soils: Comparison of five in vitro methods with Tenax as a sorption sink, *Sci. Total Environ.* 601–602 (2017) 968-974.
- [15] C. Li, R. Zhang, Y. Li, S. Zhang, P. Gao, X. Cui, L.Q. Ma., Relative bioavailability and bioaccessibility of PCBs in soils based on a mouse model and Tenax-improved physiologically-based extraction test, *Chemosphere* 186 (2017) 709-715.
- [16] Y. Zhang, X. Yang, C. Gu, Y. Bian, Z. Liu, M. Jia, F. Wang, D. Wang, X. Jiang, Prediction of Polycyclic Aromatic Hydrocarbon bioaccessibility to earthworms in spiked soils by composite extraction with Hydroxypropyl- $\beta$ -Cyclodextrin and organic acids, *Pedosphere* 27 (2017) 502-510.

- [17] F.L. Sinche, S.A. Nutile, P. Landrum, M.J. Lydy, Optimization of Tenax extraction parameters for polychlorinated biphenyls in contaminated sediments, *Talanta* 164 (2017) 386-395.
- [18] M. Crampon, J. Bodilis, F. Le Derf, F. Portet-Koltalo, Alternative techniques to HPCD to evaluate the bioaccessible fraction of soil-associated PAHs and correlation to biodegradation efficiency, *J. Hazard. Mater.* 314 (2016) 220-229.
- [19] S. Cipullo, G. Prpich, P. Campo, F. Coulon, Assessing bioavailability of complex chemical mixtures in contaminated soils: Progress made and research needs, *Sci. Total Environ.* 615 (2018) 708-723.
- [20] M. Crampon, F. Bureau, M. Akpa-Vinceslas, J. Bodilis, N. Machour, F. Le Derf, F. Portet-Koltalo, Correlations between PAH bioavailability, degrading bacteria and soil characteristics during PAH biodegradation in five diffusely contaminated dissimilar soils, *Environ. Sci. Poll. Res.* 21 (2014) 8133-8145.
- [21] F. Wong, T.F. Bidleman, Hydroxypropyl- $\beta$ -cyclodextrin as non-exhaustive extractant for organochlorine pesticides and polychlorinated biphenyls in muck soil, *Environ. Poll.* 158 (2010) 1303-1310.
- [22] O. Baltrons, M. López-Mesas, M. Vilaseca, C. Gutiérrez-Bouzán, F. Le Derf, F. Portet-Koltalo, C. Palet, Influence of a mixture of metals on PAHs biodegradation processes in soils, *Sci. Total Environ.* 628–629 (2018) 150–158.
- [23] D. Ghosal, S. Ghosh, T.K. Dutta, Y. Ahn, Current state of knowledge in microbial degradation of Polycyclic Aromatic Hydrocarbons (PAHs): A review, *Front. Microbiol.* 7 (2016) 1-27.
- [24] S.D. Siciliano, B.D. Laird, C.L. Lemieux, Polycyclic aromatic hydrocarbons are enriched but bioaccessibility reduced in brownfield soils adhered to human hand, *Chemosphere* 80 (2010) 1101-1108.

- [25] L. Ma, J. Zhang, L. Han, W. Li, L. Xu, F. Hu, H. Li, The effects of aging time on the fraction distribution and bioavailability of PAH, *Chemosphere* 86 (2012) 1072-1078.
- [26] G.C. Adeyinka, B. Moodley, Kinetic and thermodynamic studies on partitioning of polychlorinated biphenyls (PCBs) between aqueous solution and modeled individual soil particle grain sizes, *J. Environ. Sci.* 76 (2019) 100-110.
- [27] A. Wali, G. Colinet, M. Ksibi, Speciation of heavy metals by modified BCR sequential extraction in soils contaminated by phosphogypsum in Sfax, Tunisia, *Env. Res. Eng. Manag.* 4 (2014) 14–26.
- [28] F. Portet-Koltalo, N. Machour, Analytical methodologies for the control of particle-phase polycyclic aromatic compounds from diesel engine exhausts, *Diesel Engine*, ed. S. Bari, InTech Open Science (2012).
- [29] D.W. Hawker, D.W. Connell, Octanol-water partition coefficients of polychlorinated biphenyl congeners, *Environ. Sci. Technol.* 22 (1988) 382–387.

## Figure captions

Fig. 1: Cube plots representing the calculated extractability ( $F_{rap}$ ) of (A) Fluoranthene as a function of OM and clay percentages and (B) PCB153 as a function of OM and sand.

Fig. 2: Total concentrations of contaminants obtained from the exhaustive extraction through MAE and rapidly-desorbing concentrations obtained from non-exhaustive extractions through pCMCD in the **Martot** sediment core, as a function of the sediment depth (A) for PAHs (B) for PCBs.

Fig. 3: Mean extractabilities from the **Martot** sediment (averaged from all the sediment core sections) obtained through pCMCD non-exhaustive extractions (A) for PAHs, as a function of their cycle number (3-cycles: acenaphthylene, fluorene, phenanthrene, anthracene; 4-cycles: fluoranthene, pyrene, benz[*a*]anthracene, chrysene; 5-cycles: benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz[*ah*]anthracene; 6-cycles: benzo[*ghi*]perylene, indeno[*1,2,3cd*]pyrene), and (B) for PCBs, as a function of their chlorine number (3-chlorines: PCB28; 4-chlorines: PCB52; 5-chlorines: PCB101; 6-chlorines: PCB138; 7-chlorines: PCB180).

Fig. 4: Sequential extractions of TEs in four steps from the **Martot** sediment, as a function of the core depth (A) As (B) Pb (C) Cd.

Table 1: Experimental matrix for the  $2^4$  CCD, with the 4 studied factors (F), the 5 coded levels ( $-\alpha, -1, 0, +1, +\alpha$ ) and the corresponding experimental levels (into brackets).

