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Research paper

Influence of ponds on hazardous metal distribution in sediments at a catchment scale (agricultural critical zone, S-W France)

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ABSTRACT

Eight potentially toxic trace elements were investigated together with the physicochemical characteristics of sediments collected upstream, downstream, and from various ponds from three adjacent carbonated agricultural catchments in southwestern France. Geochemical indices with local references and multivariate data analysis revealed a significant enrichment of Cd, followed by Ni and Cu in sediments, originating from agricultural practices, especially in the upper catchments sensitive to erosion processes. Five other PTEs (As, Pb, Co, Cr, and Zn) mostly originated from the weathering process of the molasse. Clay minerals and/or iron oxides were the main controlling factors for most PTEs. In ponds, Cd was regulated by Ca co-precipitation favoured by the long hydraulic retention time and increased pH, whereas it was mostly controlled by silicates in stream sediments. Copper, Pb, and Cd were the highly extractable metals, suggesting the risk of a hazardous environment. Multivariate analysis revealed that several environmental factors affected the spatial variation of PTE concentrations in sediments as well as the trapping role of ponds (texture, slope, soil erosion, pond size and position, discharge, hydraulic retention time) in this area of intensive agricultural practices. Our conclusions are useful for pond management in a context of increasing water demand and climate warming.

1. Introduction

Trace elements are increasingly released into the environment due to various human activities, which include -but are not limited to- industrial emissions (Viana et al., 2008), agricultural input (Jiao et al., 2012), and urbanisation (Wei and Yang, 2010). Although essential trace elements (Cu, Zn, etc.) are indispensable for life (Mertz, 1981; Hostetler et al., 2003), some trace elements, also known as potential toxic elements (PTE, such as Cd, Pb, Hg, and Ni), can be hazardous when their concentration exceeds an acceptable level (Goldhaber, 2003). Trace elements in agricultural areas have drawn much attention because of their potential risks to the ecosystem, food, and human health (Senesil et al., 1999). The anthropogenic sources of trace elements in these areas are mainly commercial fertilisers (N'guessan et al., 2009), wastewater effluent and irrigation (Xu et al., 2010), manures (Leclerc and Laurent, 2017), and pesticides (Gimeno-García et al., 1996). For instance, commercial mineral fertilisers are responsible for up to 85% of anthropogenic Cd in French cultivated soils (Sterckeman et al., 2018). Spreading Cu-fungicides (e.g. Bordeaux mixtures) contributed to the enrichment of Cu and Zn in the soils of

French vineyards (Duplay et al., 2014).

Physical erosion leads to the removal of soil particles, which are then transported downstream as suspended matter. PTEs are mainly adsorbed onto those particles in carbonated systems with high pH conditions (N'guessan et al., 2009; Redon et al., 2013). Stream and river waters contribute to most of their transfer downstream from soils to oceans. Generally, intensively cultivated catchments undergoing traditional practices such as tillage are affected by a high soil erosion rate due to their frequent exposure to various erosive powers (such as runoff), particularly when slopes are significant (Oost et al., 2009). In addition to physical erosion, fertilisers can increase soil chemical weathering by increasing the release of base cations due to excessive protons produced during the nitrification process under intensive N-P-K fertiliser spreading (Perrin et al., 2008; Gandois et al., 2011). All the above processes enhance the transfer and deposition of suspended particulate matter along the main water channels and constitute the bottom sediments. The transfer of such sediments may be delayed by other anthropogenic objects such as reservoirs and dams, which are known to be important traps for both particles and PTEs in large basins (Audry et al., 2004; Benabdelkader et al., 2018). Such transfer of

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sediments and their anthropogenic content from upstream to downstream in the presence of ponds has rarely been evaluated in agricultural areas.

Bottom sediments are usually recognised as a sink for most PTEs (Singh et al., 2002; Çevik et al., 2009; Duan et al., 2010), and thus can be a reservoir for both anthropogenic and geogenic PTEs (Jiao et al., 2015). The accumulation of PTEs in sediments is controlled by several processes depending on the properties of both the sediments and the PTEs themselves: adsorption, absorption, and/or complexation to fine particles containing clay minerals, iron and/or manganese oxides, organic matter, and co-precipitation with other elements (Ghafari and Yusuf, 2006; Çevik et al., 2009). Sediment physicochemical properties, including pH, carbonate and organic matter contents, and redox condition, and so on, can affect these processes (Du Laing et al., 2009). The different combining processes and the sources mean that PTEs in sediments are associated with residual and/or labile phases. Anthropogenic PTEs are normally prone to bond to non-residual rather than to residual phases (Leleyter et al., 2012), which makes them more or less easily released from the sediments by water disturbance and changes in water/sediment physicochemical conditions (Duan et al., 2010). Sediments can then be a secondary source of the downstream contamination (Jiao et al., 2015). Meanwhile, metal distribution between sediments and plants may be a concern in places where vegetation is abundant, as some plants can absorb the metals through the rhizosphere (Nagajyoti et al., 2010). Evaluating the available fraction of PTEs in sediment is thus a necessary step in investigating their potential risks to the environment, and especially to living organisms.

In cultivated areas of southwestern France, numerous ponds have been constructed by local farmers for water storage, irrigation, and/or private landscaping, and a chain of several ponds can sometimes be seen along the main water channel in a given upstream agricultural catchment. The constructed ponds can store water and sediments transported by surface runoff and stormwaters, and provide a favourable environment for sedimentation (Casey et al., 2007; Frost et al., 2015) and the unintentional storage of PTEs. Few studies have examined the different distributions of PTEs in stream and pond sediments from upstream agricultural catchments, as these kinds of sediments and catchments can have different physicochemical characteristics. The position and the characteristics of the ponds that contribute to the PTE transfer downstream remain poorly understood, particularly in channels with a chain of multiple constructed ponds. Such ponds can be alternatively dredged by the owners, which question the effect of the pond management on the transfer.

To fill some of these mentioned gaps of knowledge, the stream and pond sediments from three adjacent agricultural catchments in southwestern France were collected and analysed for their physicochemical characteristics, especially for the concentrations of eight PTEs (As, Pb, Co, Cr, Zn, Cu, Ni, and Cd). The objectives of this study were to:

- (1) investigate the various sources of PTEs based on the effect of the anthropogenic activities, and to assess the contamination intensities.
- (2) identify the key physicochemical and environmental factors that regulate the contribution and distribution of PTEs, especially in stream and pond sediments.
- (3) assess the availability of PTEs in the different kinds of sediments.
- (4) and, finally, evaluate the effect of ponds on PTE transfer in catchments.

The main hypothesis was that some metals in sediments originated from anthropogenic activities and were transferred downstream, and that the presence of ponds would affect this transfer through their storage capacity according to their physicochemical and environmental characteristics.

2. Materials and methods

2.1. Sampling sites

2.1.1. Catchment characteristics

The sampling site is part of the Save basin, drained by the Save river, a left tributary of the Garonne river (southwestern France, Fig. 1). The middle and downstream part of the Save basin is mainly covered by wheat and sunflowers in rotation cultivation, and the upstream area by meadows and forests (Taghavi et al., 2011). As recorded by the Direction Départementale des Territoires (DDT), some 3000 ponds were constructed for irrigation in this area. According to the DDT database, three small adjacent agricultural catchments were considered for the study since they contained representative ponds as regards size and volume, and due to their different positions and managements in the catchment areas (Wu, PhD, in progress).

The three catchments are drained by the tributaries of the Save river, located close together on the right (Montoussé (MON), 325 ha; Mican (MIC), 277 ha) and left bank (Nuguet (NUG), 116 ha) of the middle Save basin (Fig. 1 and Table 1). The catchment slopes are in the range of what is commonly observed in the Save basin (from 0% to 20%, with 75–80% varying from 4% to 10%; Perrin et al., 2008), although MON and MIC are steeper than NUG (Table 1). The Montoussé sub-stream (900 m) and the Mican stream (3595 m) cross the village of Auradé and converge into the Boulouze stream, then to the main Save river. The Nuguet stream (2550 m) crosses the village of Marestaing in its middle course (Fig. 1).

The substratum of the sampling site is a Miocene molassic deposit, defined as “molasse” by Cayeux (1935), originating from the erosion of the Pyrenees Mountains and the subsequent sediment deposition at the end of the Tertiary Period. It consists of clays, sandstones, limestones, and calcareous sediments (Revel and Guisresse, 1995; Perrin et al., 2008). The carbonate content in molasse varies between 60% and 90% (Perrin et al., 2008). Calcic soils dominate more than 90% of the Save basin with a clay content ranging from 40% to 50%, and non-calcic soils only account for less than 10% (Perrin et al., 2008; Taghavi et al., 2011). The pH values are 7.7–8.8 and 5.9–6.9 in calcic soils and non-calcic soils, respectively. The organic content in the soils ranges from 1.0% to 2.5% (Perrin et al., 2008). As it is a traditional agricultural area, mechanical erosion due to farming and ploughing have a great impact on downward soil displacement, along with the water erosion (Revel and Guisresse, 1995). Further information about the soil composition is given in the Supplementary materials (SM Section 1).

The considered catchments are affected by an oceanic climate (Köppen–Geiger climate classification). An average annual precipitation of 621 mm and air temperature of 13.9 °C were registered in MON over the last 32 years (Ponnou-Delaffon et al., 2020). The dry and wet periods generally extend from June to August and from October to May, respectively. Intensive rainfalls occur during spring and winter, generating several significant flood events, and particularly erosive flash floods in spring. The stream discharge is mainly contributed by the surface runoff since the underground flow is very limited (Perrin et al., 2008; N'guessan et al., 2009).

