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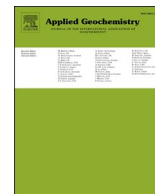
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## Evaluation of the speciation and availability of Cu, Sn, Bi and U from lacustrine sediments influenced by former mining activities

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### ABSTRACT

Managing reservoir sediments remains challenging due to their propensity to significantly sequester trace elements. Moreover, many artificial reservoirs were located downstream of former mining sites. However, the knowledge of the exact trace element speciation and its fate in sediments submitted to reoxidation and drying events, such as dredging operations, is still limited.

In this study, we examined the degree of contamination and solid speciation of trace elements and radionuclides in case of lake sediments dredging influenced by former mining activities. Finally, to assess the consequences such management *i.e.*, dredging, by mimicking drying and oxidizing conditions, Toxicity Characterizing Leaching Procedure (TCLP) tests combined with parallel chemical extractions and mineralogical analyses were performed.

Our results showed enrichments for Cu, Sn and Bi related to the former extractions activities of Charrier Cu–Sn mining site, as well as an enrichment for U partially due to the Bois-Noirs-Limouzat U mining site, in lake sediments. Moreover, the reoxidation and drying of initially anoxic sediments led to metal solid speciation dominated by: (i) Cu and Bi inherited sulfide minerals such as chalcopyrite, (ii) Cu, Bi and U associated with natural organic matter, and (iii) large grain-size refractory cassiterite SnO<sub>2</sub> crystals. Additionally, results from the TCLP indicated a limited leachability of the studied elements, confirming the significant stability of U, Cu and Bi associated with natural organic matter. Finally, Cu and U concentrations extracted by TCLP are lower than threshold values indicating that these sediments are not considered as hazardous regarding these elements.

### 1. Introduction

Anthropogenic activities have greatly influenced the geochemical cycles of Trace Elements (TE), resulting in their redistribution in environmental compartments, such as soils, wetlands and sediments (Cuvier *et al.*, 2016; Darricau *et al.*, 2021; Rainbow, 2020). Artificial reservoirs are important due to their role in water supply and/or energy production for instance. They however altered the transport of sediments and represent interesting storage areas, in which sediments are progressively segregated according to their size and density (Vörösmarty *et al.*, 2003; Frémion *et al.*, 2016). Furthermore, reservoirs built downstream of

watersheds affected by former mining activities could lead to the sequestration of elevated TE amounts in the sediments (Audry *et al.*, 2010; Friedland *et al.*, 2021; Langman *et al.*, 2020). Indeed, the release of TE from mine waste such as tailings or liquid effluents was previously widely observed into the surrounding environments (Karaca *et al.*, 2018). The accumulation of TE such as chalcophile elements (*i.e.*, Cu and Ag) and long-lived radionuclides such as U in sediments could pose a potential chemical risk to aquatic environments due to their persistence and toxicity (Burgess *et al.*, 2013; Swanson *et al.*, 1997).

Sediments can become sinks for TE. Therefore, proper management of artificial reservoirs is needed. In most cases, sediments are

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reintegrated into the downstream river. However, in certain situations, dredging and inland storage may be necessary. (Bataillard et al., 2017). Since this storage involves reclassifying sediments as waste, their long-term management requires evaluating the levels of TE contamination in sediment particles and determining the geochemical behavior of the detected TE under these new physical and chemical conditions. This includes examining the consequences of sediment oxidation. If the sediments meet the criteria indicated by the French government (Decree 09/08/2006, 2006), for being uncontaminated, they can be reused on sites, in recreational areas or in agriculture. If the sediments are contaminated and deemed hazardous, they must be neutralized, either through treatment or by being placed in a confined deposit. In the case of hazardous materials, these operations are subject to French ICPE regulations, regardless of the technique used (Decree 09/08/2006, 2006; Veron, 2008).

Among possible management actions of TE-rich reservoir sediments, mechanical excavation/dredging operation is an expensive way to deal with sediments overaccumulation in reservoir without lowering the water level (Annandale et al., 2016) and the sediment storage/repository/disposal in selected sites is one of the management strategies including deposit on bank to facilitate land farming for instance. Inland storage operations can affect the fate of TE and may result to the release of sediment-associated contaminants into the water column. This can occur through the oxidation of sulfide mineral phases or the degradation of the organic fraction of the sediments (Baran et al., 2023). Notably, the disposal of initially lacustrine anoxic sediments into open-air surface storage sites coupled to dewatering could induce reoxidation of redox-sensitive elements, such as U (Moon et al., 2007, 2009), and also a way to favor the availability of TE and their subsequent transport downstream of these sites.

The reactivity of TE species in sediments is largely influenced by their chemical form (Bissen and Frimmel, 2003; Borch et al., 2010; Sharma and Sohn, 2009). Furthermore, specific surface area, crystallinity, and geochemical affinity favor the retention of TE in mineral phases such as clay, sulfides, Fe and/or Mn oxyhydroxides, or Particulate Organic Matter (POM) in sediments (Cappuyns and Swennen, 2006; Courtin-Nomade et al., 2016; Grosbois et al., 2011; Morin and Calas, 2006; Ramirez et al., 2005). Previous studies indicated seasonally TE speciation changes in dredged sediments after land disposal (Piou et al., 2009). Strong Cu associations with POM (Lors et al., 2004), redistribution of Zn from sulfide minerals to secondary minerals such as phyllosilicates and Fe(III)-oxyhydroxides (Isaure et al., 2002) were also reported. However, the understanding of geochemical processes that control TE fate in post-dredged sediments is limited due to few studies focusing on their solid speciation.

*In situ* techniques such as X-Ray Absorption Near-Edge Structure spectroscopy (XANES) is a powerful tool, often used to obtain information on TE speciation in contaminated soils and sediments (Manceau et al., 2002; Manceau and Matynia, 2010; Morin et al., 2016; Stetten et al., 2018a, 2018b). Additionally, certified leaching tests and parallel and/or normalized sequential chemical extraction procedures generally constitute important tools to describe the easily extractable fraction of TE from lake sediments but these procedures fail to directly determine the TE chemical species. Among all known procedures, Toxicity Characterizing Leaching Procedure (TCLP) was recommended by the United States Environmental Protection Agency (US-EPA) (Bouchikhi et al., 2019; Cyr et al., 2012). TCLP was extensively used for assessing the degree of metal leachability in amended contaminated soils or ashes (Dermatas et al., 2006; Liu et al., 2019) or loess-amended dredged sediments (Zang et al., 2019). Using an acetate buffer at pH 4.93, a greater TCLP-extracted quantity of TE was expected than the use of deionized water. This procedure was rarely used to assess the availability of a TE cocktail in sediments impacted by different mining sources (Sun et al., 2006).

This study focused on the artificial reservoir of Saint-Clément, located in France (Allier, Auvergne-Rhone-Alpes). This lake is located on

a premium fishing spot river and used for recreational water activities requiring the assessment of the quality and sustainable management of the sediments. This reservoir is in the upper watershed of the Besbre river and downstream of two main former mining sites *i.e.*, the Bois-Noirs-Limouzat U mining site (Cuney, 1978) and the Charrier Cu-Sn mining site (Marcoux et al., 2022; Picot and Pierrot, 1963). Previous studies revealed significant activities of  $^{238}\text{U}$ -decay series nuclides (Morin et al., 2016; Reyss et al., 2016; Stetten et al., 2018a) and other TE (notably Cu and Sn) (Mangeret et al., 2020) in lacustrine sediments.

In this study, the evaluation of sediment contamination levels of Cu, Sn, Bi and U were assessed, and the identification of their solid speciation, and their geochemical behavior were performed in the Charrier tailing pile and sediments from a core sampled taken from the lake Saint-Clément. The main objectives were: (i) to identify the primary TE-bearing phases in Charrier samples and trace their origin; (ii) to assess the contamination status of sediments of lake Saint-Clément and identify the origin of TE; and (iii) to determine the availability of TE from these sediments under oxidizing conditions. In this study, the term “availability” was defined as the easily extractable fraction of TE in sediment samples.

## 2. Materials and methods

### 2.1. Reagents, materials, and solutions

All solutions were prepared with Milli-Q water (18.2 M $\Omega$  cm $^{-1}$  resistivity, Milli-Q water, Millipore). High-purity acids were obtained by distillation to avoid TE contamination (Savillex® DST-1000 system) from HCl (Merck, Emsure 37 %) and HNO $_3$  (VWR Chemicals, Normapur 68 %) solutions.

The following chemical products were used: hydrogen peroxide solution (VWR Chemicals, Normapur), glycerol solution (VWR Chemicals, Normapur), glacial acetic acid solution (VWR, NormaPur), sodium citrate monohydrate (Prolabo, NormaPur), sodium bicarbonate (Merck, Pro Analysis), acid ascorbic (Prolabo, Normapur), and sodium hydroxide (Prolabo, Normapur).

The following acidified standard solutions with an initial concentration of 1000 mg.L $^{-1}$  were used for the preparation of standard solutions (VWR Chemicals): Fe, Mn, Si, Al, Sn, Cu, Zn and Bi. Only the U standard solution has an initial concentration of 10 mg.L $^{-1}$  (VWR Chemicals).

Disposable polypropylene containers/coning tubes (VWR) were employed in all experiments.

### 2.2. Site description and sampling procedures

The upper Besbre watershed is located in the Massif of Bois-Noirs (Massif Central, France) (Fig. 1).

It includes two main former mines: the Bois-Noir-Limouzat site and the Charrier mine. The operated U ore body of the Bois-Noirs Limouzat mine was a pitchblende hosted-vein deposit associated with quartz veins (Cuney, 1978) where U extraction took place from 1955 to 1980. The river Besbre still receives up to date the treated mine waters from the Bois-Noir-Limouzat site, supplying the lake Saint-Clément located at approximately 20 km downstream (Fig. 1).