Experiment number	F1 Clay	F2 Sand	F3 OM	F4 Ageing
1	- 1 (6%)	- 1 (15%)	- 1 (3%)	- 1 (30 d)
2	- 1 (6%)	- 1 (15%)	- 1 (3%)	+ 1 (88 d)
3	- 1 (6%)	- 1 (15%)	+ 1 (7%)	- 1 (30 d)
4	- 1 (6%)	- 1 (15%)	+ 1 (7%)	+ 1 (88 d)
5	- 1 (6%)	+ 1 (35%)	- 1 (3%)	- 1 (30 d)
6	- 1 (6%)	+ 1 (35%)	- 1 (3%)	+ 1 (88 d)
7	- 1 (6%)	+ 1 (35%)	+ 1 (7%)	- 1 (30 d)
8	- 1 (6%)	+ 1 (35%)	+ 1 (7%)	+ 1 (88 d)
9	+ 1 (14%)	- 1 (15%)	- 1 (3%)	- 1 (30 d)
10	+ 1 (14%)	- 1 (15%)	- 1 (3%)	+ 1 (88 d)
11	+ 1 (14%)	- 1 (15%)	+ 1 (7%)	- 1 (30 d)
12	+ 1 (14%)	- 1 (15%)	+ 1 (7%)	+ 1 (88 d)
13	+ 1 (14%)	+ 1 (35%)	- 1 (3%)	- 1 (30 d)
14	+ 1 (14%)	+ 1 (35%)	- 1 (3%)	+ 1 (88 d)
15	+ 1 (14%)	+ 1 (35%)	+ 1 (7%)	- 1 (30 d)
16	+ 1 (14%)	+ 1 (35%)	+ 1 (7%)	+ 1 (88 d)
17	0 (10%)	0 (25%)	0 (5%)	0 (59 d)
18	0 (10%)	0 (25%)	0 (5%)	0 (59 d)
19	0 (10%)	0 (25%)	0 (5%)	0 (59 d)
20	0 (10%)	0 (25%)	0 (5%)	0 (59 d)
21	0 (10%)	0 (25%)	0 (5%)	0 (59 d)
22	0 (10%)	0 (25%)	0 (5%)	0 (59 d)
23	0 (10%)	0 (25%)	0 (5%)	0 (59 d)
24	0 (10%)	0 (25%)	0 (5%)	0 (59 d)
25	$-\alpha$ (2%)	0 (25%)	0 (5%)	0 (59 d)
26	$+\alpha$ (18%)	0 (25%)	0 (5%)	0 (59 d)
27	0 (10%)	$-\alpha$ (5%)	0 (5%)	0 (59 d)
28	0 (10%)	$+\alpha$ (45%)	0 (5%)	0 (59 d)
29	0 (10%)	0 (25%)	$-\alpha$ (1%)	0 (59 d)
30	0 (10%)	0 (25%)	$+\alpha$ (9%)	0 (59 d)
31	0 (10%)	0 (25%)	0 (5%)	$-\alpha$ (1 d)
32	0 (10%)	0 (25%)	0 (5%)	$+\alpha$ (117 d)

Table 2: Results obtained from the CCD as regards the median extractability (%) of PAHs/PCBs through pCMCD non-exhaustive extractions, with the coefficient of determination of the model ( $r^2$ ), the adjusted coefficient of determination ( $r^2_{adj}$ ), the p-value corresponding to ANOVA, ranking of the most influential factors and interactions (quadratic modeling) and the p-value corresponding of the lack-of-fit test (LOF).

<b>HAP compounds</b>	Fluorene	Phenanthrene	Fluoranthene	Pyrene	Benzo[b]- fluoranthene	Benzo[a]pyrene	Benzo[ghi]- perylene
$r^2$	0.17	0.22	0.76	0.67	0.77	0.66	0.51
$r^2_{adj}$	- 0.50	- 0.51	0.72	0.64	0.75	0.59	0.49
ANOVA p-value	0.9932	0.9875	<0.0001	<0.0001	<0.0001	<0.0001	0.0001
LOF test p-value	-	-	0.0916	0.0789	0.0099	0.0281	<0.0001
Influential factors	(a)	(a)	OM>Clay×OM> Clay>OM×OM	OM>Clay>OM <sup>2</sup>	OM>OM <sup>2</sup>	Aging>Aging <sup>2</sup> > OM>Clay×OM	OM>Aging <sup>2</sup> > OM <sup>2</sup>
Median extractability (%)	24.6	39.8	24.6	18.8	9.8	1.8	1.2
Log <b>Kow</b> (b)	4.18	4.52	5.20	5.18	5.78	6.50	7.10
<b>PCB compounds</b>	PCB28	PCB52	PCB101	PCB153	PCB138	PCB180	PCB209
$r^2$	0.50	0.22	0.90	0.84	0.88	0.799	0.605
$r^2_{adj}$	0.48	0.20	0.88	0.81	0.86	0.785	0.562
ANOVA p-value	<0.0001	0.0064	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
LOF test p-value	0.0070	0.002	0.3600	0.3170	0.4767	0.2200	0.6300

Influential factors	OM	OM	OM>OM <sup>2</sup> >sand× OM>aging>clay	OM>OM <sup>2</sup> >Sand> sand×OM>clay	OM>OM <sup>2</sup> >Aging >sand×OM	OM>OM <sup>2</sup>	OM>Aging> OM <sup>2</sup>
Median extractability (%)	15.1	19.2	10.8	9.1	7.4	2.2	0.6
Log <b>K<sub>ow</sub></b> (c)	5.67	5.84	6.38	6.92	6.83	7.36	8.18