More than 90% of each catchment area is cultivated. During the sampling period, wheat and sunflower were the dominating crops, with some colza. The spreading of N-P-K fertilisers for wheat usually occurs between mid-January and March with an optional addition in April (Paul et al., 2015). The amount of fertiliser applied in these catchments is close to the demands of the crop, which is around 110 kg N ha⁻¹ a⁻¹ (Ponnou-Delaffon et al., 2020).

2.1.2. Pond characteristics

Table 1 provides detailed information about the sampling ponds. Samples were collected from nine ponds, and, if they were connected to the stream, their up and down drainage streams: two ponds in MON, four ponds in MIC, and three ponds in NUG (Fig. 1; NUG4 was not

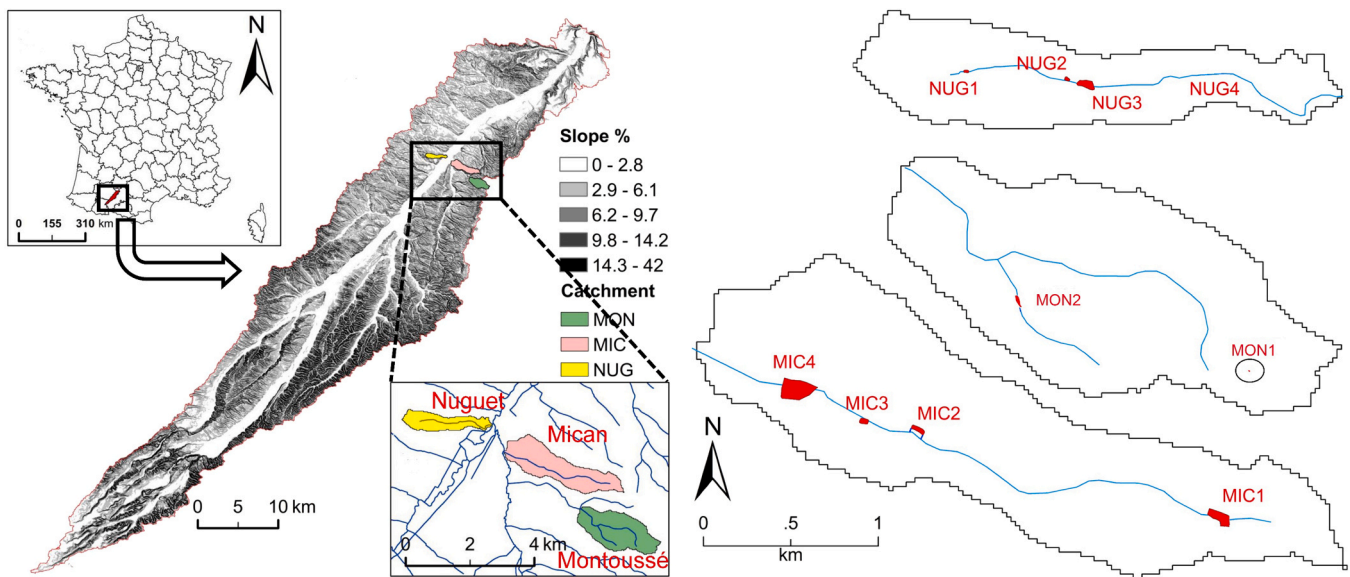


Fig. 1. Location of the studied ponds and the three relative catchments (Montoussé (MON), Mican (MIC), Nuguet (NUG)) within the Save basin, southwestern France.

Table 1

Characteristics of the sampled streams and ponds, and of their relative catchments. Distance = distance ratio between the distance from source to a pond and the stream total length (from 0 to 1 indicating from upstream to downstream); HRT = hydraulic retention time (pond volume / (Q_{outlet} - Q_{inlet}), with Q the discharge velocity); YC = year of pond construction, YD = year of sediment dredging.

Catchment	Montoussé (MON)		Mican (MIC)				Nuguet (NUG)			
Area (ha)	325		277				116			
Slope (%)	6.59 ± 3.10		4.44 ± 2.49				4.01 ± 2.56			
Stream length (m)	900		3595				2550			
Stream elevation (m)	226.4 ~ 192.7		220.6 ~ 149.0				190.4 ~ 146.0			
Pond	MON1	MON2	MIC1	MIC2	MIC3	MIC4	NUG1	NUG2	NUG3	NUG4
Longitude	1.0936	1.0773	1.0762	1.0547	1.0509	1.0460	1.0073	1.0145	1.0157	1.0246
Latitude	43.548	43.5513	43.5656	43.5696	43.5699	43.5715	43.5815	43.5813	43.5810	43.5818
Distance	NA	0.064	0.068	0.598	0.691	0.789	0.075	0.306	0.329	0.627
Slope (%)	2.72	4.49	1.81	3.94	1.03	1.46	1.46	1.62	3.15	1.63
Area (m ²)	80	1050	4200	2500	1566	18,000	480	550	3800	3641
Volume (m ³)	23.0	1520.7	8515.7	2183.7	1123.3	62,213.3	169.3	293.3	10,144.7	5481.3
HRT (day)	NA	41.8	1202.0	186.8	13.5	1956.7	26.8	41.4	1151.1	379.9
YC	1970	1970	1977	1960s	Late 1970s	1965	Before 1970s	1970s	Early 1980s	1995
YD	Never	2015	Never	1999	Never	1985	1980s	1990s	^a	Never
Connection	Isolated	Connected	Connected	^b	Connected	^c	Connected	Connected	Connected	Connected

^a Only the border was dredged a little.

^b This pond is disconnected during high floods periods with large loads of suspended matters and connected the rest of the time. It was connected to the Mican stream while sampling.

^c This pond was disconnected unless the owner opens its valve linked to the channel very scarcely, not in flood conditions. It was disconnected while sampling.

sampled inside the pond, see below). MON1 is a very small, isolated pond, which is not connected to the Montoussé stream, in the very upstream Montoussé catchment. MON2 is surrounded by wheat, and its pond sediments were dredged in 2015. In MIC and MON, the first three ponds (MIC1 to MIC3 and NUG1 to NUG3, respectively) were connected to the stream during the sampling campaign, whereas MIC4 was disconnected. NUG4 is located downstream in the Nuguet stream and was not sampled because of the effect on the quality of waters and sediments from the exudate of the Marestaing village residential wastewater treatment plant (WWTP) upstream of the pond. This would compromise detection of the effect of agricultural activity. MIC1, MIC4, and NUG3 are recognised as large ponds in size, and consistently have the longest hydraulic retention time (HRT, Table 1). MIC3 is a shallow pond due to significant sediment accumulation as it has never been dredged since its establishment in the 1960s (Table 1). There is almost no vegetation in these ponds. Some *Typha latifolia* L. grows at the very upstream source of NUG. A cover of seasonal floating plants was

observed in the borders of NUG2, but this cover was very limited relative to its large surface area. Organic debris, mainly decayed fallen leaves from the trees in the surrounding, covered the upper part of pond bed in NUG3. NUG2 and NUG3 are also closely linked (Fig. 1), and thus the stream outlet of NUG2 was identified as the stream inlet of NUG3.

2.2. Sampling strategies and sample pre-treatments

Sediment samples were collected from streams and ponds (see SM Fig. 1 for the sampling strategic schema). The sampling campaign was carried out from mid-March to early April in 2016, during the late wet season of the Save basin after the fertiliser spreading period. No significant flood events were noted either before or during the sampling campaign, and thus the water discharge corresponded to a recession flow, which usually occurred at that time (Perrin et al., 2008; Paul et al., 2015; Ponnou-Delaffon et al., 2020).

Stream sediments at the inlet/outlet of the ponds (SM Fig. 1) were

collected by hands in sterilised non-powder gloves from the surface layers of stream sediments (< 4 cm, beneath the water-sediment interface). Pond sediments were collected using a straight core sampler. The sampler was inserted vertically into the benthic sediment and sealed by a rubber stopper at the tail end to obtain a core of sediment. Firstly, the surface layer (S) of the sediment (0 – 4 cm) was extracted from each core. Secondly, the rest of sediment was sliced into one or two layers (called deeper (D) and bottom (B) layers) depending on the sedimentation and change of sediment colours, supposed to represent different oxic and organic conditions. The number of sediment sampling points in each pond was determined by its surface area. For normal sized ponds, sediments were taken from the central part of a pond (CP), and for the largest ones, samples were collected from the upper part (UP), central part (CP), and lower part (LP) inside these ponds (SM Fig. 1).

The sediment samples were put in plastic containers, and kept in coolers during transportation to the laboratory, where samples were then dried in an oven at 40 °C. The dry sediments were gently homogenised in an agate mortar, and then they were sieved into three fractions, a fine fraction (<63 µm), a coarse fraction (63 µm – 2 mm), and the coarser fraction (>2 mm), following very well established protocols (N'guessan et al., 2009; Benabdelkader et al., 2018). Each fraction was weighed and conserved in a dry place for further analyses.

2.3. Physicochemical analyses

The texture of the fine and the coarse fractions (< 63 µm and 63 µm – 2 mm, respectively) of the sediments was measured using a laser diffraction particle distribution analyser (LA-960, HORIBA). The organic carbon content (Corg, %) was determined using an element analyser (Flash2000, ThermoFisher) after decarbonation with 1 mol l⁻¹ HCl on a heat block (40 °C) until the complete disappearance of effervescence.