The Charrier mine was located at 15 km upstream of lake Saint-Clément (Fig. 1). It was exploited episodically for Cu, Sn and also Fe and Ag from 1872 to 1953 (Marcoux et al., 2022). The initially exploited mineralization of the Charrier site was mainly composed of sulfides *i.e.*, chalcopyrite (CuFeS $_2$ ), chalcocite (Cu $_2$ S) and bornite (Cu $_5$ FeS $_4$ ), and oxides *i.e.*, cassiterite (SnO $_2$ ) and magnetite (FeO $_3$ ) associated to Bi mineralization composed of bismuthinite (Bi $_2$ S $_3$ ) and emplectite (CuBiS $_2$ ). Indium bearing phases were also reported (Marcoux et al., 2022; Muraio et al., 1991; Picot and Pierrot, 1963). The ore processing was exclusively mechanical, consisting of a first phase of crushing and grinding, then a second phase of separation by gravimetry, flotation cell,

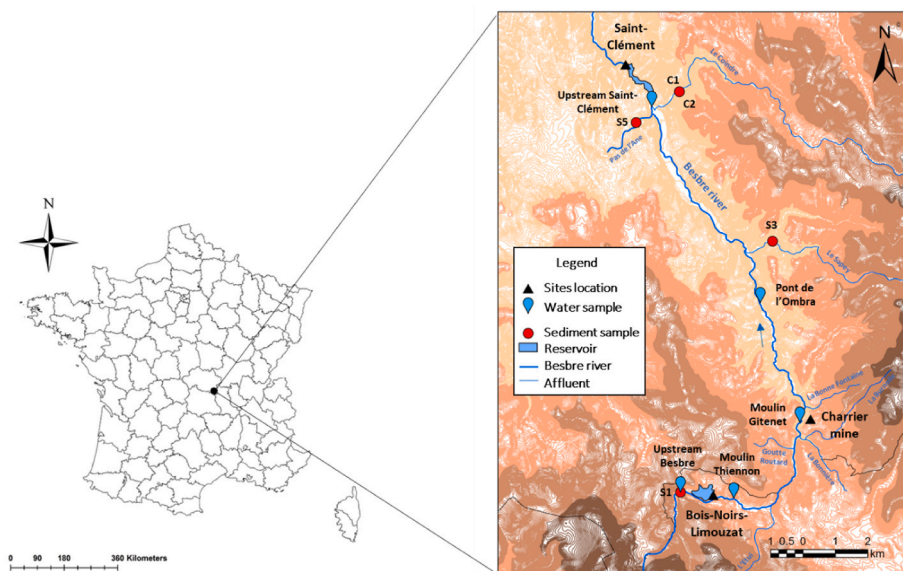


Fig. 1. Local geochemical background sediment sampling locations (red circles), and watershed local chemical surface water sampling location (blue icons).

electromagnetism and then shaking (Marcoux et al., 2022). The Charrier tailing pile is still directly in contact with the atmosphere with no containment system and is located near a tributary of the river Besbre (Fig. 1). Various events, including flooding and the reprofiling of the Charrier mine tailing pile in 1999, could lead to the potential release of TE from the pile to the surrounding environment, notably through particle transport.

The sediments of lake Saint-Clément were previously studied for identifying uranium (U) and radium-226 ( $^{226}\text{Ra}$ ) trapping mechanisms (Morin et al., 2016; Stetten et al., 2018a; Mangeret et al., 2020). Analyses of sediment cores showed significant concentrations of stable chemical elements (Fe, Mn, Cu, Zn) and U at various depths (Mangeret et al., 2020). Moreover, the decrease in dissolved U concentration in sediment pore waters with depth was found correlated with the organic carbon mineralization associated with the reduction of Fe(III) and Mn (III/IV) oxyhydroxides (Stetten et al., 2018a). Complete reduction of U (VI) to U(IV) was demonstrated at 15 cm below the sediment-water interface. U speciation in sediments was identified mainly as mononuclear U(IV) species associated with C or P groups (60–80%) and accompanied by crystalline phases, including minerals inherited from the host granite (*i.e.*, monazite and zircon), at the surface (Stetten et al., 2018a), or ningyoite-like nanocrystals of U(IV)-phosphate, in a deeper sediment samples (Morin et al., 2016). However, less is known about the solid speciation of TE sequestered, except for U, and their sensitivity to oxidative events such as sediment excavation/dredging operations and surface storage.

Three types of samples were collected (Fig. 1): (1) materials from the Charrier mining site dedicated to trace the origin of TE in (2) oxidized sediments from the Lake Saint-Clément and (3) pristine sediments representative of the local geochemical background of the upper Besbre watershed, which were required for the calculation of contamination indexes. Here are details on the samples collected.

- (1) In 2021, four tailing samples were collected from the Charrier pile along a high-low transect. A soil sample near the tailing pile and two sediments samples downstream of the pile were also collected. Fig. S1 displays all sampling location.
- (2) A 143-cm length sediment core was sampled in 2013 at approximately 120 m upstream of the dam within PVC liners using a 63 mm diameter Uwitec® gravity hand corer (see more details in Stetten et al., 2018a). The sediment core was sampled every 2 cm. To reflect geochemical variations, sediments samples at 6, 10, 16,

18, 22, 24, 26, 28, 32, 34, 38, 40, 44, 50, 60, 70, 80, 92, 96, 100, and 102 cm were selected for chemical and/or mineralogical analyses.

- (3) Stream pristine sediments, S0, S3, S5, C1 and C2 were sampled respectively from the upstream of the Besbre River, the Sapey, the Pas de l'Àne and the Coindre streams in April 2013 using a high-density polyethylene (HDPE) shovel, in the first 10 cm of the surface sediment. These samples were considered as not influenced by previous mining activities due to their location (Fig. 1).

### 2.3. Elemental analyses of soil/sediment samples

#### 2.3.1. Soil/sediment treatment

Tailings, soil and sediment samples were dried at 40 °C in a stream room (VWR Venti-Line), then stored in polypropylene containers under laboratory temperature ( $20 \pm 2$  °C). All samples were finely ground in an agate mortar before alkaline fusion and parallel chemical extractions.

#### 2.3.2. Total organic carbon

Total Carbon (TC) and Total Inorganic Carbon (TIC) contents of Charrier tailing samples were determined by CHNS analyses (FlashSmart, Thermo Scientific). TIC values were determined on dried and finely ground samples after calcination at 550 °C for 5 h in a muffle furnace. Total Organic Carbon (TOC) was determined by subtracting TIC from TC.

#### 2.3.3. Alkaline fusion procedure

Total element contents *i.e.*, Fe, Mn, Si, Al, U, Sn, Cu, Zn, Bi, were determined after alkaline fusion in solid samples (Carignan et al., 2001). Briefly, 150 mg of finely ground sample were placed on a 900 mg powder mixture of  $\text{LiBO}_2/\text{LiBr}$  (98.2 and 1.5% w/w, respectively; SPEX Fusion Flux, Pure) in a platinum crucible (5AUPTKAX, KITCO). The platinum crucible was then placed in a Katanax K1 Prime furnace, with a two-temperature level program: (i) at 600 °C to oxidize the reduced elements and POM for 5 min, and (ii) at 985 °C during 10 min to merge the sample. Finally, once cooled at room temperature, the fusion melt was totally dissolved in 200 mL of a solution containing 1.0 M  $\text{HNO}_3$ , 1.4 M  $\text{H}_2\text{O}_2$  and 0.5 M glycerol. The dissolution of fusion melt was enhanced by ultrasonic treatment (2–5 min).

#### 2.3.4. Parallel chemical extractions

In order to study the distribution of TE in the solid phase and the



associated risk assessment related to former mining activities (*i.e.*, Bi, Cu, Sn, and U), three single-step extractions were applied to Charrier tailings and oxidized sediment samples from the 2013C7 core. Sediment sample selection was based on the geochemical index values. For the three single-step extractions, the mixture was continuously and vigorously shaken with an orbital shaker (250 rpm; BIOBLOCK scientific). The first single-extraction consisted to quantify the fraction of TE associated with easily reducible amorphous iron (III) and manganese (III/IV) (oxy)-hydroxides from 200 mg of soil/sediment sample using 5 mL of Citrate-Bicarbonate-Ascorbate (CBA) agent (pH = 7.5, 0.7 M NaHCO<sub>3</sub>, 0.2 M trisodium citrate dihydrate and 0.1 M ascorbic acid) for 24 h (Haese et al., 2000; Hyacinthe et al., 2006; Hyacinthe and Van Cappellen, 2004). Indeed, amorphous iron (III) and manganese (III/IV) (oxy)-hydroxides were known as important TE-bearing phases in contaminated sediments (Chuan et al., 1996; Courtin-Nomade et al., 2016; Romero et al., 2007). The second single-extraction targeted the fraction mainly exchangeable, bound to POM, amorphous and poorly-crystallized iron (III) and manganese (III/IV) (oxy)-hydroxides, carbonates, phosphates, and acid-volatile sulfides (Cooper and Morse, 1998; Larmer et al., 2006; Leleyter et al., 2012; Ruban et al., 2001; Yu et al., 2021). These phases are known to play an important role in the retention of TE. 200 mg of soil/sediment sample were placed in 5 mL of 1 M HCl solution for 24 h. The third single extraction undertaken was the application of TCLP to first assess the environmental impact of sediment management strategies. This protocol was formerly used to mimic the TE leaching during the storage of potentially hazardous materials (EPA, 1992). The TCLP test was also widely used to evaluate the efficiency of TE immobilization in sediments by different types of materials (Krcmar et al., 2013; Ma et al., 2022). Moreover, this extraction could be used as an analogue of the BCR F1 fraction, targeting the acid-soluble fraction of TE. For this purpose, 250 mg of soil/sediment samples were placed in 5 mL of 0.25 M acetic acid solution at pH 4.93 (adjusted with dilute NaOH solution) for 18 h. No pH variations were encountered during these experiments. After each single-step extraction, the mixtures were centrifuged at 14,000 rpm for 10 min, then filtered at 0.45 µm (filter syringe with acetate cellulose filter membrane, VWR) and acidified at 0.3 M HNO<sub>3</sub> before elemental analysis. The solid residual fraction was dried at 40 °C and stored for mineralogical analyses to assess the potential transformation of TE-bearing phases and/or re-precipitation phenomenon during these single-step extractions.