(a) No influential factor could emerge from the CCD modeling

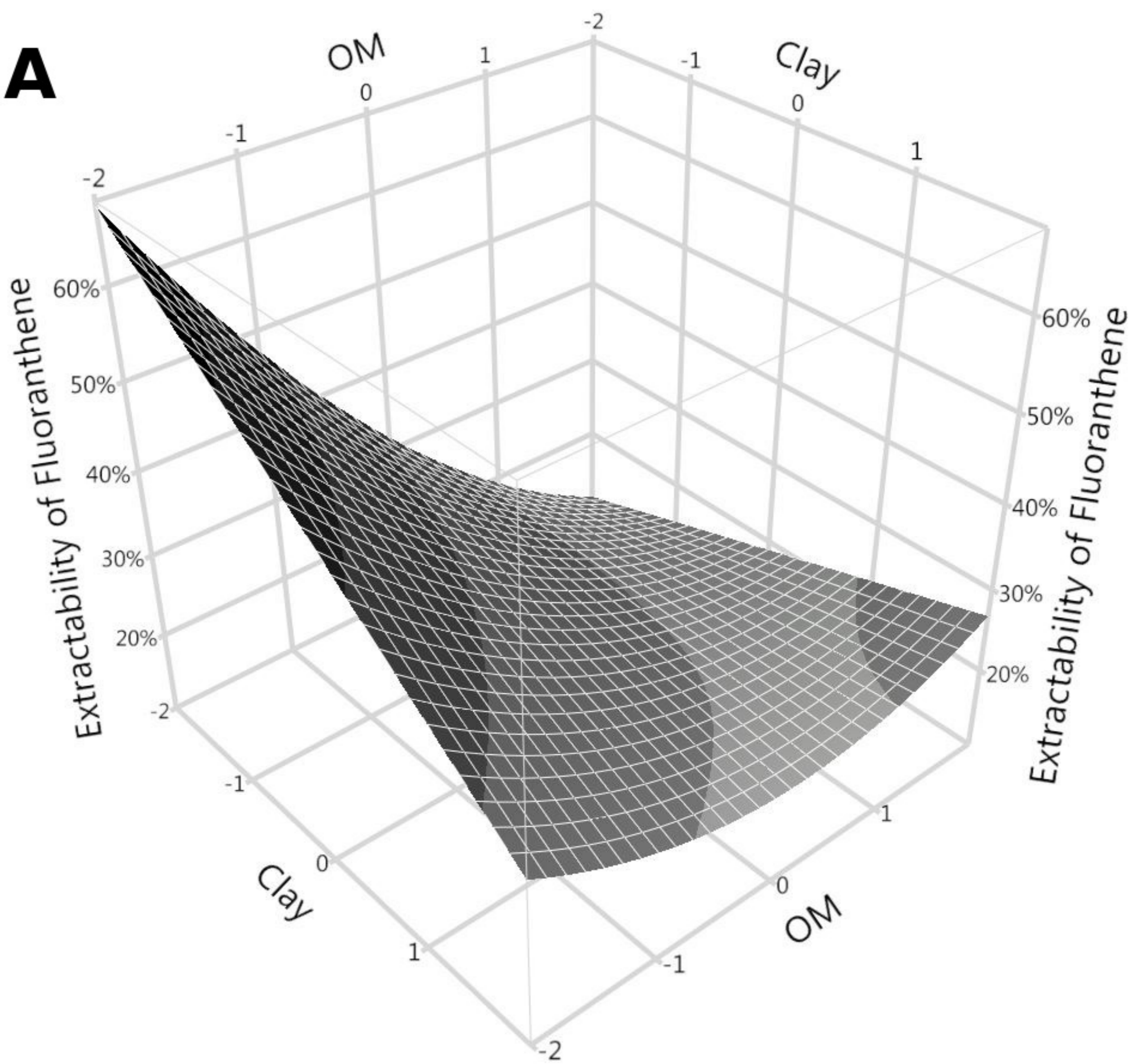
(b) [28]

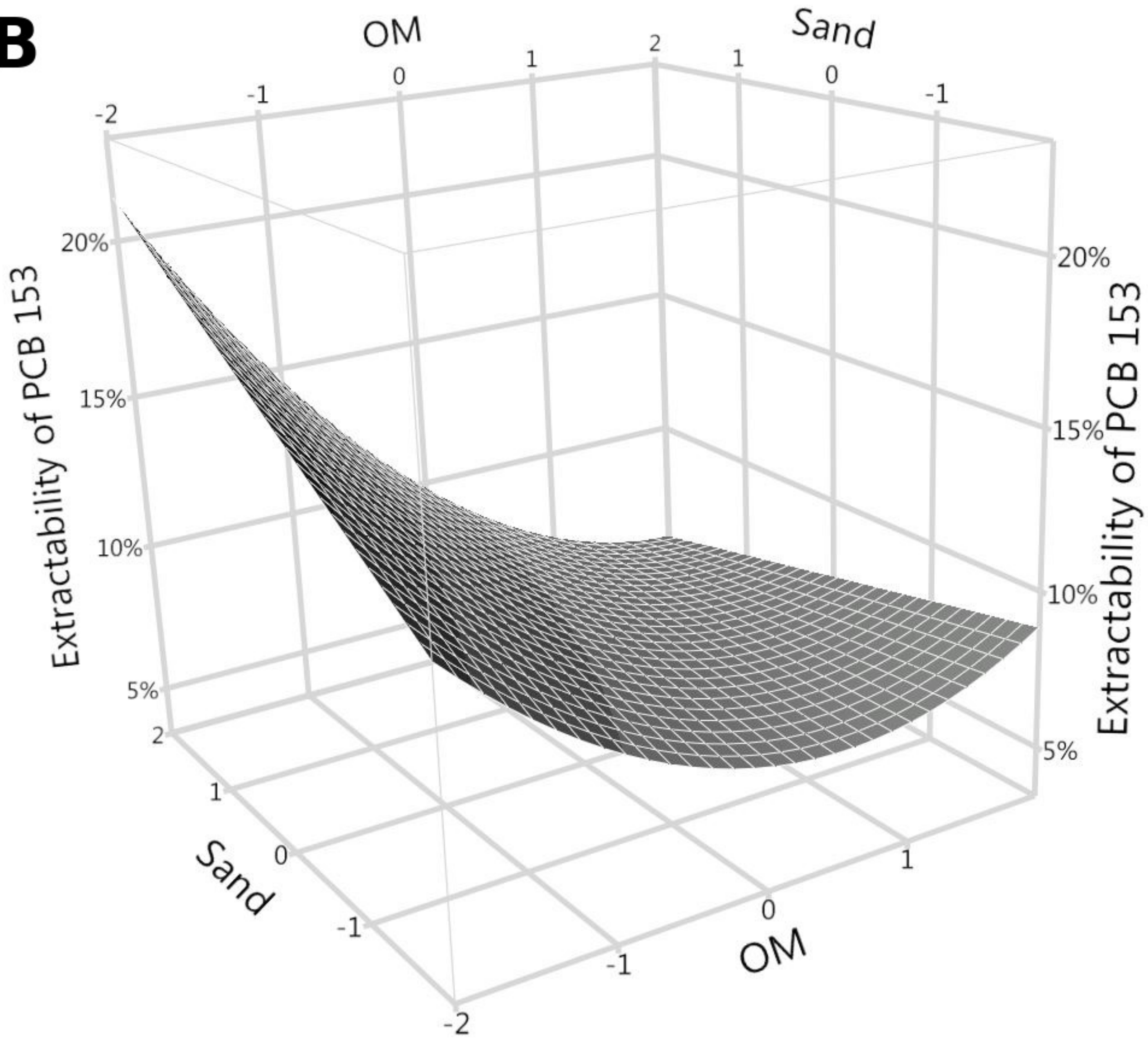
(c) [29]