Mineralisation was performed on the 63 µm fraction owing to its dominance and the affinity for metals (Probst et al., 1999). Sediments were totally digested with a mixture of HF/HNO₃/H₂O₂ under a well-validated multiple step procedure in the laboratory clean room. This process has been successfully applied in many studies, particularly for studies in similar carbonated context (Benabdelkader et al., 2018; Bur et al., 2009; N'guessan et al., 2009). Blanks and standard sediments (SUD-1, WQB-1, and STSD-3) were treated using the same digestion procedure. SM Section 2 provides a detailed protocol for the sediment digestion.

A single EDTA extraction procedure was applied to sediments for the measurement of the available fraction of trace elements (SM Section 2). A solution of 1 g sediment and 10 ml of EDTA-2Na (0.05 mol l⁻¹, ethylenediaminetetraacetic acid disodium salt dihydrate) was gently mixed for 1 h at the ambient temperature (20 °C). The extracted solution was then filtered through a 0.22 µm filter membrane. Two blanks were treated by the same process.

The major elements (Ca, Al, Fe, Mg, Mn) were analysed with an inductively coupled plasma-optical emission spectrometer (ICP-OES, Thermo IRIS Interpid II XDL) at the Laboratory of Functional Ecology and Environment (Toulouse, France). The trace elements (Zn, Cr, Ni, Cu, Pb, As, Co, Sc, Cs, Pb) were measured using an inductively coupled plasma-mass spectrometer (ICP-MS, Perkin-Elmer ELAN 6000) at the GET-OMP (Geoscience Environment Toulouse-Observatory Midi-Pyrénées) analytical platform. Recovery for the standard sediments ranged from 85% and 110%, and the blanks were below the detection limits. The detection limits of ICP-OES for major elements are 0.5 µg l⁻¹. The detection limits of ICP-MS for trace elements are between 10⁻³ and 10⁻² µg l⁻¹.

2.4. Data treatment

2.4.1. Geoaccumulation index

The geoaccumulation index (I_{geo}) was introduced to assess the degree of contamination by a given element in sediment (Müller, 1969),

which is expressed as follows:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \quad (1)$$

Where C_n is the concentration of an element, B_n is the background concentration of the corresponding element. A correction factor of 1.5 is used to correct the fluctuation of background value due to the lithogenic effect. Seven classes of I_{geo} are defined ranging from Class 0 ($I_{geo} \leq 0$, unpolluted) to Class 6 ($I_{geo} \geq 5$, extremely polluted), where Class 1 ($0 < I_{geo} < 1$) reflects an uncontaminated to moderately contaminated situation and Class 2 ($1 < I_{geo} < 2$) indicates moderate contamination. The local molasse bedrock was used as the background material.

2.4.2. Enrichment factor

The enrichment factor (EF) has been widely applied to evaluate the anthropogenic contribution of metal to the total concentration in a river sediment (Chester and Stoner, 1973).

$$EF = \frac{\left(\frac{C_i}{RE}\right)_{sample}}{\left(\frac{C_i}{RE}\right)_{background}} \quad (2)$$

Where C_i is the concentration of a given element, and RE is the concentration of the reference element. The local molasse bedrock and Cs were selected as the reference material and the reference element, respectively. The selection process for the normaliser element and the bedrock material chosen in this study is demonstrated in the Supplementary material (SM Section 3).

2.4.3. Anthropogenic contribution

The total concentration of a given element in the sediment could be considered the consequence of both lithogenic and anthropogenic activity. Assuming that the lithogenic ratio of a given element to the reference element remains the same between the molasse and the sediment sample, the lithogenic element concentration could be calculated as follows:

$$C_{lithogenic} = RE_{sample} \times \left(\frac{C_i}{RE}\right)_{molasse} \quad (3)$$

Where $C_{lithogenic}$ is the lithogenic concentration of a certain trace element, RE_{sample} is the concentration of reference element in the sediment, and C_i is the concentration of a certain trace element in the background bedrock.

The anthropogenic concentration, then, can be obtained as the difference between the total and the lithogenic contribution. The anthropogenic contribution (%) is calculated as follows:

$$Anthropogeniccontribution(\%) = \frac{(C_i)_{sample} - RE_{sample} \times (C_i/RE)_{molasse}}{(C_i)_{sample}} \times 100\% \quad (4)$$

2.4.4. Statistical analyses

The statistical analysis was conducted in R (version 3.4). The Shapiro-Wilk test, accompanied by the quantile-comparison plot, was used to test the normality of a parameter. The permutation *t*-test was applied to compare the differences of given values between groups. The Spearman correlation coefficient was applied to calculate correlations among various parameters. Principle component analysis (PCA) was carried out based on z-scored data to investigate the factors that could affect the behaviour of major and trace elements in stream and pond sediments, respectively. The Kaiser-Meyer-Olkin measure of sampling adequacy and Bartlett's test of sphericity were conducted before PCA to test the feasibility of performing PCA with the data.

3. Results

3.1. Concentrations of major elements and eight potential toxic elements (PTE) in sediments

The descriptive statistics of the concentrations of concerned elements in all sediments are shown in Table 2. The average concentrations of major elements were in the increasing order of Mn < Mg < Fe < Al < Ca. Iron, Al, and Mn were in the range of concentrations measured in various stream sediments from the Gascogne region, while Mg and Ca were a little bit higher (N'guessan et al., 2009). The concentrations exceeded the molasse content in the same region (N'guessan et al., 2009). In terms of the chemical composition for major elements (Fig. 2A), Ca + Mg (%) varied from 21.4% (NUG1-CP-D, near the non-carbonate end-member [Ca < 15%]) to 59.3% (MIC2-CP-D, near the carbonate end-member [Ca > 60%]), with a mean of $44.3 \pm 7.9\%$. There was a significant difference between the MON/MIC and NUG catchments ($p < 0.01$). The relative percentage of Ca was lower in the NUG sediment than in the MON/MIC sediments although few NUG sediments fell into the cluster of the MON/MIC group.

This study focused on eight PTEs as regards their potential hazard to the environment and the living organisms. The order of PTEs was Cd < Co < As < Pb < Cu < Ni < Cr < Zn according to the average concentration (Table 2). Arsenic, Pb, Co, and Cd fell in the range of concentrations of stream sediments in the Gascogne region (N'guessan et al., 2009) with less value dispersion around the mean, while Cr, Zn, Cu, and Ni were slightly greater, particularly with higher maximum and minimum values (Table 2). As with major elements, the mean concentrations of PTEs were greater than the molasse background value, except for As. The ratios of mean concentration in sediments to the local background value were: 0.95 (As), 1.15 (Pb), 1.20 (Co), 1.36 (Cr), 1.38 (Zn), 1.62 (Cu), 1.75 (Ni), and 2.40 (Cd). The concentrations of PTEs were always higher in MON and MIC than in NUG, particularly for Cd, Cu, Ni, and Zn (Fig. 3B). The pond sediments exhibited higher PTE concentrations than the stream sediments (Fig. 3C), however, no significant differences were found between the surface and deeper layers of the pond sediments (Fig. 3D).

3.2. Sediment texture

The sediment texture (Shepard's classification) was shown in Fig. 2B. There was no difference in sediment textures between the three

catchments. Although most of sediments fall in the clayey-silt domain, the texture differed significantly between stream and pond sediments ($p < 0.01$). Stream sediments are located between sandy-silt and silty-sand domains, with most in the clayey-silt and sandy-silt domains, whereas pond sediments were in the clayey-silt domain, except for two (MIC1-LP-D and NUG3-LP-D) near the border of the silty-clay domain. The lowest clay content (17.4%) was found in NUG3-CP-S and the highest sand content (51.4%) was in NUG1-IN in the very upstream of NUG. As a whole, the pond sediments normally contained more fine particles than the stream sediments, especially for the fine fractions (< 63 μm). This observation was also supported by the granulometry of particle size distribution (SM Fig. 2).

3.3. Contamination indices

3.3.1. Geoaccumulation index (I_{geo})

Table 3 showed the descriptive statistics of I_{geo} for eight PTEs in all sediments. The values of I_{geo} were in the order of As < Pb < Co < Cr < Zn < Cu < Ni < Cd, and were either negative or between 0 and 1, which indicated unpolluted to moderately polluted sediments for the PTEs considered. The values of three PTEs (As, Pb, and Co) were always negative, except that As in MON2-OUT was the only sample with I_{geo} greater than 0. The average values of I_{geo} for Cr and Zn were -0.16 ± 0.21 and -0.15 ± 0.26 , respectively. Copper, Ni, and Cd presented the highest I_{geo} in the average between 0.07 and 0.58, with a maximum value for Cd of 1.6 (MON2-IN).

3.3.2. Enrichment factor (EF)

The order of EF was As < Pb < Co < Cr < Zn < Cu < Ni < Cd, for all sediments (Fig. 4A), which is the same as that of I_{geo} . A threshold of 2 was accepted to discriminate whether a certain element was enriched in sediment. This threshold could be decreased to 1.5 if a local reference material is used to calculate EF (Hernandez et al., 2003; Roussiez et al., 2005; N'guessan et al., 2009; Benabdelkader et al., 2018). The EF of the first five elements, particularly for As, were lower than the threshold of 1.5, although a few outliers were higher than 1.5. Although the average value of EF(Cu) did not exceed 1.5, 25% of sediments (sediments mainly from upstream ponds in three catchments, respectively) exhibited an EF (Cu) value exceeding 1.5. The average EF (Ni) was not different from the threshold of 1.5 ($p = 0.14$). Cadmium had an average EF value greater than 1.5 ($p < 0.001$). It was the most enriched element with a mean EF value of 1.99 ± 0.60 , but also had the most dispersed values and a

Table 2

Concentration of major elements and eight potentially toxic elements (PTE) in sediments and other materials.