### 2.3.5. Elemental analyses

Total element concentrations in extracts (diluted at least 100-fold for alkaline fusion and single-step extraction using 0.3 M HNO<sub>3</sub> solution) were determined by ICP-OES (Thermo Fisher ICAP™ 7600 Duo) or ICP-MS/MS (Agilent 8800, Agilent Technologies) depending on the concentration level. Measurements were performed at the LUTECE and PATERSON platforms (IRSN, Fontenay-aux-Roses, France). Spectrometers were calibrated using standard solutions with a matrix close to that of dilute extracts when it was possible (with a minimum acceptable R<sup>2</sup> > 0.995), and the blank correction was applied when necessary. Quality controls using standard solutions with similar concentration levels found in real samples were regularly performed. In order to validate alkaline fusion procedure, standard materials was analyzed: SARM standards granites GA (Govinoaraju and De La Roche, 1977) and Tibet Sediment (NCS DC 70317; Colin et al., 2021). Results of control analysis quality are displayed in Table S1 with correct extraction yields using alkaline fusion (80–120%). Quantification limits are found in Table S2. Elemental analyses of pristine sediments (S1, S3 and S5) were performed at the “Service d’Analyses des Roches et Minéraux” Analysis Service (SARM, CNRS, Vandoeuvre-lès-Nancy, France). Details on their analytical procedures can be found at <https://sarm.cnrs.fr/index.html/>.

### 2.4. Mineralogical analysis

Bulk powder X-Ray Diffraction (XRD) analyses were performed to

identify the major mineral phases on a Panalytical at GEOPS facility (Orsay, France) ranging from 0 to 80°2θ (CuK<sub>α</sub> = 1.5418 Å) with a step size of 0.017° and a Scan Step Time of 775.335 s.

Solid samples were embedded using Epoxy resin (EpoFix, Struers), polished and analyzed for mineralogical identification, textures, and chemical composition using Scanning Electron Microscopy (SEM) and Electron Probe MicroAnalysis (EPMA). Secondary Electron (SE) images were obtained with SEM Phenom™ Pro X at the GEOPS facility (Orsay, France) equipped with an Energy Dispersive Spectrometry (EDS) system with a voltage of 15 keV. EPMA analyses were performed on SEM-selected particles at 15 kV with a 4 nA beam current on a CAMECA SX Five (Camparis, Sorbonne Université, France) previously calibrated with selected standards (OSU, Ecce Terra). For the sake of representativeness, two to three analyses were carried out on each particle when it was large enough (>5 µm) and sufficiently homogeneous. When the investigated area included several particles, each particle was analyzed two to three times according to its size.

### 2.5. Geochemical index methods

Several geochemical indexes were reported in the literature to estimate the degree of contamination induced by anthropogenic activities (Sakan et al., 2015a). The geoaccumulation index ( $I_{geo}$ ) and the enrichment factor ( $EF$ ) were commonly used to assess metal contamination in sediments. Both are based on “geochemical background” data, making them possible to identify the contamination of anthropogenic origin (Rubio et al., 2000; Sakan et al., 2015b).

The  $EF$  was used for assessing whether the presence of an element in sediment samples was linked to anthropogenic activities. It represents the actual contamination level in sediment and is used for tracing heavy metal enrichment (Balls et al., 1997).

The  $EF$  leads to compare each value with the given background level and was defined according to Eq. (1):

$$EF_M^{(C)} = \left( \frac{\{M\}_{\text{sample}} / \{X\}_{\text{sample}}}{\{M\}_{\text{background}} / \{X\}_{\text{background}}} \right) \quad \text{Eq. 1}$$

where  $\{M\}$  is the amount of the potentially enriched element (mg.kg<sup>-1</sup>) and  $\{X\}$  the amount of the invariant element or proxy element (mg.kg<sup>-1</sup>). The subscripts “sample” and “background” refer to the sample and background values, respectively. The proxy element chosen (C) for this study is aluminum (Al), which is a conservative element considered suitable for normalization due to its relative abundance in the Earth’s crust and therefore its low tendency to be heavily influenced by human activities (Jain et al., 2005). The  $EF$  values were interpreted as:  $EF < 1$  no enrichment;  $EF < 3$  is minor;  $EF = 3-5$  is moderate;  $EF = 5-10$  is moderately severe;  $EF = 10-25$  is severe;  $EF = 25-50$  is very severe; and  $EF > 50$  is extremely severe (Acevedo-Figueroa et al., 2006; Sakan et al., 2015b).

The  $I_{geo}$  was used as a second index to identify and qualify contaminated sediments. This quantitative measurement of metal pollution in sediments was used as a reference to estimate the extent of metal pollution (Müller, 1969; Sakan et al., 2015a). The  $I_{geo}$  values in sediments of lake Saint-Clément were calculated using Eq. (2):

$$I_{geo_n} = \log_2 \left( \frac{\{C_n\}}{1.5\{B_n\}} \right) \quad \text{Eq. 2}$$

where  $\{C_n\}$  is the content of the element of interest  $n$  measured,  $\{B_n\}$  the geochemical background for the element (mg.kg<sup>-1</sup>), and 1.5 the factor attributed to lithogenic variations in the sediment.  $I_{geo}$  is based on a qualitative pollution intensity scale, sediments can be classified as uncontaminated/unpolluted  $I_{geo} < 0$ ; unpolluted to moderately polluted for  $0 \leq I_{geo} < 1$ ; moderately polluted for  $1 \leq I_{geo} < 2$ ; moderately to highly polluted for  $2 \leq I_{geo} < 3$ ; highly polluted for  $3 \leq I_{geo} < 4$ ; highly to extremely polluted for  $4 \leq I_{geo} < 5$ ; and extremely polluted for  $I_{geo} \geq 5$ .

In this study, the background average composition level was calcu-

lated with sediments sampled from stream pristine sediment samples (S1, S3, S5, C1 and C2), respectively sampled upstream of the former mining site of Bois-Noirs-Limouzat (S1), in different Besbre tributary streams: Sapey (S3), Pas de l'Ane (S5), Coindre (C1, C2) (Fig. 1, Table S3). These reference sites were privileged for the calculations of  $EF$  (Eq. (1)) and  $I_{geo}$  (Eq. (2)) rather than the average continental crust composition in order to better reflect the lithology of the upper Besbre watershed.

## 2.6. Micro-X-ray fluorescence ( $\mu$ -XRF) and micro-X-ray absorption spectroscopy ( $\mu$ -XAS)

$\mu$ -XRF mapping and  $\mu$ -XANES analyses of Charrier tailings and two sediment samples from the lake Saint-Clément were conducted at the SOLEIL beamline PUMA (Paris, France). A Kirkpatrick–Baez (KB) mirror focused the X-rays to a spot of 10  $\mu$ m (H) x 5  $\mu$ m (V) on the sample, which was mounted at an angle of 45° towards the beam. An optical microscope (homemade) with a scientific CMOS camera (Hamamatsu Orca) focused on sample position allowed for the proper alignment and the observation of the analyzed spot. Data were collected at room atmosphere and temperature. A silicon drift detector (Rayspec) installed at 90° from the incident beam permitted to acquire the XRF signal.

The samples were embedded in epoxy resin and prepared according to the same procedure used for SEM observations, their thickness being reduced to a 100  $\mu$ m size. The samples were then fixed with Kapton tape on a pierced Teflon support.

The incident beam energy was selected using a Si(111) double crystal monochromator and set to 20 keV in order to scan the sample for  $\mu$ -XRF mapping. The calibration of the emission spectrum energy was done by the SOLEIL detector group. The PyMca software was used to convert the XRF spectra to element-specific fluorescence intensity maps through batch curve fitting of emission lines for the elements of interest (including Cu K $\alpha$  and Bi L $\alpha$ ) (Solé et al., 2007).  $\mu$ -XRF maps of diverse size were acquired with a counting time of 0.1 s per point and a step size between 10 and 6  $\mu$ m under a continuous scanning mode (FLYSCAN). Finally, after  $\mu$ -XRF mapping, Cu and Bi-rich points of interest were analyzed by  $\mu$ -XANES at the Cu–K-edge and/or Bi L<sup>III</sup>-edge with a step size of 0.5 eV around the absorption edge. The  $\mu$ -XANES spectra were then treated using the ATHENA software. In addition, ATHENA was used for Linear Combination Fitting (LCF) analyses (Ravel and Newville, 2005).

More than 20 reference standards were prepared as thin sample pellets. The corresponding spectra were acquired for calibration purposes and to identify Cu compounds and LCF calculations. Reference spectra acquired were verified according to XRD analyses (Figs. S4 and S5). Standards for Cu were: Cu(I) oxide, Cu(II) oxide, Cu-foil, CuS, Cu<sub>2</sub>S, CuSO<sub>4</sub>, Shattuckite (Cu<sub>5</sub>(SiO<sub>3</sub>)<sub>5</sub>(OH)<sub>2</sub>), Kobyashevite (Cu<sub>5</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>4H<sub>2</sub>O), Chalcantite (CuSO<sub>4</sub> 5H<sub>2</sub>O), Yvonite (Cu(AsO<sub>3</sub>OH)), Pushcharovskite (Cu(AsO<sub>3</sub>OH) 1.5(H<sub>2</sub>O)), Azurite (Cu<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>), Malachite (Cu<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>), CuCO<sub>3</sub>, Cu acetate, CuF<sub>2</sub>, CuCl<sub>2</sub>, and dopped goethite with 0.7 wt% Cu and 0.5 wt% Cu and dopped ferrihydrite with 0.3 wt% Cu and 0.5 wt% Cu. All acquired spectra were compared both to

reference standards and to spectra available in the literature.