Table 3: Mean percentages of extracted trace elements all along the **Martot** sediment core through sequential extractions in 4 steps.

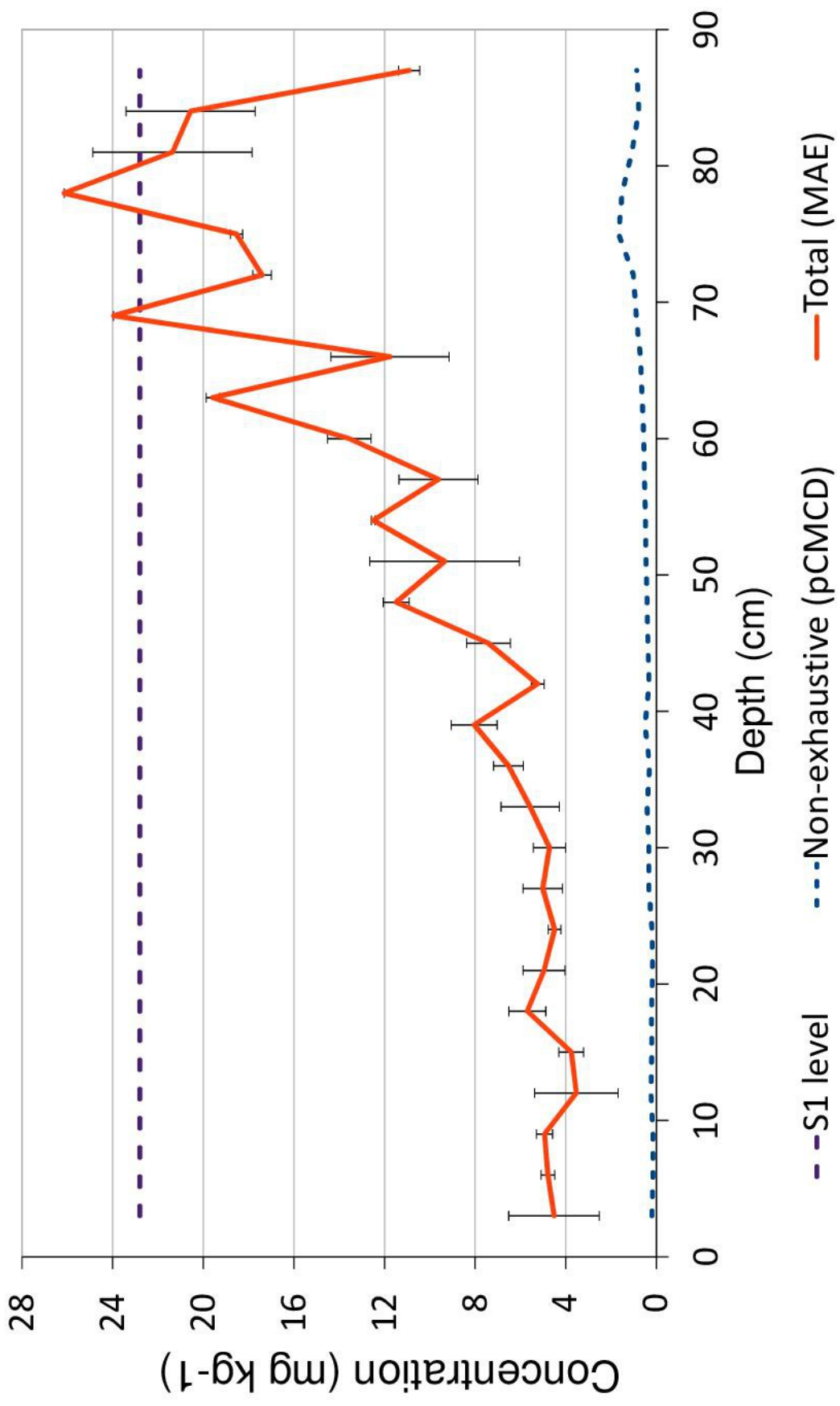
Extracted fractions (%)	As	Cd	Cr	Cu	Ni	Pb	Zn	<i>Mean</i>
Step 1: Exchangeable	17.9	3.6	0.1	0.4	9.3	0.7	15.3	6.8
Step 2: Reducible	17.3	43.9	0.7	1.5	6.3	6.5	31.9	15.4
Step 3: Oxidizable	14.0	37.6	40.2	51.3	25.9	25.7	27.5	31.7
Step 4: Residual	50.8	15.0	59.0	46.8	58.5	67.1	25.3	46.1