	This study			Gascogne ^a			Molasse ^b	UCC ^c	PAAS ^d
	Min	Max	Mean (SD)	Min	Max	Mean			
<i>Major element (mg g⁻¹)</i>									
Al	43.44	92.48	68.91(13.79)	31.87	98.17	52.99	46.53	77.44	189.00
Ca	26.36	129.56	71.10(22.64)	2.01	104.50	29.18	48.85	29.45	13.00
Mg	4.96	13.36	9.73(2.18)	1.64	8.76	4.36	3.60	13.50	22.00
Fe	21.57	43.65	33.01(5.94)	17.63	60.09	28.59	28.43	30.89	72.00
Mn	0.41	4.52	1.01(0.76)	0.36	2.41	1.05	0.55	0.53	1.10
<i>Potential toxic element (PTE) ($\mu\text{g g}^{-1}$)</i>									
As	8.17	27.32	16.27(3.97)	8.77	27.48	17.19	17.19	2.00	NA
Pb	18.19	28.52	24.58(2.56)	16.52	41.94	21.45	21.45	17.00	20.00
Co	9.65	17.88	14.58(2.03)	8.15	33.16	12.19	12.19	11.60	23.00
Cr	52.08	97.09	78.36(11.4)	33.49	84.98	52.98	57.56	35.00	110.00
Zn	66.63	147.52	111.55(19.69)	55.46	140.59	80.96	80.96	52.00	85.00
Cu	16.86	42.62	29.16(6.64)	11.25	29.62	18.04	18.04	14.30	50.00
Ni	26.62	60.75	46.49(9.03)	17.01	43.92	26.73	26.73	18.60	55.00
Cd	0.23	0.67	0.48(0.15)	0.11	0.79	0.20	0.20	0.10	NA
Cs	3.83	9.09	6.54(1.41)	2.24	5.97	5.50	5.50	5.80	15.00
Sc	7.17	14.06	11.17(2.00)	6.30	21.88	12.97	14.48	7.00	16.00

^a Gascogne stream sediments (N'guessan et al., 2009).

^b Molasse is the local background bedrock of Gascogne (N'guessan et al., 2009).

^c Upper Continental Crust (Hans Wedepohl, 1995).

^d Post Archean Australia Shale (McLennan, 2001). NA: data not available.

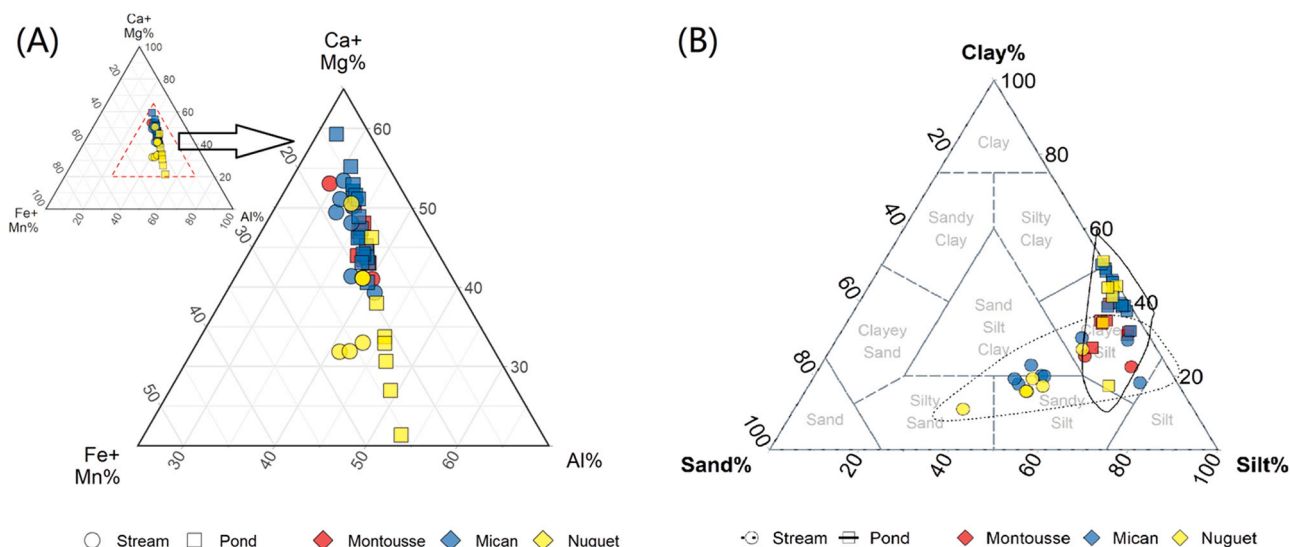


Fig. 2. Ternary diagrams for (A) major elements composition, and (B) sediment texture. Stream and pond sediments are indicated by round and square points, respectively. The red, blue, and yellow colours correspond to the Montoussé (MON), Mican (MIC), and Nuguet (NUG) catchments, respectively. For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.

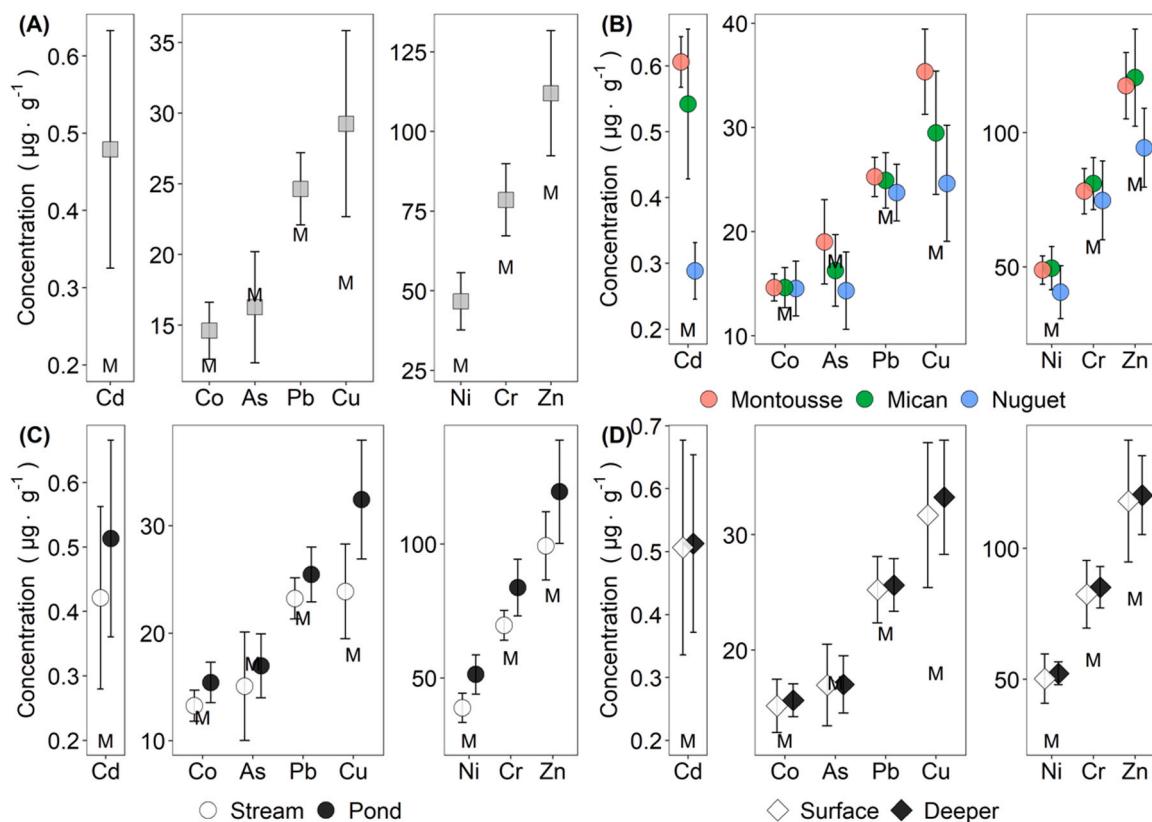


Fig. 3. Mean concentrations and standard variation of eight potential toxic elements (PTE): (A) all sediments; (B) by different catchments (Montoussé/Mican/Nuguet); (C) by different sediment types (stream/pond sediments); (D) by different layers of pond sediments (surface/deeper layers). “M” indicates the concentration of a given element in the background molasse. (Data from N’guessan et al., 2009).

maximum value reaching 3.40 in MIC1-OUT (the upstream MIC catchment).

The same EF pattern was observed for the three adjacent catchments (Fig. 4B), particularly from As to Cr, even if NUG had more dispersed values. Only the differences in the mean values of EF between MIC and NUG catchments were tested statistically, because the sediment samples

in MON were from only two ponds, of which one is isolated from the drainage stream. The mean value of three elements showed a significant difference between MIC and NUG, e.g. Zn (MIC > NUG, $p = 0.013$), Ni (MIC > NUG, $p < 0.001$), and Cd (MIC > NUG, $p < 0.001$). It should be noted that the upstream sediments usually had relatively high EF values, which were particularly observed in the ponds in the MON and MIC

Table 3

Geoaccumulation index (I_{geo}) of eight potential toxic elements (PTE) in all sediments.

Element	Min	Max	Mean	SD
As	-1.66	0.08	-0.71	0.38
Pb	-0.82	-0.17	-0.40	0.15
Co	-0.92	-0.03	-0.34	0.21
Cr	-0.73	0.17	-0.16	0.21
Zn	-0.87	0.28	-0.15	0.26
Cu	-0.68	0.66	0.07	0.34
Ni	-0.59	0.60	0.18	0.30
Cd	-0.40	1.16	0.58	0.52

catchments, for Cd and Cu.