## 3. Results and discussion

### 3.1. Charrier tailings and the surrounding environment

#### 3.1.1. Bulk chemical composition and mineralogy

The elemental composition of Charrier tailings samples indicated significant Bi, Cu and Sn contents reaching 720, 2077 and 4900 mg kg<sup>-1</sup>, respectively (Table 1). Bi contents were significantly higher than those found for the geochemical background and the continental crust, the average value being respectively 1.4 mg kg<sup>-1</sup> (Table 1, Table S3) and 0.12 mg kg<sup>-1</sup> (Wedepohl, 1995). Extreme Bi enrichments (up to 100 mg kg<sup>-1</sup>) were already reported in some other granite areas, such as the highly fractionated Variscan Podlesí granite (Czech Republic) (Breiter et al., 2006).

TC and TOC contents in tailings, soils and sediments were determined below 0.5% (Table 1), indicating that mineral compounds were predominant in these samples.

Charrier tailings, soils and stream sediments collected a few meters downstream of the pile contained similar levels of Si, Al, Fe, Mn, Cu, Zn, Sn and Bi were found in compared to the background values (Table 1, Table S3). This suggests that tailings particles have been transported to the surrounding environment. The small stream located downstream of Charrier thus directly supplied TE-enriched particles to the Besbre river and the Lake Saint-Clément, depositing TE-rich particles in these sediments.

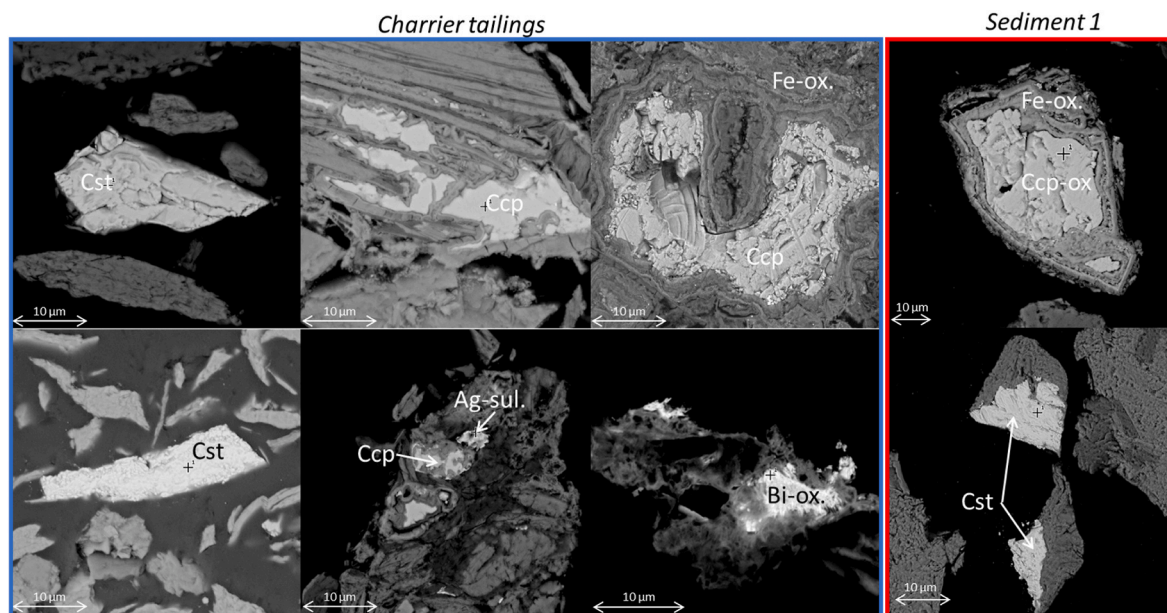
Major element composition, characterized by significant Al and Fe contents compared to the local geochemical background (Table 1, Table S3), was consistent with the mineralogy of Charrier tailings, dominated by Fe-rich chamosite-type chlorite (Fe<sup>2+</sup>, Mg, Al, Fe<sup>3+</sup>)<sub>6</sub>(Si, Al)<sub>4</sub>O<sub>10</sub>(OH, O)<sub>8</sub>, quartz (SiO<sub>2</sub>), and muscovite (KAl<sub>2</sub>(AlSi<sub>3</sub>O<sub>10</sub>)(OH, F)<sub>2</sub>) (Fig. S2). The mineralogical data were consistent with the presence of ferrous and cupro-stanniferous clusters in chloritized and biotite gangues, as previously observed in the Charrier deposit (Marcoux et al., 2022; Picot and Pierrot, 1963).

Additionally, accessory minerals included refractory species such as Ti-oxides (Ti-O<sub>x</sub>), barite (BaSO<sub>4</sub>), and Rare Earth Elements (REE) phosphates (data not shown). Primary minerals related to the extraction of Sn and Cu are also present. As previously described Fe-enriched single particles often contained Cassiterite (SnO<sub>2</sub>) crystals (79 wt% Sn, 21 wt% O) (Table S4) (Lerouge et al., 2017). Inclusions of residual ore minerals, specifically Cu-sulfides like chalcopyrite (30 wt% Fe, 35 wt% Cu, 35 wt% S), were observed within other minerals (Fig. 2). Some of these inclusions were oxidized and surrounded by Fe oxides (Fig. 2). Bi oxide minerals were observed as single particles, inclusions and coatings on Fe or Cu sulfides. Finally, rare Bi oxides and Cu–Bi–Ag rich sulfides (Fig. 2 and Tables S4 and S5) were also identified. The studied tailings were produced during the extraction process's flotation step (Marcoux et al., 2022). The presence of sulfide mineral inclusions was expected since they had not yet been separated. Marcoux et al. (2022) also observed Cu and Bi sulfides, as well as Ag and Se contents in bornites from the initial

**Table 1**

Total elemental contents for samples from Charrier Tailings (sampling locations in Fig. S1). Data were expressed as metal oxides in wt% for Si, Al, Fe and Mn and in mg. kg<sup>-1</sup> for Cu, Sn and Bi and in % for TC and TOC. RSD referred to relative standard deviation. Quantification limits are found in Table S2.

|  | RSD        | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MnO  | Cu   | Zn   | Sn   | Bi   | TC   | TOC  |
|--|------------|------------------|--------------------------------|--------------------------------|------|------|------|------|------|------|------|
|  |            | <2%              | <2%                            | <5%                            | <5%  | <5%  | <10% | <5%  | <10% | <10% | <10% |
| Charrier tailings                          | Top 1      | 36.8             | 18.0                           | 25.3                           | 0.72 | 859  | 858  | 2280 | 134  | 0.12 | 0.12 |
|  | Top 2      | 42.8             | 20.4                           | 29.8                           | 0.88 | 2077 | 1426 | 4832 | 729  | 0.10 | 0.05 |
|  | Middle 1   | 29.6             | 19.2                           | 32.4                           | 0.96 | 1319 | 1253 | 4765 | 306  | 0.09 | 0.05 |
|  | Middle 2   | 28.3             | 19.3                           | 33.4                           | 0.98 | 1732 | 1288 | 4912 | 336  | 0.08 | 0.04 |
|  | Down       | 34.1             | 18.2                           | 28.0                           | 0.86 | 1613 | 1035 | 2358 | 131  | 0.17 | 0.14 |
| Environment close to the Charrier tailings | Soil       | 38.9             | 18.0                           | 23.0                           | 0.70 | 1197 | 844  | 2152 | 142  | 0.29 | 0.25 |
|  | Sediment A | 41.5             | 17.4                           | 21.8                           | 0.65 | 1130 | 784  | 1943 | 141  | 0.43 | 0.39 |
|  | Sediment B | 36.5             | 18.2                           | 26.5                           | 0.80 | 1459 | 952  | 2593 | 167  | 0.35 | 0.35 |



**Fig. 2.** SEM images of cassiterite (Cst), chalcopyrite (Ccp) Bi oxides (Bi-ox.), Ag-sulfides (Ag-sul.), and Fe oxides (Fe-ox.) observed in bulk samples from (blue) Charrier tailings and (red) the sediments sampled in the stream downstream of the tailing pile.

### Charrier mineralization.

Chalcopyrite crystals and cassiterite inclusions were found in chamosite and Fe oxides in sediments downstream of the tailing pile (Fig. 2 and Tables S4 and S5), indicating the input of particles from the tailing pile in the stream.

### 3.1.2. Sn, Cu and Bi distribution and speciation

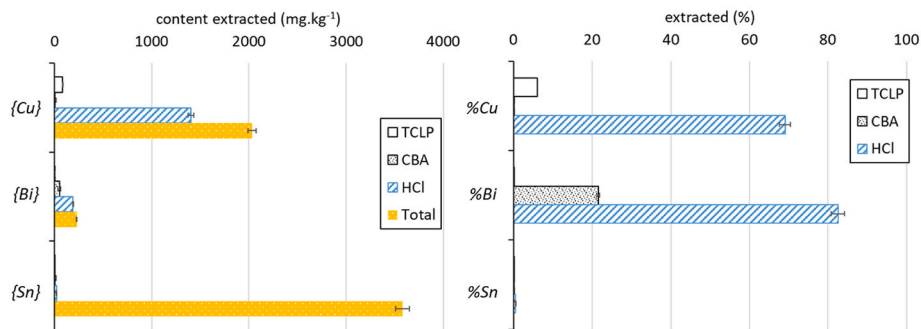
**Tin** – 1 M HCl and CBA parallel chemical extractions indicated no relevant associations with dissolved Fe-compounds in the extractants (*i. e.*, amorphous and/or poorly Fe-oxyhydroxides). Indeed, extracted Sn contents were still below 1 % (Fig. 3). Post-extractions SEM observations revealed the presence of Cassiterite and its refractory nature (Dill et al., 2006; Lottermoser and Ashley, 2006).