**A**

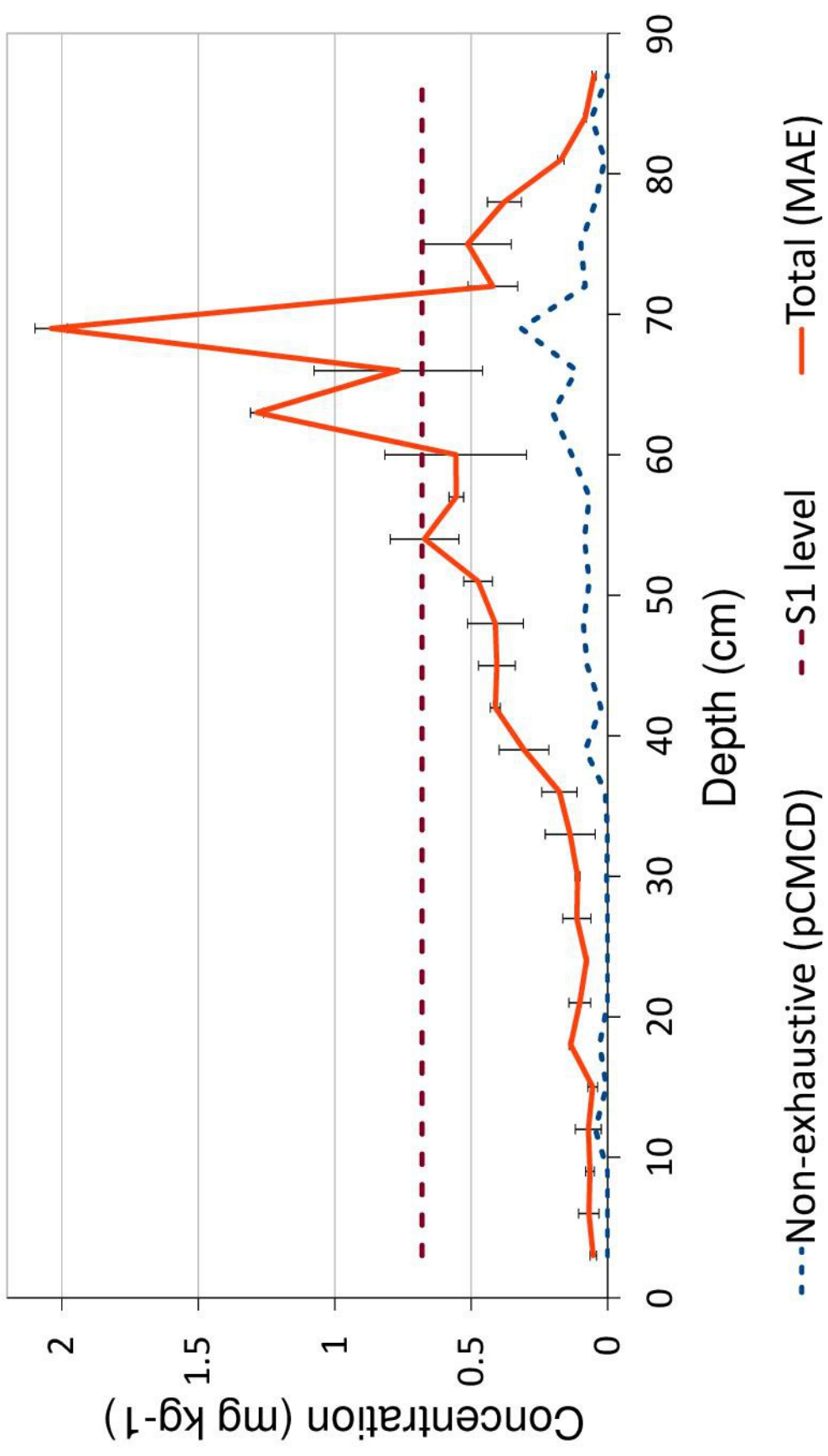


**B**

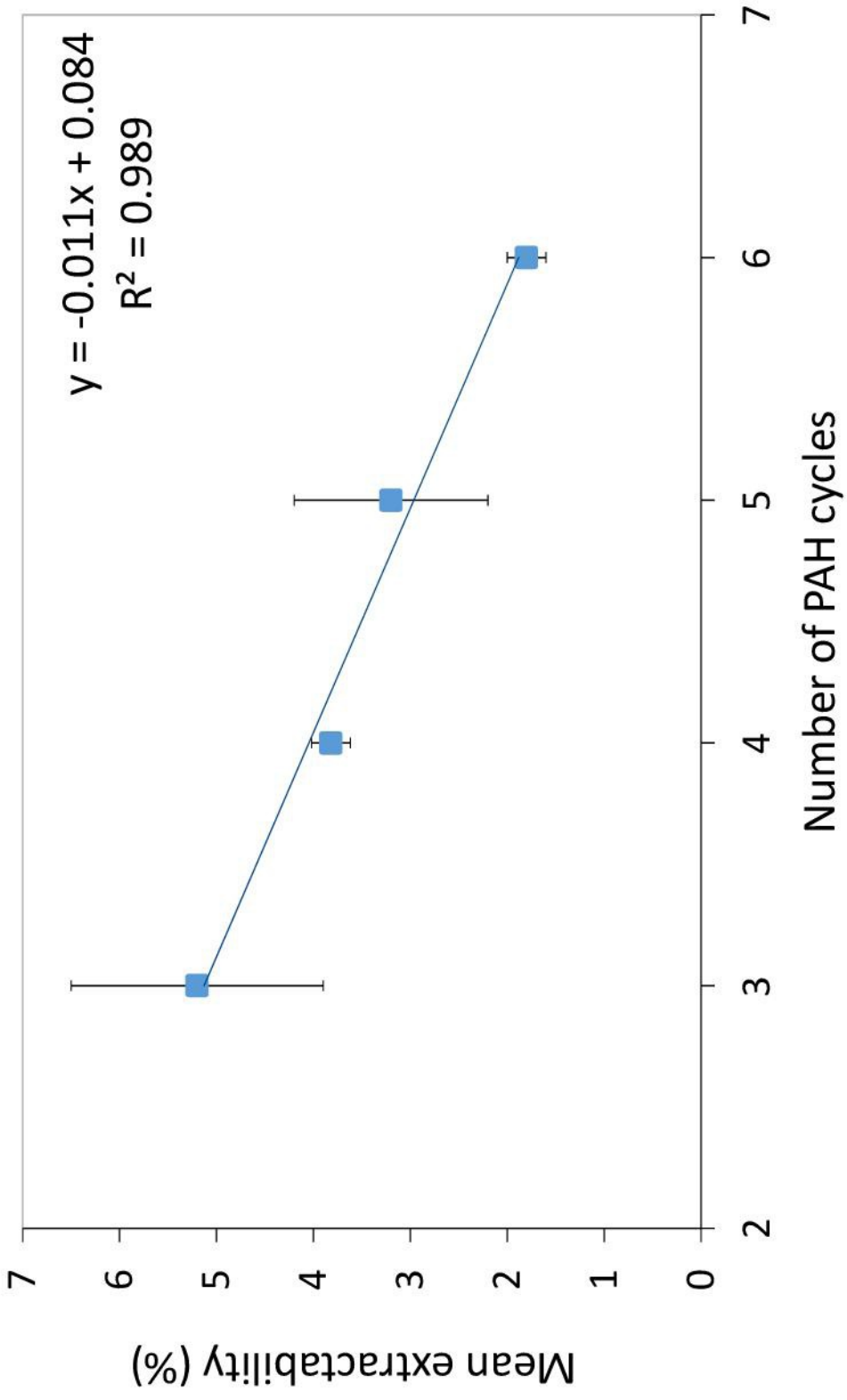