The EF of six elements (As, Pb, Co, Cr, Zn, and Ni) of stream sediments were also significantly greater than those of pond sediments ($p < 0.05$ for Ni, $p < 0.001$ for the others) (Fig. 4C). Interestingly, although Cu and Cd had relatively high EF values, they were not significantly different between stream and pond sediments. No significant differences in EF were observed between surface and deeper pond sediments for each element (Fig. 4D), and a very consistent dispersion of the EF values was observed for all the trace elements in pond sediments.

3.4. Principal component analysis (PCA) and correlation matrix (CM)

Three principal component analyses (Fig. 5) were performed, based on (A) all sediments, (B) stream sediments, and (C) pond sediments in order to inspect the potentially different factors, which can control the PTE concentrations in stream and/or pond sediments, and in different conditions (e.g. catchments, sediment types, sediment depths). The general input variables included the concentrations of five major elements and eight PTEs, the sediment texture (clay, silt, and sand), the pH, and the organic carbon content

(C_{org}) of the sediments. Additionally, to assess the catchment-scale environmental effect, the stream discharge (Q) was introduced into the PCA for stream sediments, and the hydraulic retention time (HRT) and the surface area of the sub-catchment of a given pond (UC.Area) were added to the PCA for pond sediments. The main results are shown in Table 4 and Fig. 5. The eigenvalues of the components are shown in SM Table 1. The Spearman correlation matrix between PTE concentrations, EFs, and the main factors are presented in SM Fig. 6.

3.4.1. All sediments

The first three principal components (PC) accounted for 89.1% of the total variance, 65.8% for PC1, 12.7% for PC2, and 10.6% for PC3 respectively (SM Table 1). Major elements (Al, Ca, Mg, Fe, and Mn) and most PTEs (except As and Cd) were positively linked to PC1 due to their high loadings (>0.80) and contributions (Table 4 and Fig. 5A). PC2 was mainly positively associated with Ca and Cd (loading > 0.6). Arsenic and Mn were positively related to PC3 (loading > 0.60), and Ca was negative (loading = -0.51). In the individual scores of all sediments (Fig. 5A right), stream or pond sediments were mainly characterised by PC1, as stream sediments usually had negative scores and pond sediments were positive. The pond sediments from the upstream pond in each catchment (e.g. MON2, MIC1, and NUG1) normally scored higher in PC1. Sediments from different catchments were distinguished by PC2 as sediments from MON and MIC scored positive, and were higher than those from NUG.

The considered PTEs for all sediments were closely positively inter-related (SM Fig. 6A, $p < 0.01$). These PTEs were positively linked to Al, Mg, and Fe ($p < 0.01$). Zinc, Ni, and Cd were also positively related to Ca ($p < 0.01$). All the elements (except for Ca, Mn, As, and Cd) were positively associated with the clay content and negatively linked to the sand content. Aluminium, Mg, Cr and Ni were negatively linked to C_{org} ,

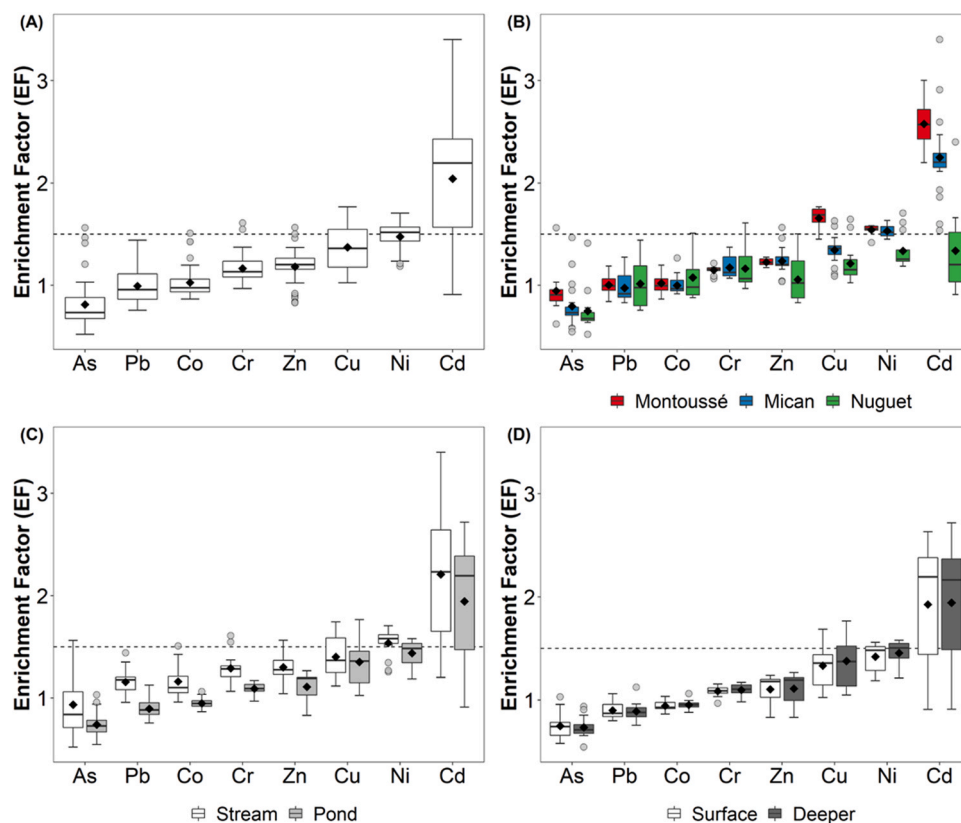


Fig. 4. Enrichment factors (EF) of trace elements: (A) all samples; (B) by different catchments (Montoussé/Mican/Nuguet); (C) by different sediment types (stream/pond sediments); (D) by different layers of pond sediments (surface/deeper layers).

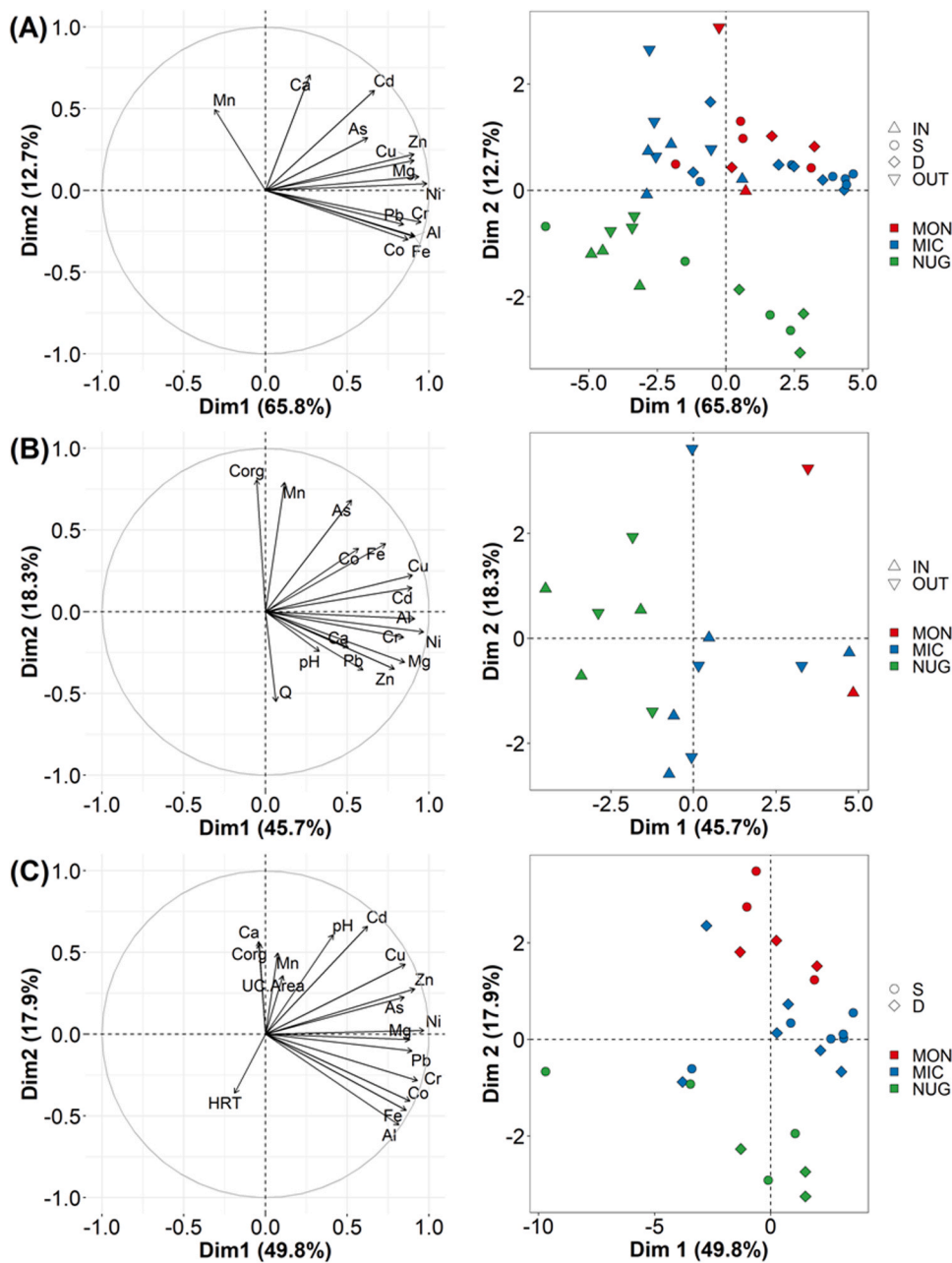


Fig. 5. First two dimensions (also known as ‘axes’ or ‘components’) of principal component analysis (PCA) for: (A) all sediments; (B) stream sediments; (C) pond sediments. The left column represents the variable loadings of PCA, while the right shows the individual scores. The PCA was calculated based on the concentrations of major and trace elements. Other physicochemical variables were abbreviated as follows: Corg = organic carbon content, Q = discharge, HRT = hydraulic retention time, and UC. Area = upstream sub-catchment area. Catchments were differentiated by colours (MON = Montoussé, MIC = Mican, NUG = Nuguet in the legend). Sediments were classified into different symbols (IN = Inlet (stream sediment), S = Surface layer (pond sediment), D = Deeper layer (pond sediment), OUT = Outlet (stream sediment) in the legend).

and Mn showed a positive relationship ($p < 0.01$). The pH value positively affected Pb, Zn, Cu, and Cd.