**Copper** – The results of parallel extraction experiments showed that 70% of Cu was extracted using a 1 M HCl solution (Fig. 3). Post-extraction SEM observations revealed the presence of small-sized (<5 μm) chalcopyrite and pyrite crystals. Previous studies have found that Cu-sulfide compounds, such as covellite (CuS), chalcocite (Cu<sub>2</sub>S), and chalcopyrite (CuFeS<sub>2</sub>), have low solubility in HCl solution (0.5–6 M) was previously found in several studies (Cooper and Morse, 1998; Heron et al., 1994; Praharaj and Fortin, 2004; Ueshima et al., 2019). The CBA agent resulted in the extraction of less than 1 % of Cu (as shown in

Fig. 3), suggesting that it was not likely associated with amorphous Fe (III)-(oxy)hydroxides in the tailing samples. These single-step extractions indicate that Cu was primarily associated with other phases. The TCLP single-step extraction revealed that up to 6 % of Cu was extracted (Fig. 3). A low amount of Cu in the tailings was found to be in a leachable form and could potentially be mobilized and transported by runoff water (Gil-Díaz et al., 2021; Phillips and Chappie, 1995). This copper could be distributed within the tailings pile and transported to the nearby stream, which feeds the Besbre river.

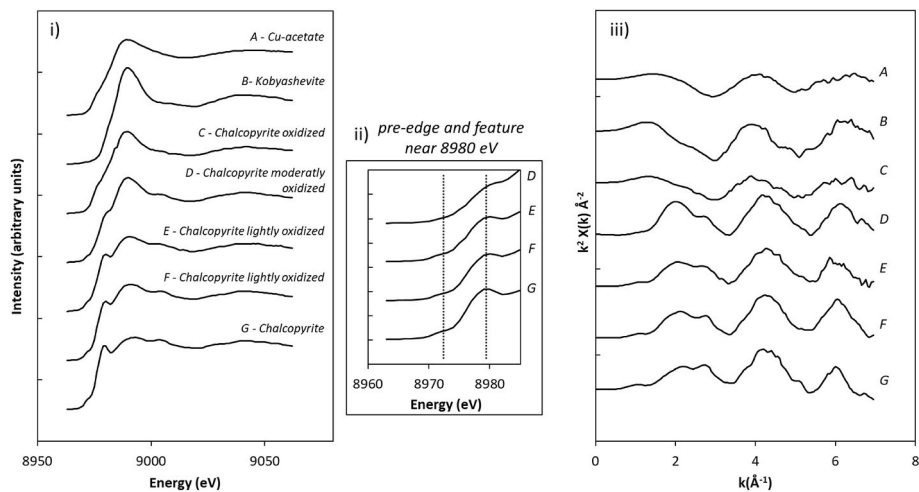
The μ-XRF maps revealed that Cu was mainly in the form of isolated particles (Fig. S3). Various μ-XANES spectra were acquired from a wide range of Cu-enriched zones and particles that were identified using μ-XRF mapping. By comparing these spectra with references compound spectra from the literature, it was possible to identify several Cu-bearing phases in the tailings (Cervi et al., 2021; England et al., 1999; Feng et al., 2022; Mikhlín et al., 2021; Ohta and Kubota, 2016; Sekine et al., 2017).

LCF fit analysis of Cu-μ-XANES spectra with reference compounds suggested the best fitting results for Cu speciation for some unidentified spectra (Table S6). Cu-μ-XANES spectra from “G” to “D” (Fig. 4i) showed clear trends illustrated by the progressive loss of the pre-edge and the feature near 8980 eV (Fig. 4ii) as observed for oxidized chalcopyrite (England et al., 1999). The existence of chalcopyrite (spectra G) and



**Fig. 3.** Average Cu, Bi and Sn contents extracted by the TCLP leaching test, 1 M HCl single-step extraction, CBA single-step extraction and alkaline fusion (total) from Charrier tailing samples (Top 2, Table 1). Conversion from extracted amount to percentage was calculated using  $\%M = 100 \times (\{M\}_{\text{single-step extraction}} / \{M\}_{\text{total}})$ . {M} referred to the amount of metal (mg.kg<sup>-1</sup>), subscript “single-step extraction” to the amount extracted by single step extraction (TCLP, 1 M HCl or CBA), and subscript “total” to the total metal amount obtained by alkaline fusion.





**Fig. 4.** Cu K-edge  $\mu$ -XANES spectra illustrating the diverse Cu-bearing phases in the Charrier tailing samples (“Top 1”, “Middle 2” and “Down”) in i) derivative spectra and iii) Fourier-transform magnitude spectra (iii). An enlargement of some Cu K-edge  $\mu$ -XANES spectra was found in ii) and highlighted the oxidation of chalcopyrite. The comparisons with references and LCF fit allowed to identify the Cu-bearing phases. The closest standard mineral phases were reported. The results of LCF fit were described in Table S7.

oxidized Cu phases such as kobyashevite (spectra B), a Cu-bearing sulfate, could be assumed in the Charrier tailings (Fig. 4, Table S6).

No differences in the main Cu-speciation were found between the “Top”, “Middle” and “Down” tailings samples. The obtained spectra were mainly similar to the reference compound kobyashevite (see Figs. S4 and S5). The XANES spectra of kobyashevite are similar to those of Cu doped Fe-oxide and goethite. However, certain distinguishing features, such as a shoulder peak and pre-edge region, as well as an oscillation tendency observed in the Fourier-transform magnitude spectra, allowed for the selection of the appropriate references to identify Cu-speciation in the samples (Fig. S6). Rare Cu association with organic compounds were found (spectra A, Table S6), which was expected given low TOC amount (<0.5%), and thus organic matter in the tailings (Table 1). Few Cu association with Fe oxides could also be highlighted (Figs. S6 and S7), which supports the results obtained from the CBA extraction (Fig. 3). Several oxidized Cu-bearing phases were found and could be related to the storage type of these tailings. Chalcopyrite crystals inherited from the mineralization could have oxidized over the years due to exposure to atmospheric conditions and runoff water (Courtin-Nomade et al., 2009; Hofmann and Schuwirth, 2008; Kimball et al., 2010). The weathering of these secondary Cu-bearing phases could lead to the formation of secondary sulfate minerals that are observed in the tailings (Ohta and Kubota, 2016).

Cu-speciation, as determined by  $\mu$ -XANES on the Soil and Sediment 1 & 2 sampled near the tailings pile (Fig. S1), highlights the same main Cu-speciation with weathered sulfides to Cu-sulfate (Fig. S7, Table S7). These results confirm the transport of particles from the Charrier tailing pile, in the stream and the soils downstream.

**Bismuth** – The results of parallel chemical extractions showed that over 80% of the total Bi was extracted using 1 M HCl extraction, while almost 20% was extracted using the CBA agent (Fig. 3). The 1 M HCl extraction procedure was largely employed to extract metals from exchange sites in soils and sediments (Leleyter et al., 2012). However, for the case of Bi, hydrometallurgical processes dedicated to the production of Bi from sulfides such as bismuthinite were developed, based on the combination of catalyzers (e. g., Cu) and concentrated acids, including HCl (Ding et al., 2016; Ha et al., 2015; Shen et al., 2019; Yang et al., 2009). The reaction between Bi and concentrated HCl generated strong aqueous complexes,  $\text{BiCl}_3(\text{aq})$  and  $\text{BiCl}_4^-$  (Reyes-Aguilera et al., 2008). The presence of sulfide species in the Charrier tailings suggests that a significant portion of Bi may be associated with these species.