A



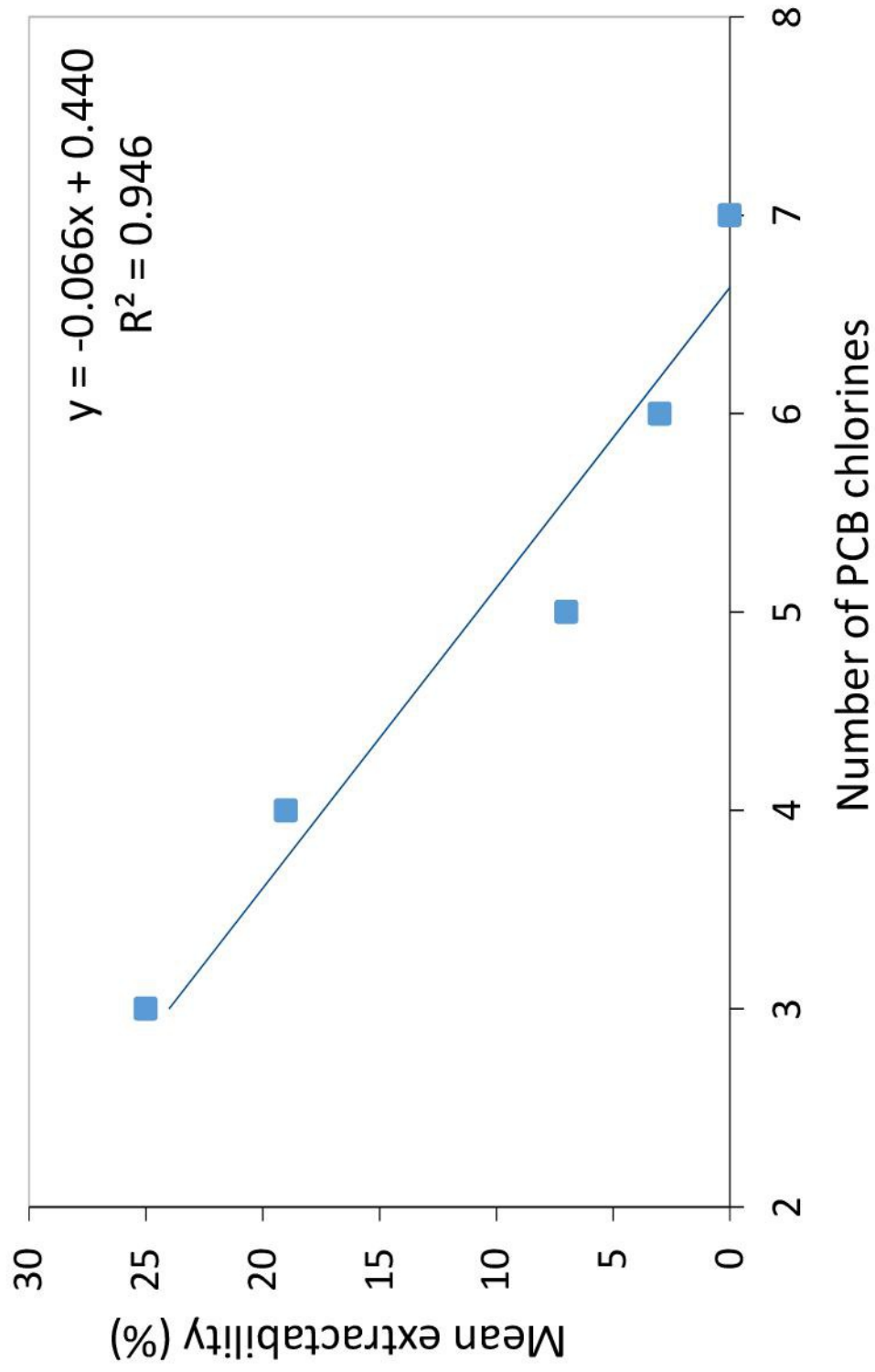
**B**

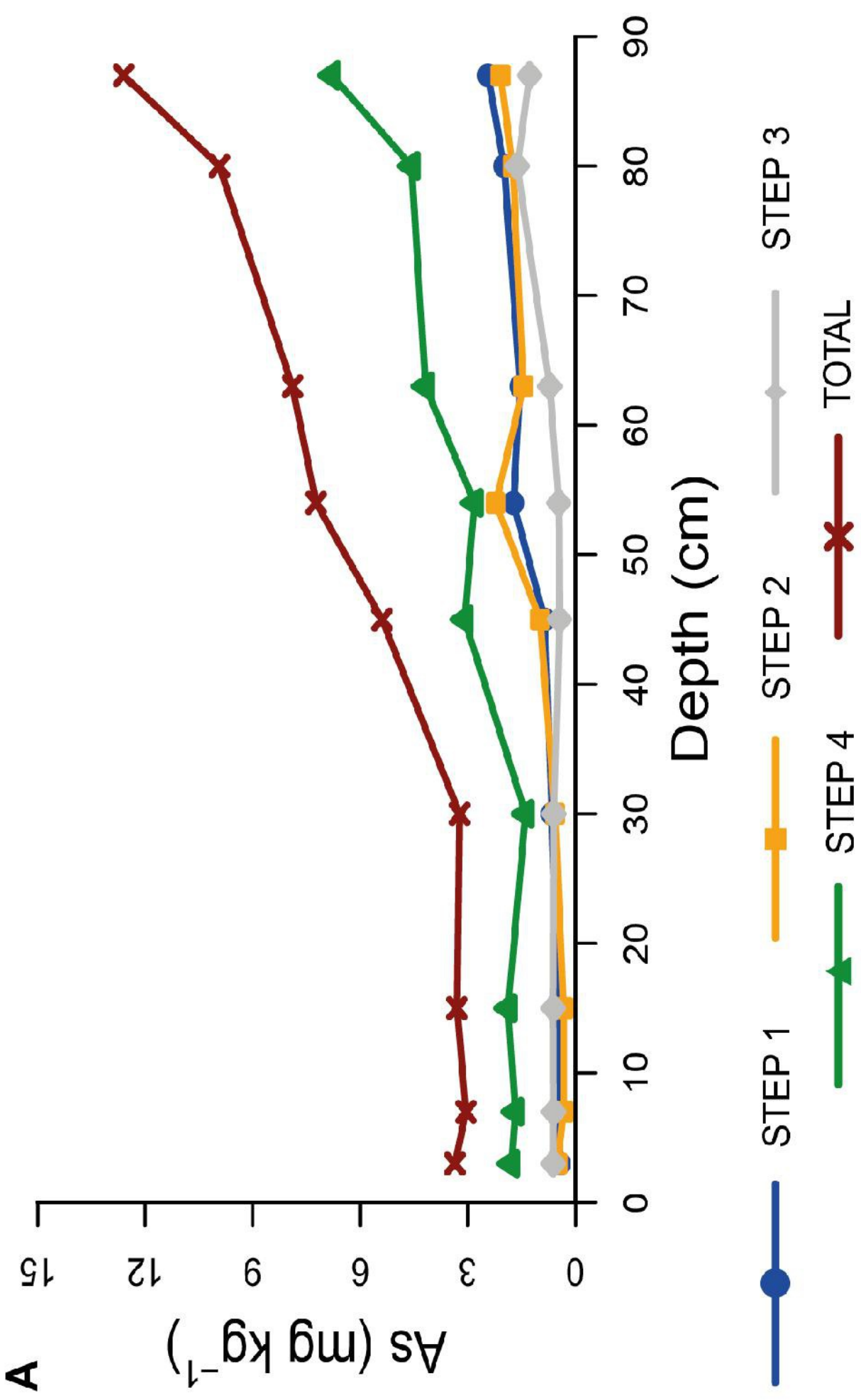