3.4.2. Stream sediments

79.4% of the total variance was explained by PC1 (45.7%), PC2 (18.3%), and PC3 (15.4%) (SM Table 1). In PC1 (Fig. 5B left and Table 4), high positive loadings (> 0.70) were observed for Al, Mg, Fe, Cr, Zn, Cu, Ni, and Cd. In PC2, high positive loadings (> 0.65) were observed for Mn, As, and C_{org}, and a negative high loading (-0.55) for Q. PC3 was positively contributed by Ca and Q, and negatively contributed by Pb and pH. Stream sediments from the different catchments were separated by PC1 (Fig. 5B right), and the most positive scores were for stream sediments in MON and MIC, particularly those located in the very upstream part (e.g. MON2-IN and MIC1-IN), whereas the negative scores were for those in NUG (Fig. 5B right). No obvious differences were observed for the inlet and outlet sediments of the ponds.

3.4.3. Pond sediments

82.3% of the total variance (SM Table 1) was explained by the first three PCs (49.8% by PC1, 17.9% by PC2, 14.7% by PC3, respectively). The positive high loadings (> 0.80) of most major and trace elements (except for Ca, Mn, and Cd) were observed in PC1 (Fig. 5C left and Table 4). PC2 was mainly positively contributed by Cd, pH, Ca, and C_{org} (loading > 0.55), and negatively contributed by Al (loading = -0.55). Calcium and HRT showed high positive loadings (> 0.70) in PC3, while C_{org} possessed a high negative loading (= -0.68). Most pond sediments in MIC and MON showed positive scores in PC2 (Fig. 5C right), while those in NUG scored negatively. The highest score in PC2 was for MON2. No differences were observed between the pond sediments of the surface layer and the deeper layer.

Finally, the complementary data of the correlation coefficients presented in SM Figs. 6B and 6C indicated that in both stream and pond sediments, Co, Cr, Zn, and Ni were positively related to Al, Mg, and Fe. In stream sediments, most major element and PTEs (except for Mn, As,

Table 4
Relationships and contributions of variables to principal components of principal component analyses for (A) all sediments; (B) stream sediments; and (C) pond sediments. The % symbol stands for the contribution (%) of a given variable to a dimension. Bold fonts indicate significant factors in the component. Corg = organic carbon content, Q = discharge, HRT = hydraulic retention time, and UC.Area = upstream sub-catchment area.

Variable	(A) All sediments						(B) Stream sediments						(C) Pond sediments					
	PC1		PC2		PC3		PC1		PC2		PC3		PC1		PC2		PC3	
	r	%	r	%	r	%	r	%	r	%	r	%	r	%	r	%	r	%
Al	0.91	9.76	-0.28	4.73	0.01	0.01	0.91	11.38	-0.04	0.06	-0.06	0.13	0.82	7.86	-0.55	10.14	-0.08	0.24
Ca	0.27	0.85	0.71	30.39	-0.51	19.00	0.51	3.49	-0.22	1.61	0.66	17.80	-0.04	0.02	0.57	10.62	0.73	21.60
Mg	0.94	10.31	0.08	0.44	-0.22	3.61	0.85	9.90	0.31	3.25	0.23	2.13	0.22	0.03	-0.03	0.03	0.39	6.21
Fe	0.91	9.71	-0.28	4.89	0.16	1.81	0.73	7.37	0.42	5.91	0.10	0.44	0.86	8.73	-0.47	7.15	-0.11	0.51
Mn	-0.31	1.13	14.88	14.88	0.74	39.62	0.12	0.18	0.79	21.36	0.36	5.41	0.08	0.07	0.50	8.13	-0.48	9.15
As	0.62	4.56	0.32	6.32	0.63	28.41	0.52	3.77	0.68	15.91	0.30	3.65	0.85	8.49	0.23	1.68	-0.41	6.84
Pb	0.84	8.34	-0.21	2.62	0.05	0.16	0.60	4.85	-0.36	4.34	-0.64	16.67	0.90	9.49	-0.10	0.34	-0.10	0.42
Co	0.87	8.90	-0.30	5.49	0.24	4.22	0.57	4.42	0.39	5.13	-0.49	9.84	0.88	9.22	-0.41	5.48	-0.08	0.28
Cr	0.95	10.58	-0.19	2.29	0.02	0.03	0.84	9.75	-0.16	0.84	0.08	0.25	0.93	10.18	-0.28	2.64	-0.01	0.00
Zn	0.91	9.65	0.22	2.98	-0.18	2.40	0.79	8.50	-0.35	4.18	0.23	2.07	0.91	9.83	0.28	2.53	0.23	2.18
Cu	0.91	9.66	0.18	2.05	0.04	0.11	0.90	11.06	0.22	1.71	-0.26	2.72	0.85	8.61	0.43	6.05	-0.15	0.85
Ni	0.99	11.38	0.04	0.11	-0.09	0.57	0.97	12.79	-0.12	0.51	0.10	0.40	0.97	11.09	0.02	0.02	0.16	1.03
Cd	0.67	5.18	0.61	22.82	-0.03	0.05	0.90	10.97	0.15	0.73	-0.05	0.09	0.62	4.59	0.66	14.37	0.27	2.91
Corg	-	-	-	-	-	-	-0.05	0.04	0.81	22.20	0.08	0.25	-0.04	0.02	0.55	10.11	-0.68	18.63
pH	-	-	-	-	-	-	0.33	1.47	-0.24	2.01	-0.62	15.62	0.41	2.02	0.61	12.20	0.14	0.81
Q	-	-	-	-	-	-	0.06	0.06	-0.55	10.25	0.74	22.53	-	-	-	-	-	-
UC.Area	-	-	-	-	-	-	-	-	-	-	-	-	0.11	0.13	0.36	4.23	0.42	7.23
HRT	-	-	-	-	-	-	-	-	-	-	-	-	-0.19	0.43	-0.36	4.28	0.72	21.09

and Pb) were positively linked to the clay content and also to silt (for Cu and Cd as ex.), while in pond sediments (SM Fig. 6B), such relationships with clays were only observed for Al, Mg, Fe, Pb, Co, Cr, and Ni (SM Fig. 6C). Most elements were linked to silt content. Arsenic was only positively associated with Mn and Corg in stream sediments (SM Fig. 6B). Cadmium was positively related to Al, Fe, and clay in stream sediments, and it was positively linked to Ca, pH, and the surface area of the sub-catchment of a given pond (UC.Area). Additionally, in pond sediments, As, Zn, Cu, and Cd was positively related to pH. The UC.Area, Ca, and pH exhibited positive correlations.

3.5. EDTA extraction

A single EDTA extraction was performed to assess the available fraction, where anthropogenic metal can be fixed and consequently be easily accessed by living organisms (Sahuquillo et al., 2003; Leleyter et al., 2012). Table 5 presents the concentrations of the available fractions and the proportions of the total concentrations in all sediments. The order of the available fraction was Cr < As < Ni < Zn < Co < Cu < Pb < Cd (Fig. 6). This pattern was commonly observed in sediments from the considered catchments/types/layers, although the sequences of Zn and Co may sometimes be reversed in MON sediments, or in surface pond sediments.

Considering all sediments, the available fraction of five PTEs (Cr, As, Ni, Zn, and Co) was very low (less than 5%, ranging from 0.09 ± 0.03–4.91 ± 3.17%, although some outliers did reach 10% for Zn and Co), whereas it was relatively high for Cu, Pb, and Cd (20.50 ± 5.78, 30.6 ± 7.97, and 47.86 ± 12.19%, respectively). The highest available fractions of Cu, Pb, and Cd were normally observed in MON2, MIC1, MIC4, and NUG1. Although the proportion of the available fraction in MIC appeared to be higher than in NUG, the differences were only significant (p < 0.05) for As, Pb, Co, and Ni, while two elements (Cu and Cd) with large available fractions were not statistically different between MIC and NUG (Fig. 6B). No significant differences were observed between surface and deeper layers of pond sediments (particularly for Cu, Pb, or Cd), nor between stream and pond sediments, despite a higher extraction for stream compared with pond, particularly for the less extracted elements (Fig. 6C and Fig. 6D).