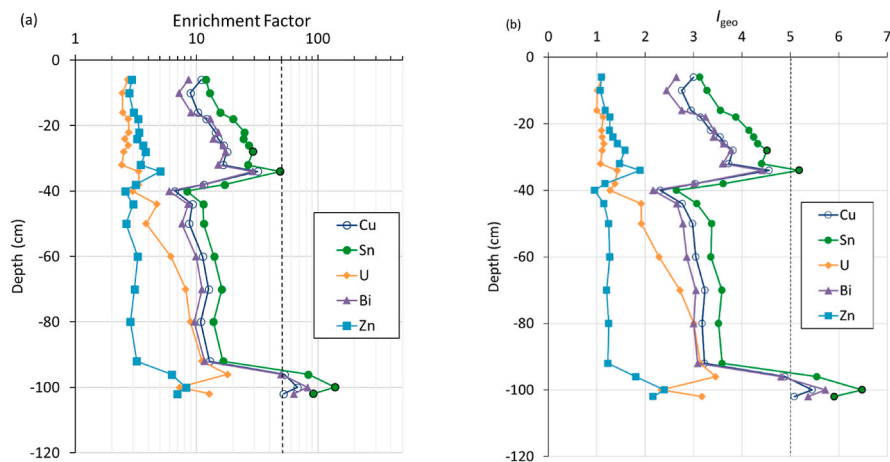
### 3.2. Saint-Clément sediments

#### 3.2.1. Contaminant indexes and origin of TE

Contaminant indexes are often used to trace the degree of TE enrichments in sediments influenced by past anthropogenic activities (Audry et al., 2004; Delgado et al., 2012; Yang et al., 2017).  $EF$  values were calculated using Eq. (1) for Cu, Sn, Bi, Zn and U in the sediments of lake Saint-Clément to determine the impact of past mining activities (Fig. 5a). Data employed for calculations are available in supplementary file (Tables S3 and S8). The results indicated that these metals were enriched ( $EF > 1$ ) to varying degrees, from moderate to extremely severe enrichment. The contamination indexes for Cu, Bi, and Sn, indicate a strong ( $EF > 10$ ) to an extremely severe ( $EF > 50$ ) enrichment throughout the sediment core, as well as at 34 cm deep and 96–100 cm depth. The  $EF$ s for U were found moderate to moderately severe throughout the core and severe ( $EF > 10$ ) at depths of 92 and 102 cm.  $I_{\text{geo}}$  values showed the same trends as those in the lake sediments (Fig. 5b), indicating a high to extremely high enrichment for Cu, Sn, and U. The lake sediments were considered highly enriched ( $I_{\text{geo}} > 3$ ) for Cu and Sn and extremely enriched ( $I_{\text{geo}} > 5$ ) at depths of 34 and 96 cm. For U, the sediments were considered moderately polluted ( $I_{\text{geo}} > 1$ ) throughout the core, except at 60 cm (moderately highly polluted) and at depths of 92, 96, and 102 cm (highly polluted). These indexes consequently highlighted significant anthropogenic inputs of these metals, which could be linked to former mining activities (Da Silva et al., 2005; Hadjipanagiotou et al., 2020; Liu et al., 2021). For U, the high  $EF$ s could be partially linked to former U mining activities of the Bois-Noirs Limouzat mine (Mangeret et al., 2020; Reyss et al., 2016) and the deposition of U-rich accessory minerals originated from granite (Morin et al., 2016). Indeed, significant activities of  $^{238}\text{U}$  daughter isotopes (i.e.,  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$ ), with several  $\text{Bq} \cdot \text{g}^{-1}$ , were formerly detected and attributed to these activities (Reyss et al., 2016).

The variations of Fe, Mn, Cu, Sn, and Bi contents with depth in sediments showed similar trends (Table S8). Furthermore, significant contents are observed for some trace elements  $\{\text{Sn}\}_{-34\text{cm}} = 919 \text{ mg kg}^{-1}$  and  $\{\text{Sn}\}_{-100\text{cm}} = 2265 \text{ mg kg}^{-1}$ ,  $\{\text{Cu}\}_{-34\text{cm}} = 452 \text{ mg kg}^{-1}$  and  $\{\text{Cu}\}_{-100\text{cm}} = 838 \text{ mg kg}^{-1}$ ,  $\{\text{Bi}\}_{-34\text{cm}} = 31 \text{ mg kg}^{-1}$  and  $\{\text{Bi}\}_{-100\text{cm}} = 77 \text{ mg kg}^{-1}$ . Additionally, U contents showed an increase with depth, with two peaks at depths of 96 cm and 102 cm with respectively 370 and 309  $\text{mg kg}^{-1}$ . Two significant Bi, Cu, Sn, and Zn content peaks,  $EF$  and  $I_{\text{geo}}$  values at depths of 34 and 100 cm suggested that two significant events took place in the upper Besbre watershed. The recent peak at 34 cm depth





**Fig. 5.** EF (a) and  $I_{geo}$  (b) indexes obtained for Cu, Sn, Bi, Zn, and U in the 2013C7 sediment core of lake Saint-Clément. The dotted lines showed the highest contamination limits for each index. Black circles indicated the sediment depths where mineralogical analyses (SEM and EPMA) were performed.

was successfully dated to 1999 according to radiogeochronological methods based on the  $^{228}\text{Ra}$  excess and  $^{137}\text{Cs}$  measurements (Reyss et al., 2016), leading to a sedimentation rate of  $2.6 \text{ cm.y}^{-1}$ . According to documents from the French Environment agency DRIRE, the removal of mine buildings and remodeling of the Charrier tailings pile took place in 1999 (GEODERIS, 2021). This event may be the cause of the high EF of Cu, Sn and Bi observed at depth of 34 cm, the origin of higher EF and  $I_{geo}$  for TE between depths of 92–102 cm is difficult to identify and may be linked to the site's history and/or to exceptional hydrological events that transported Charrier tailings into the Saint-Clément Lake via the Besbre River (Batson et al., 1996; Zonta et al., 2005). Indeed, several important daily flow rate values for the Besbre River were recorded between 1977 and 1985. The highest value,  $33.5 \text{ m}^3 \text{ s}^{-1}$  was recorded in July 1977 at the Chatel-Montagne station located near the lake Saint-Clément dam (HydroPortail, 2023). The high flow rates may contribute to the transport of TE-enriched particles from the Charrier tailing pile. Strong correlations were found for the total content of Bi, Cu, Sn and Fe ( $R^2 = 0.96\text{--}0.98$ ), suggesting a potential common origin for these elements. The analysis of total element content, FE and  $I_{geo}$  depth profiles (Fig. 5, Table S8) reflects the past mining activities in the upper Besbre watershed, as well as the transportation of TE by suspended particles in river waters, likely due to storm or flood events, as was previously reported (Da Silva et al., 2005; Parsons et al., 2012). Overall, the TE mobilization downstream of mining sites is primarily controlled by: (1) the distance from the mine waste source, (2) the hydrological conditions of the river, including wet and dry seasonal variations and flooding events (Pirrie et al., 1997; Salvarredy-Aranguren et al., 2008; Silva et al., 2014; Yim, 1981). The next section will discuss mineralogical, elemental and speciation investigations on the sediment particles of Lake Saint-Clément to confirm the mining origin for the studied TE.

### 3.2.2. Sediment mineralogy

Mineralogical analyses were preferentially conducted on sediment samples enriched in TE (Sn, Bi, Cu and U) at depths of 34 cm, 100 cm, and 102 cm depth, as well as on samples with lower TE enrichments (*i.e.*, at depths of 6, 24, and 70 cm) to provide an overview of the sediment's mineralogical composition. The investigation of Fe solid speciation was also monitored in Stetten et al. (2018a) due to its influence on biogeochemical processes involved in the metal cycle.

The sediments of lake Saint-Clément were found to contain mainly detrital minerals from granite including quartz, micas, K-feldspars (mainly microcline), and phyllosilicates such as chamosite-type chlorites (Fig. S8), consistent with previous studies (Morin et al., 2016; Stetten et al., 2018a). Sediments sampled at 6 and 70 cm depth had

higher quartz contents. In contrast, the XRD analyses of sediment samples taken at depths of 24, 34, and 100 cm showed lower quartz contents and significant diffraction peaks of chamosite. The abundance of chamosite in the sediment, along with high EF and  $I_{geo}$  of Cu, Sn, and Bi, suggests the transport of fine-grained particles from the Charrier tailings to the Besbre River., as demonstrated in other mining-influenced watersheds (Pascaud et al., 2015).

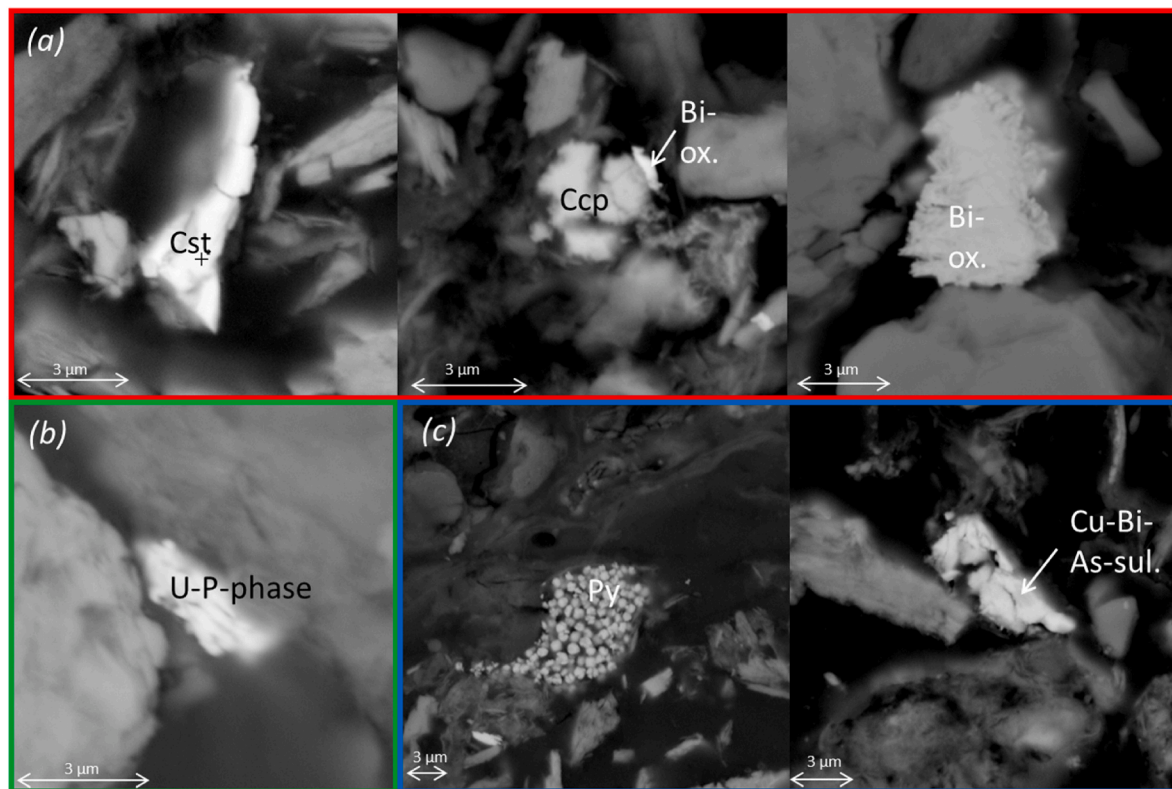
### 3.2.3. Fe, Sn, Cu, Bi and U speciation in sediments

**Iron** – SEM observations identified small sphalerite ((Zn,Fe)S) and pyrite crystals ( $\text{FeS}_2$ ). The morphology of the pyrite crystals similar to framboidal habits suggests an authigenic origin. Fe-oxides were also observed, with a chemical composition of 86.4 wt% FeO, indicating the presence of magnetite or wüstite, as previously reported in other studies (Marcoux et al., 2022) (Table S4). Additionally, traces of Fe were also observed in cassiterite crystals (Fig. 6).