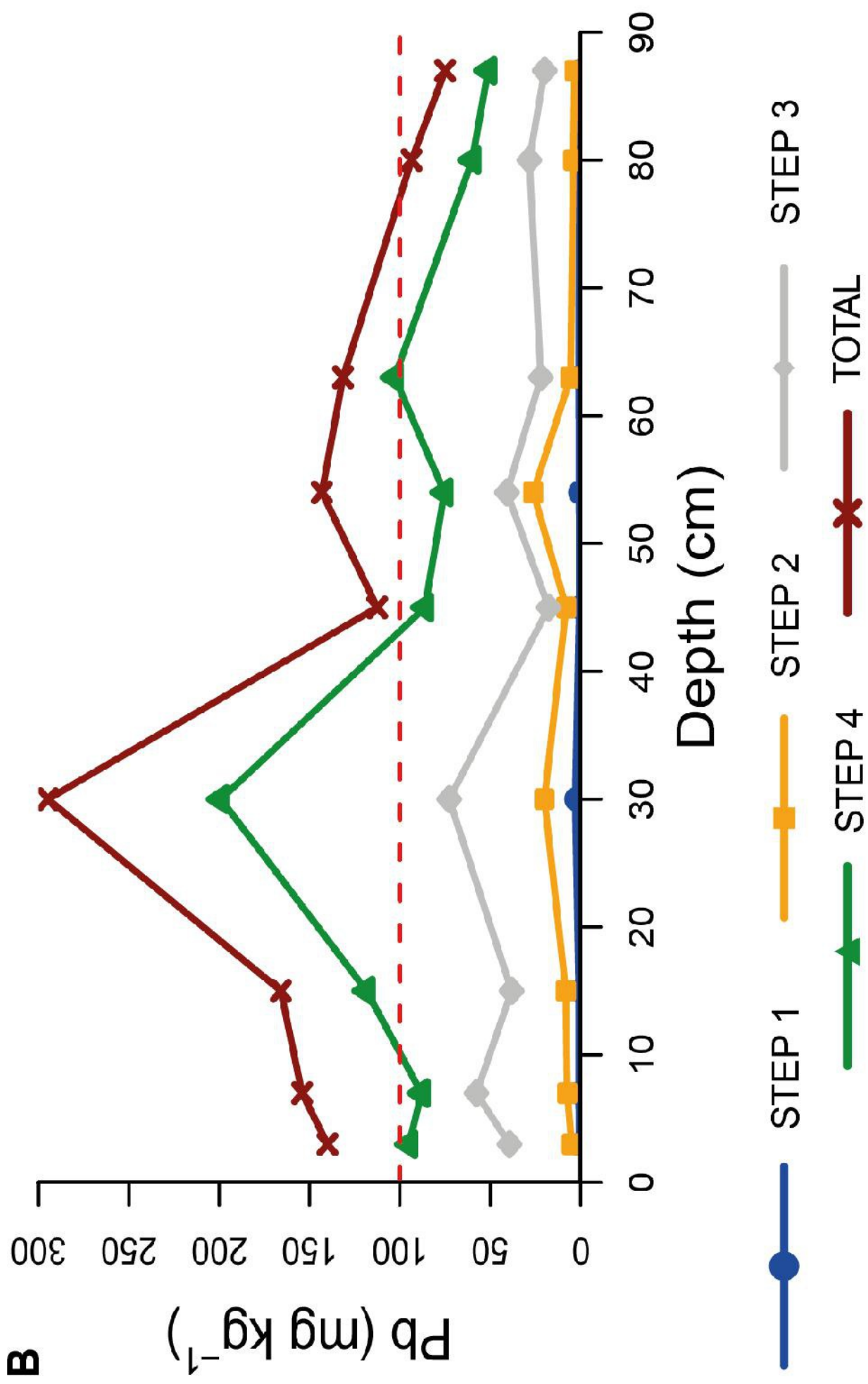
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