4. Discussion

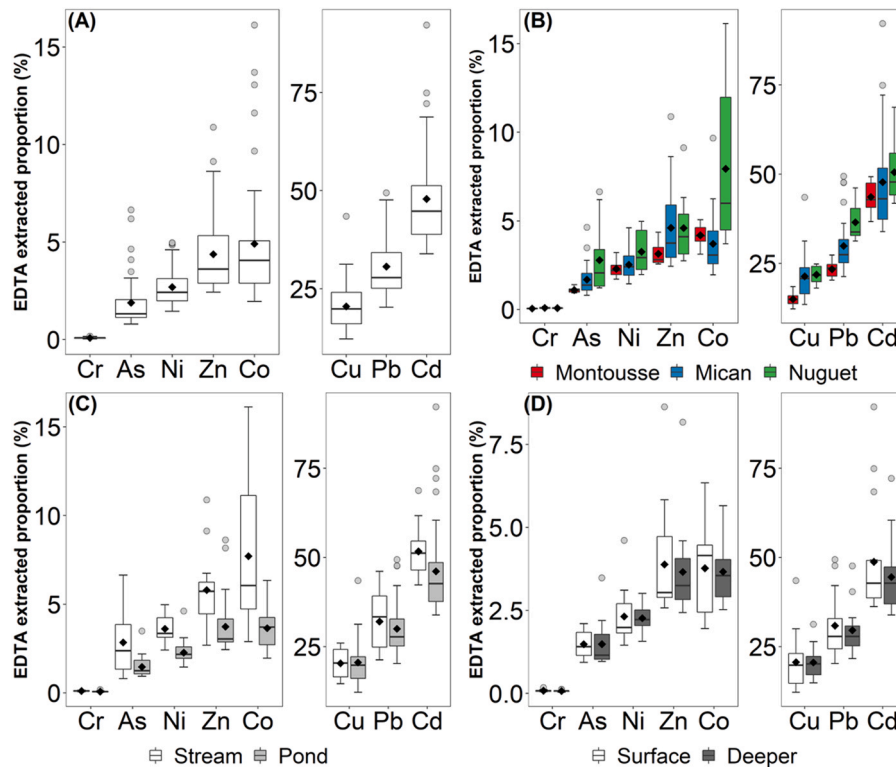
4.1. Natural vs. anthropogenic origins of PTEs in sediments, and their contributions

The concentrations of eight PTEs fell into the range of those determined in other streams from the same Gascogne region (Bur et al., 2009; N'guessan et al., 2009), though slightly higher values were observed for Cu, Ni, Cr, and Zn, which may indicate the similar origins and distributions of eight PTEs in the three catchments compared to those in Gascogne region. Copper, Ni, and Cd showed the greatest accumulation in the sediments as their average concentrations were 1.62 ~ 2.40 times higher than the background concentrations of molasse, while other five PTEs were barely accumulated (Table 2), suggesting a natural origin of the molasse through the mineral weathering processes (N'guessan et al., 2009). The same ascending order observed between I_{geo} and EF indicated a convincing result that Cd was the most enriched PTE in most sediments. Cadmium contamination was, however, far lower than that originated from mining exploitation where concentrations can reach 100–200 times the background value, such as in the dam from the Cajarc reservoir on the Lot river (Audry et al., 2004) or in the Milluni reservoir in Bolivia (Salvarredy-Aranguren et al., 2008).

EF could also indicate whether a PTE in the sediment is of anthropogenic origin (Ghafari et al., 2011). As confirmed by low EF values (< 1.5), five PTEs (As, Pb, Co, Cr, and Zn) mainly originated from the weathering process of the molasse (Zhang and Liu, 2002; N'guessan et al., 2009; Tang et al., 2010), which is a mainly carbonated event also

Table 5Concentration ($\mu\text{g g}^{-1}$) of metal in the available fraction and its proportion (%) of the total concentration in all sediments using EDTA extraction.

Element	Min		Max		Mean		SD	
	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	%
As	0.12	0.80	0.8	6.64	0.28	1.89	0.16	1.30
Pb	4.41	20.27	13.38	49.40	7.40	30.63	2.14	7.97
Co	0.32	1.95	2.33	16.12	0.70	4.91	0.44	3.17
Cr	0.03	0.04	0.11	0.18	0.07	0.09	0.02	0.03
Zn	2.77	2.44	12.71	10.88	4.72	4.38	2.04	1.97
Cu	3.12	12.22	10.94	43.47	5.66	20.50	1.57	5.78
Ni	0.83	1.45	1.84	4.97	1.19	2.69	0.25	0.93
Cd	0.10	33.89	0.48	92.17	0.22	47.86	0.09	12.19

**Fig. 6.** Available fractions (%) of eight potential toxic elements (PTE) extracted by EDTA: (A) all samples; (B) by different catchments (Montoussé/Mican/Nuguet); (C) by different sediment types (stream/pond sediments); (D) by different layers of pond sediments (surface/deeper layers).

containing some silicate minerals (Bur et al., 2009). Although Cu and Ni were not considered enriched in most sediments due to $EF < 1.5$, they showed greater EF values (> 1.5) in some very upstream sediments, meaning that the anthropogenic contribution of Cu and Ni to these places cannot be neglected.

The quantitative anthropogenic contribution (AC, %) indicated no obvious anthropogenic contribution for As, Pb, and Co. Chromium and Zn exhibited an AC of 13%, but with a very variable range of values, confirming if anything a relatively low contamination of these elements (in accordance with the interpretation of I_{geo} values). Conversely, Cu, Ni, and Cd reached an average AC of 25%, 32%, and 45%, respectively, which is consistent with previous observations on soils and suspended particulate matters transported during flood events (Roussiez et al., 2013). The supply of Cu, Ni, and Cd mainly resulted from spreading fertiliser and fungicide in the surrounding soils, as revealed by the analysis of fertilisers used in the area (Roussiez et al., 2013). Farmers use mainly synthetic fertilisers (from phosphate exploitation) for wheat and sunflowers cultivation, and Bordeaux mixtures for ancient vineyards. Similar contaminations were observed in an agricultural catchment cultivated for several decades (Jiao et al., 2015), and Cd proved to be the highest enriched trace element due to fertiliser spreading in other

agricultural catchments (Ghreat et al., 2011; Bing et al., 2016; Liao et al., 2019; Mao et al., 2020).

The absence of differences between both concentrations and EF s for As, Pb, Co, and Cr among the three catchments also argued for their natural origin. The higher anthropogenic impact of Zn, Ni, and Cd in MON and MIC compared with NUG, shown by the concentrations and EF s, might result from the effect of environmental catchment characteristics and/or the physicochemical settings of sediments (see Section 4.2), since these catchments involve similar agricultural practices and land cover. Indeed, the MON and MIC catchments have steeper slopes (Table 1) and higher carbonate content than NUG, and the anthropogenic PTEs were particularly associated with Ca (SM Fig. 6A). Redon et al. (2013) also reported a higher trace element content in calcareous agricultural soils from the Midi-Pyrénées region compared with non-calcareous soils. We thus propose that the arable soil erosion was responsible for the accumulation of anthropogenic Ni and Cd due to the presence of carbonated soil in these catchments (Bur et al., 2012; Benabdelkader et al., 2018). The highest contamination for Ni and Cd was always observed in the upstream ponds (MON2, MIC1, and NUG1) of the three catchments. These ponds were the first repository of sediments that originated from the soil erosion of upstream catchments

without the effect of discharge dilution (N'guessan et al., 2009). The effect of soil erosion regulating anthropogenically originating elements, especially Cd, were also reported by other studies (Bing et al., 2016; Benabdelkader et al., 2018; Liao et al., 2019). The greater anthropogenic contribution of Cu in sediments from MON compared to MIC and NUG could be related to Bordeaux mixture application in two parcels of vineyards that were pulled up in the recent decades (in sub-catchment of MON2, see the land use map in Ponnou-Delaffon et al. (2020)). The average PTE concentrations in sediments from ponds were always higher than in streams in relation to higher clay content in pond sediments (Fig. 3C and SM Fig. 2) since these elements were strongly positively related to the clay content (Fig. 5A and SM Fig. 6.). The mostly naturally originating PTEs (As, Pb, Co, Cr, and Zn), however were lower in ponds than in stream sediments, even if EFs were low, which was the opposite of the pattern of concentrations, while the EFs of Cu and Cd showed no difference. One explanation could be the higher content of fine particles in pond sediments. Indeed, the concentration of the reference element (Cs), used as the normaliser in the EF calculation, was higher in the pond sediments. Meanwhile, Al, Cs, and Fe showed the same high correlations ($r = 0.93$, $p < 0.001$) to the clay content (SM Fig. 6A) as other metals. The higher accumulation of the reference element may unintentionally restrain the EF. It can also be confirmed by EF values based on Fe showing less affinity to fine particles, as the EF difference between stream and pond sediments was minimised (SM Fig. 7). In the pond sediments, the absence of a statistical difference between PTE enrichment in surface and deeper sediments (Fig. 3D) indicated the probable similar natural or anthropogenic origin of PTEs in these sediments.

4.2. Distribution of PTE concentration and its controlling factors

The PCA (Table 4 and Fig. 5) and the correlation matrix (SM Fig. 6) allowed the controlling factors for the PTEs to be investigated. Three preliminary tests (Bartlett's test of sphericity, the KMO test, and the determinant test) showed that the following PCA results were reliable.

For all sediments, the significant positive interrelations among PTEs and their low EF values (SM Fig. 6A and Section 3.4) confirmed the main origin as from the natural weathering process, as discussed above in Section 4.1. Most PTEs (except As and Cd) were controlled by clay minerals and/or iron oxides due to their high loadings and high associations with Al and Fe in PC1 (Fig. 5A). The same phenomenon has been observed in other stream sediments in the Gascogne region (N'guessan et al., 2009). The positive relationship between As, Mn, and Corg in stream sediments indicated that As was associated with manganese oxides and/or complicated by sediment organic matters, which were also found in various stream conditions (Salvarredy-Aranguren et al., 2008).