1 M HCl and CBA extractions extracted less than 35% and 25% of Fe, respectively (Fig. S9). Compared to the study by Stetten et al. (2018a), the amount of Fe extracted by CBA was higher, ranging from 8 to 20% from anoxic sediments of the lake Saint-Clément. The higher Fe contents extracted by 1 M HCl may reflect a pool of exchangeable Fe, bound to POM and/or poorly crystalline Fe-oxyhydroxides. Additionally, the majority of Fe was mainly found to be associated with refractory mineral phases (60–75 %; Fig. S9). As demonstrated by Stetten et al. (2018a), XANES and EXAFS analyses revealed that Fe was primarily present as structural Fe(II) and Fe(III) in phyllosilicate minerals in well-preserved sediments. Fe was mainly incorporated into clay minerals such as illite, biotite, or chlorite like chamosites, which could contain up to 29 wt% Fe, as previously found in the sediments of Lake Saint-Clément (Stetten et al., 2018a). Pyrite crystals were also observed from SEM observations in the solid residues of 1 M HCl extraction (Fig. S10), they can be considered as minor Fe-bearing species.

**Tin** – The main Sn-bearing phases observed were unaltered cassiterite grains with variable sizes, up to  $10 \mu\text{m}$  (Fig. 6). Chemical analyses of these crystals indicated the presence of low TE concentrations, including Pb (up to 2 wt%), Fe (up to 1.6 wt%), and Bi (up to 3.9 wt%) (Table S4). Cassiterite has very low solubility (Dill et al., 2006; Lottermoser and Ashley, 2006), making it an interesting proxy for tracing the metal discharges from the Charrier site. Furthermore, investigations using the two single-step extractions resulted in very low Sn contents extracted, below 1 % (Fig. S11). Post extraction SEM analyses confirmed the preservation of cassiterite (Fig. S10).

**Copper** – Cu sulfides of small size, ranging from 10 to less than  $3 \mu\text{m}$ , were observed (Fig. 6). These sulfide species, mainly found as unweathered chalcocopyrite and framboidal pyrite, had Cu content between



**Fig. 6.** SEM images of cassiterite (Cst), chalcopyrite (Ccp), Bi-oxide (Bi-ox.), framboidal pyrite (Py), Cu–Bi–As sulfide (Cu–Bi–As sul.), U-rich zircon (U-Zrn), and a U and P-rich autunite-like mineral phase (U-phase.) observed in the sediment core 2013C7 of the Saint-Clément Lake at (a) 34 cm depth where a peak of metal concentrations related to the remodeling of the Charrier tailing pile at 1999 was found (red box) (b) 100 (green box) and (c) 102 cm depth (blue box) sediment samples, where significant peaks of metals were detected.

26 and 33 wt%. They were not associated with other mineral phases. Selective extraction experiments showed that 38–58% of Cu was extracted by 1 M HCl solution (Fig. 7). SEM observations after chemical extractions revealed the presence of small size chalcopyrite and pyrite crystals (Fig. S10), as well as other refractory minerals such as Ti-oxides and zircon, similarly to Charrier tailings. The CBA extraction yielded only 5–9% of Cu, indicating a low contribution of Fe oxyhydroxides to Cu solid speciation in the sediments of Lake Saint-Clément. Furthermore, the significant TOC contents ranging from 8.5 to 12 wt% (Stetten et al., 2018a), suggests a possible association between Cu with POM.

Chalcopyrite and sphalerite are sulfide minerals that can be oxidized in uncovered tailing piles, potentially providing a source of Cu and/or Fe in natural systems downstream (Courtin-Nomade et al., 2009; Hofmann and Schuwirth, 2008; Kimball et al., 2010). As previously suggested, this oxidation could cause Cu redistribution from the original mineral ores and become sequestered onto major natural sorbents such as POM (Manceau et al., 2002; Manceau and Matynia, 2010). It may also be associated with poorly crystalline Fe and Mn oxyhydroxides (Scheinost et al., 2001) and/or as secondary sulfide minerals (Audry et al., 2010) in river and lake sediments. Laboratory incubation experiments of sediments were conducted on sediments spiked with  $\text{Cu}^{2+}$  and amended with organic matter under suboxic and anoxic conditions. The experiments promoted the precipitation of covellite and chalcopyrite (Cervi et al., 2021).

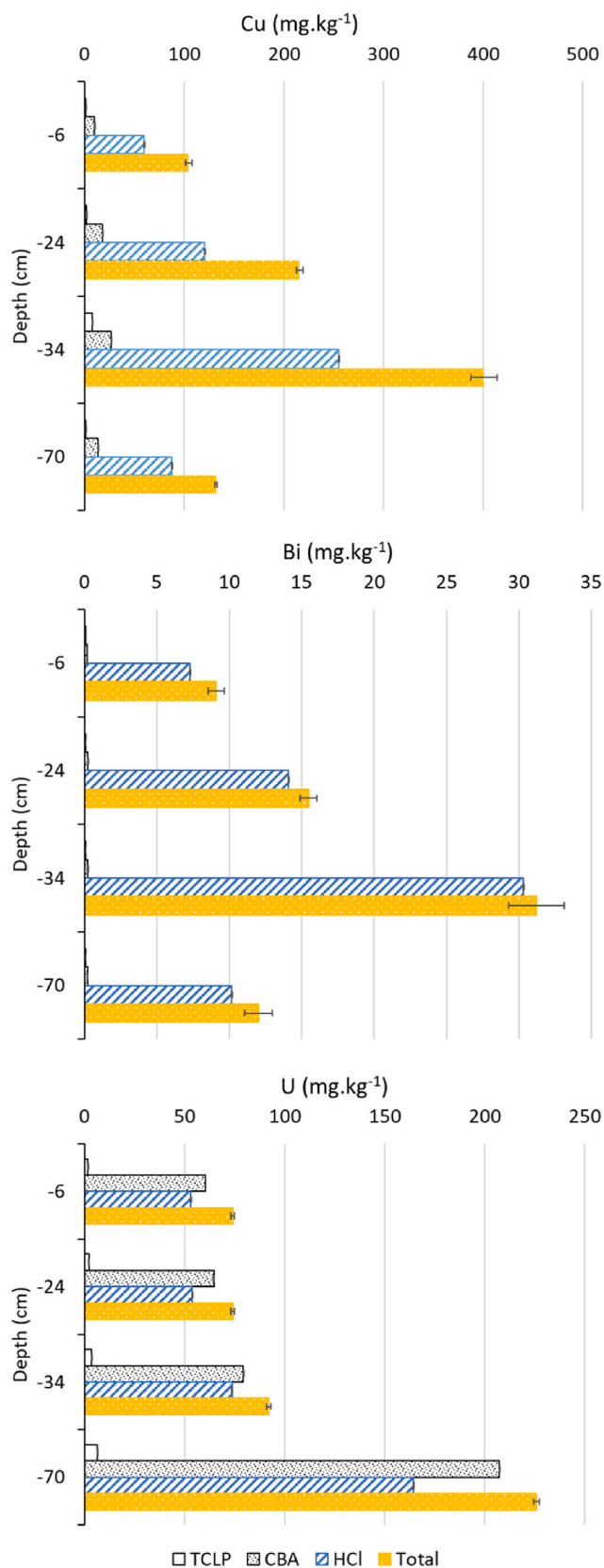
$\mu$ -XRF maps of sediments sampled at a depth of 100 cm showed that Cu was primarily present as isolated high-grade particles (Fig. S12).  $\mu$ -XANES analyses of individual particles revealed that Cu was mainly associated with chalcopyrite, with varying degrees of oxidation (Fig. 8). Rare Cu-sulfate particles were also identified in the sediments (Fig. 8, Table S6), suggesting that Cu was mainly present as reduced species. The observations suggest that sediment reoxidation does not fully oxidize Cu-bearing phases.

In Lake Saint-Clément sediments, Cu is mainly present as sulfides (inherited from the Charrier tailings or secondary sulfide minerals), associated with OM and to a lesser extent as Fe(III) and/or Mn(III/IV) oxyhydroxides.

**Bismuth** - TE impurities such as Ag (up to 3 wt%), and Bi (up to 0.8 wt%) were detected in some Cu-rich sulfide minerals from Charrier tailings (Table S5). Additionally a Cu–Bi–As-rich sulfide phase was identified (Fig. 6). Bi-oxides (Fig. 6) and rare Ag-rich phases (30 wt%) containing Se (15 wt%) and Cu (5 wt%) were also found (Table S5). Parallel chemical extractions of the sediment samples showed that 70–95% of total Bi was extracted by 1 M HCl extraction, similar to Charrier tailings samples. Less than 2% of Bi was extracted with the CBA agent targeting TE associated with poorly crystalline Fe(III) and/or Mn (III/IV) oxyhydroxides. This suggests that Bi has a weak association with these phases.

There is limited knowledge about the geochemical behavior of Bi in soils contaminated by mining activities (Hällström et al., 2018). Bi was discovered to be poorly soluble in waters under moderately acidic and oxidizing conditions and enriched in sediments due to particulate transport downstream of a Cu–W mine (Jung et al., 2002). These results suggest that Bi speciation in sediments of Lake Saint-Clément may be in the form of easily extractable species, possibly associated with POM and inherited sulfide minerals from the Charrier tailings. This is likely due to the significant TOC (10–15 wt%) and the presence of Bi-containing phases, such as sulfides and oxides, in the sediments. Recent studies have shown that Bi(III) has a strong association with dissolved and soil organic matter in batch experiments (Laborda et al., 2008; Kleja et al., 2022).