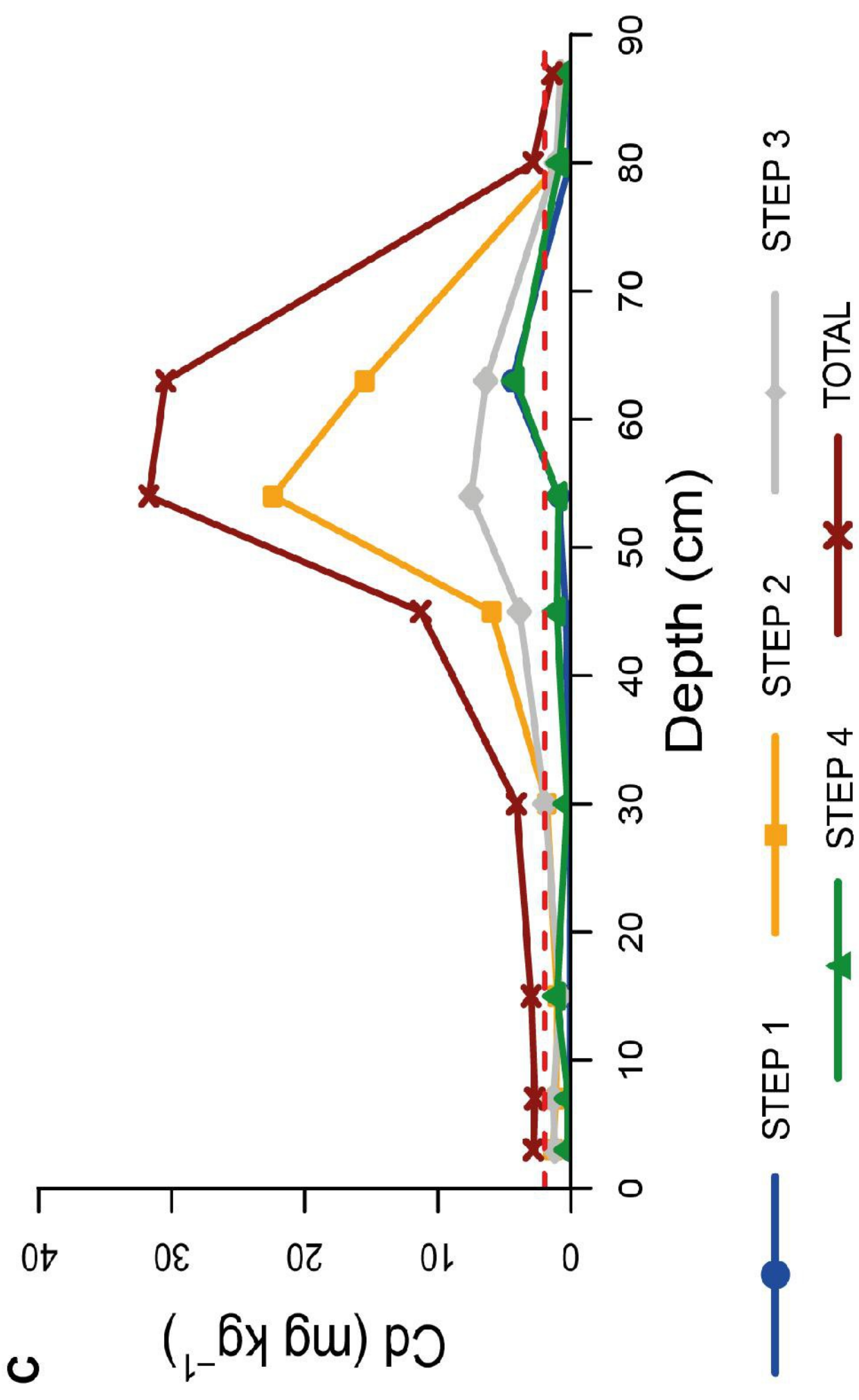


**B**











Sediment core