The fine sediments in the ponds can provide a higher specific surface area that favours the adsorption process of metals (Leleyter and Probst, 1999; Duan et al., 2010) and explains why PTE concentrations in pond sediments were higher than in stream sediments (Fig. 5A). As explained above, Cd, and to a less extent Ni and Cu, originated from anthropogenic agricultural inputs, were eroded from soil during storm events (Ponnou-Delaffon et al., 2020) and transported to accumulate in sediments downstream. Since carbonate minerals contain low Cd, the strong link between Ca and Cd in intensively agricultural areas suggest that Cd was controlled by calcite co-precipitation under the $pH > 8$ condition (N'guessan et al., 2009; Benabdelkader et al., 2018; Ponnou-Delaffon et al., 2020) (SM Fig. 6 and PC3 in Table 4C). Considering the higher temperatures in ponds and the higher hydraulic retention time (HRT), this co-precipitation process might be particularly enhanced (Fig. 5C and SM Fig. 6), however, in stream sediments, Cd was more controlled by silicates (clay and iron oxides).

Since the three catchments were closely adjacent and the geomorphological characteristics were similar except on the slope (Table 1), the hydrodynamic condition which affects the soil erosion (Duan et al.,

2010) might be a main controlling factor. The steeper slopes of the catchments (MON and MIC) favoured a greater soil erosion and transport of Cd from the fertilisers into the downstream river systems. The NUG sediments were also less carbonated (Fig. 5A), which resulted in less Cd control. Compared to other ponds in the Mican catchment, the lowest Cd concentration found in MIC4 pond could be explained by its position downstream, which undergoes a strong dilution (Fig. 1 and Table 1).

4.3. Availability of PTE in sediments

Both low EF (Fig. 4) and available fraction (Fig. 6) for As, Co, Cr, and Zn indicated their limited potential environmental risk to the aquatic system, which was consistent with the natural origin of these PTEs (Benabdelkader et al., 2018). Although the anthropogenic contribution of Ni was significant (Section 4.1), Ni showed a low extractability (Fig. 6). This may be a result of binding strength, since Ni formed a strong binding to clay minerals in sediments (Yoo et al., 2013). The similar low extractability of Ni was observed in other studies (Hamdoun et al., 2015; Kouassi et al., 2019). Copper, Pb, and Cd exhibited high available fractions in increasing order, which was observed in other catchments with agricultural practices (Roussiez et al., 2013; Guo et al., 2018). A complexation process could have mobilised these three PTEs. Previous studies have shown that the availability of Cu and Pb with EDTA was attributed to their high complexation constants with EDTA, and due to the high affinity of Cu and Pb to Fe oxides (SM Fig. 6). These PTEs can be remobilised with the complexation of Fe oxides (Sahuquillo et al., 2003). Copper and Cd both had high EF and a high available fraction that evidenced their potential environmental risk to the aquatic system if physicochemical conditions changes allowed desorption processes. Although Pb was mostly of natural origin in the agricultural catchments, its mobility can be significant (Bur et al., 2009; Benabdelkader et al., 2018). Similar observations were also made by Leleyter and Baraud (2005) relative to EDTA extraction in the Vire river sediments.

Interestingly, the average available fraction was always lower in the Mican catchment than in the Nuguet catchment, in opposition to the higher degree of anthropogenic contribution. This could result from the higher calcium carbonate content in MON and MIC, which is consistent with the significant ($p < 0.01$) negative relationship between available fractions of most PTEs and available Ca concentrations (SM Fig. 8). The dissolution of calcite by excessive EDTA during the extraction process increased at high pH values (Papassiopi et al., 1999), contributing to the precipitation of released PTEs and their re-adsorption onto fine particles (Manouchehri et al., 2006). Contrary to expected results, the higher proportion of available fraction of PTEs in stream sediments (Fig. 6C) was associated with coarse particles (as attested by the positive correlation to sand and negative to clays, SM Fig. 8). The probable higher oxides content in pond sediments may provide a more specific surface for metal binding.

4.4. Effect of ponds on PTE transfer in catchments

The distribution of PTE needs to be specifically regulated since the spatial variation of PTE concentrations observed in close adjacent catchments was non negligible. This is specifically important for the anthropogenically originated elements, so as to reduce the potential environmental risk to the ecosystem in a limited geographic area. In agricultural catchments, constructed ponds have proved to be an effective way to control this risk (Frost et al., 2015; Jiao et al., 2015). In this study, the constructed ponds may be a sink for PTEs as the pond sediments concentrated more PTEs than the stream sediments.

As discussed before, the large surface area and the steeper slopes led to the higher input of PTEs due to the more intensive fertiliser application, the greater soil erosion, and surface runoff. The streams located in the upstream catchments were thus normally confronted with higher PTE concentrations than downstream, which may be reflected in the

higher PTE enrichment in MON and MIC than in NUG. However, the discharge dilution was an important factor in minimising the PTE loads exported to a tributary of the next order, as revealed by the Mican stream, where a greater decrease of Cu, Ni and Cd was observed in its downstream section compared to NUG.

The storage function of the pond was evidenced in this study, since in general, the PTE concentration was higher in the inlet of a given pond than in the outlet. MIC3 and NUG1 were two exceptions, however MIC3 was never dredged, the long-term (several decades) accumulation of sediments led to the lowest pond water depth of all the studied ponds. Although the pond sediments in MIC3 accumulated PTEs in the same way as other pond sediments, the low water depth and water volume limited the effective accumulation of fresh suspended matter from its upstream inlet. Meanwhile, the low water depth made MIC3 much vulnerable to the turbulence process by upstream discharge. Sediment re-suspension could occur in pond sediments during high discharge periods. This contributed to particulate transfer downstream with adsorbed/complexed PTEs, and contributed to PTE desorption, which make this pond only temporary sinks for PTEs (Acevedo-Figueroa et al., 2006). Although no statistical difference was observed in PTE concentration between the surface and relative deeper sediment in ponds as a whole, the concentration was higher in surface sediments than in deeper sediments in the Mican catchment, except in the Nuguet catchment. Due to the larger pond volume and longer HRT in the MIC pond than in NUG pond, the MIC pond exhibited a better retention capacity for fine particles, and thus the MIC ponds demonstrated a better PTE storage function than the NUG ponds. In the MON2 pond, the surface pond sediment was supposed to accumulate more anthropogenically originating PTEs, however, recent sediment dredging activity (one year before the sampling campaign), meant that the PTE concentration in its surface sediment was lower than in the deeper sediments. The dredging activity enabled the accumulated PTEs in pond sediments to be removed, however, the treatment of the contaminated sediments after excavation needs to be managed.

5. Conclusion

This study, firstly, assessed the contamination of potential toxic elements (PTE) in both stream and pond sediments in the three adjacent agricultural catchments in southwestern France. According to the geo-accumulation index (I_{geo}) and the enrichment factor (EF), As, Pb, Co, Cr, and Zn were not enriched in sediments, indicating their natural origin from the molasse bedrock weathering process. Cadmium was the most enriched element ($EF > 1.5$), and the average EFs of Cu and Ni were close to 1.5. The use of local molasse bedrock and Cs as the reference element in calculating EF assured the accuracy of interpretation regarding the potential natural/anthropogenic sources for PTEs. The anthropogenic contribution (AC, %) quantifies a significant anthropogenic impact on Cu, Ni, and Cd, in increasing order. The spread of agricultural mineral fertiliser and pesticides in upstream soils was the main anthropogenic source for Cu, Ni, and Cd, and the Bordeaux mixtures used in the ancient vineyards also contributed to Cu. In general, a higher EF was observed in sediments from upstream catchments and in MIC compared to NUG, and there was no difference between surface and depth of ponds.

The highest finer particle content contributed to the highest concentration observed in ponds. Clay minerals and/or iron oxides were key factors in the distribution of most PTEs (except for As and Cd). Cadmium showed different controlling factors between stream and pond sediments. In stream sediments, Cd was more controlled by silicates (clay and iron oxides), while in pond sediments, longer hydraulic retention time and increased water temperature contributed to Cd co-precipitation with calcite due to higher pH conditions and Ca content. This explained the difference in the control of Cd observed between MIC and NUG catchments. Arsenic was bound to manganese oxides and/or complexed with organic matter in stream sediments.

In general, Cu, Pb, and Cd showed the highest EDTA extractability, suggesting a hazardous potential environmental risk, whereas the lower Ni extractability may be due to a lesser extraction efficiency of the extractant. Extractability was affected by the calcite content in sediments due to the dissolution of calcite and the consequent pH increase, since the highest anthropogenically affected sediments (MIC) exhibited the lower extractability. Surprisingly, the coarse sediments from streams supported a higher proportion of extractable PTEs.

The geomorphological properties of the catchments and the management of constructed ponds can affect the spatial variation of PTE concentrations. The larger surface area of an upper sub-catchment and the steeper slope leads to higher PTE accumulation in stream and pond sediments, especially for anthropogenically originating elements, relative to intensive fertiliser spreading, the greater soil erosion and surface runoff. The increasing discharge along the channel contributes to the dilution of PTEs downstream. While the constructed pond having a considerable hydraulic retention time can be a sink for fine particles and PTEs, the non-dredged ponds were vulnerable to particle resuspension and the transfer of PTEs downstream. Ponds temporarily ensure a storage of sediments, and sediment dredging activity therefore contributes to regularly remove the PTEs associated with the accumulated sediments, but this involves planning for their downstream treatment.

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CRediT authorship contribution statement

Both authors contributed to the study conception and design. The first draft of the manuscript was written by Xinda Wu (XW) and Anne Probst (AP) commented on previous versions of the manuscript. Both authors approved the final manuscript. **X. Wu:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. **A. Probst:** Conceptualization, Methodology, Validation, Investigation, Data curation, Writing - review and editing, Supervision, Project administration, Funding acquisition..

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2021.125077](https://doi.org/10.1016/j.jhazmat.2021.125077).

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