**Uranium** - The sediment samples at a depth of 100 cm contained various crystalline phases enriched with uranium, including zircon and a phosphate-rich phase similar in composition to autunite (Fig. 6). The CBA solution extracted over 80% of U, while the 1 M HCl solution



**Fig. 7.** Cu, Bi, and U contents (mg.kg<sup>-1</sup>) extracted by chemical extraction HCl 1 M, CBA, and by normalized test TCLCP of 2013C7 Saint-Clément Lake 6, 24, 34, and 70 cm depth sediments samples and of Charrier tailings sample. The conversion from extracted amount to percentage were displayed in Fig. S11.

extracted between 65 and 80% (Fig. 7). These results are consistent with previous chemical extraction tests conducted on well-preserved sediments of the Saint-Clément Lake using a 1 M NaHCO<sub>3</sub> solution. The tests indicated that 60–84% of U was in the form of mononuclear U(IV) species (Morin et al., 2016; Stetten et al., 2018a). Additionally, the presence of uranium phosphate minerals in sediment samples at a depth of 100 cm, which are estimated to have been deposited between 1978 and 1980, indicates the existence of previously deposited inherited U species.

### 3.3. Environmental influence analysis

To evaluate the impact of sediment excavation/dredging and inland storage in France, the total metal contents (mg.kg<sup>-1</sup>) in sediments were compared to threshold values (S1) established in the French Environment Code for managing rivers and canal sediments (Decree 09/08/2006, 2006). The influence of the sediment management strategies was deemed “normal” or comparable to the geochemical background if the total TE contents were below the threshold values S1, and “negative” if they exceeded the thresholds S1.

Total average (>260 mg kg<sup>-1</sup>), median (180 mg kg<sup>-1</sup>), and maximum (840 mg kg<sup>-1</sup>) Cu contents measured from all the sample from the sediment core were reported in Table 2. The values exceed the S1 limit value (100 mg kg<sup>-1</sup>) for Cu (Table 2), indicating a potential negative impact of sediment management strategies on Cu. However, the S1 threshold was not defined for each trace element, including U. Therefore, threshold values alone cannot be used to make decisions about sediment management (Peddicord et al., 1998).

Sediment Quality Guidelines (SQGs) are useful tools for assessing the quality of freshwater sediments (MacDonald et al., 2000). They include a threshold effect concentration (TEC) and a probable effect concentration (PEC). The quality of sediments is a concern for Lake Saint-Clément, which is a recreational area, including a fishing spot. The total Cu contents exceeded the SQGs threshold values, 149 and 31,6 mg kg<sup>-1</sup> for PEC and TEC respectively (Table 2) (MacDonald et al., 2000). This indicates a potential toxicological risk for this element. It is important to note that SQGs do not consider possible interactions of contaminants, and are not defined for each contaminant of concern.

To assess the effects of a specific management, such as dredging and inland deposits, case-specific effects-based testing is required. Complementary studies, including ecotoxicological and leaching tests, are also necessary.

**TCLP** – To aid in the assessment of sediment dredging operations impact, the TCLP leaching test was performed instead of using European standards. This test was chosen because it defined threshold levels for more elements relevant to our study. While the TCLP leaching test alone cannot fully assess the consequences of dredging operations, it does provide initial information on the mobility and leachability of TE. To evaluate the leachate data collected for Cu, Zn, and U, threshold values established by US-EPA were proposed. These regulatory values are based on 100 times the National Interim Primary Drinking Water Standards for metals (Marguí et al., 2004) and can serve as a useful point of comparison. Regulatory standards have been established for 9 TE including Cu and Zn, as Maximum Contaminant Level Goals (MCLG). For U, the WHO drinking-water guidance value of 30 µg.L<sup>-1</sup> have been used for evaluation of TCLP results (WHO, 2011) (Table 2).

The concentrations of TE TCLP in the leachates were significantly lower than the reference values (Table 2). This indicates that dredged lake sediments can be considered as non-hazardous waste with respect to the EPA’s defined threshold values for Cu, Zn and U. The TCLP leaching test procedure is close to the F1 fraction of the BCR sequential extraction protocol, targeting metals associated with the exchangeable, water- and acid-soluble fractions from previous works (Marguí et al., 2004; Unda-Calvo et al., 2017). Therefore, this test can be considered as an analogue of the BCR F1 fraction.

The sediments of lake Saint-Clément (Morin et al., 2016; Stetten



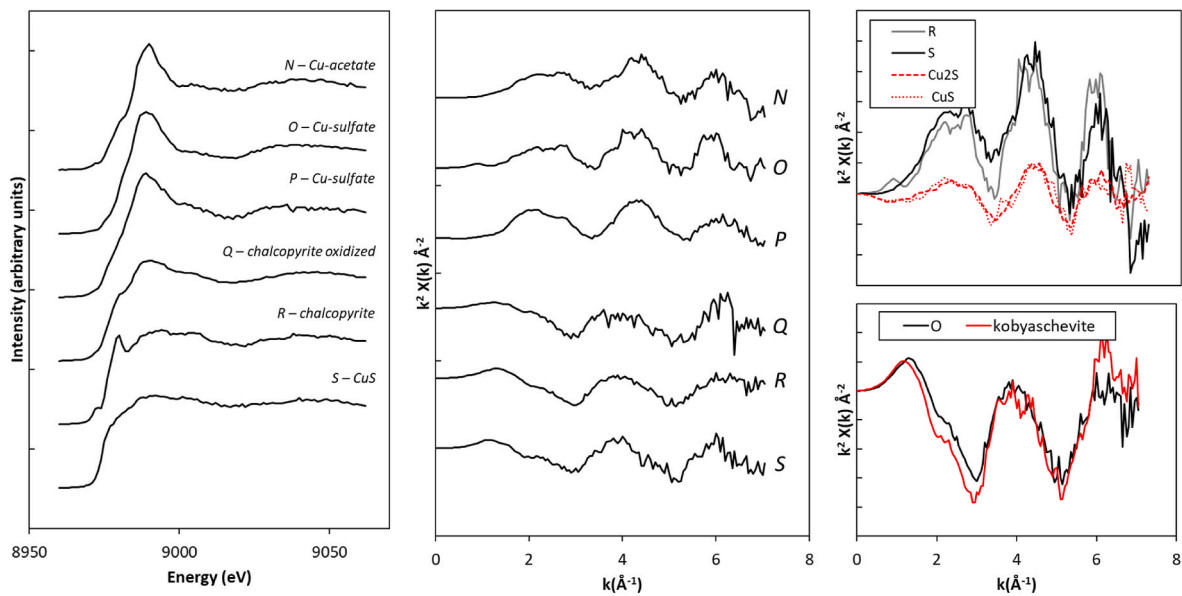


Fig. 8. Cu K-edge  $\mu$ -XANES spectra illustrating the diverse Cu-bearing phases in the Saint-Clément sediment samples (34 and 100 depth). Comparison with references and LCF fit allowed to identify the Cu-bearing phases as sulfide to few sulfates close to Kobyashevite. LCF results were reported in Table S7.

Table 2

Comparison between total average Cu and Zn contents in sediments of lake Saint-Clément and S1 threshold values. TCLP average concentrations were also reported (see Fig. 7) a compared with TCLP threshold values and Waste Criteria, ND = Not Defined, \*\* => derived guidelines from WHO (2011) for U and from US-EPA (1992) for Cu and Zn.

| Substance | Content in the sediment |                     |                     | French "total" threshold value |                       | Extracted concentration and content |                       | American extracted threshold value |
|-----------|-------------------------|---------------------|---------------------|--------------------------------|-----------------------|-------------------------------------|-----------------------|------------------------------------|
|           | Average                 | Median              | Maximum             | S1                             | TCLP leachate content | TCLP extracted content              | TCLP threshold values |                                    |
|           | mg.kg <sup>-1</sup>     | mg.kg <sup>-1</sup> | mg.kg <sup>-1</sup> | mg.kg <sup>-1</sup>            | μg.L <sup>-1</sup>    | mg.kg <sup>-1</sup>                 | μg.L <sup>-1</sup>    |                                    |
| Cu        | 260                     | 180                 | 840                 | 100                            | 116                   | 2.9                                 | 100,000**             |                                    |
| Zn        | 300                     | 270                 | 590                 | 300                            | 155                   | 3                                   | 500,000**             |                                    |
| U         | 143                     | 89                  | 376                 | ND                             | 184                   | 3.6                                 | 3000**                |                                    |

et al., 2018a), like in wetland soils (Lefebvre et al., 2022; Stetten et al., 2018b, 2020) and in U roll-front deposits (Bhattacharyya et al., 2017) have been found to contain mononuclear U(IV) or U(VI) associated with C, Si, or P groups, which serve as the main host for U. It was suggested that acetate ligands may have a poor ability to complex uranyl species (Jiang et al., 2002) compared to particulate organic matter or bicarbonate ions (Seder-Colomina et al., 2018, 2022), which could explain the low U content extracted from sediments during TCLP tests. These findings highlight the importance of considering the complexation ability of ligands when analyzing U content in sediments. In oxic soils, Cu is also present as stable Cu(II) complexes with natural organic matter, as found in other studies (Karlsson et al., 2006; Manceau and Matynia, 2010). Previous BCR soil extraction studies have shown that acetate ions have a low ability to desorb Cu from organic matter-rich matrices, such as soil and sediments (Qin et al., 2004).

This initial environmental assessment did not identify any potential impact on the availability of Cu, Sn, Bi, and U content if lake sediments were dredged and disposed of inland. The environmental and health effects of Bi were not established due to limited information on its mobility and its toxicity (Murata, 2006; Hällström et al., 2018). However, a recent study suggested that metallic Bi is redistributed in oxic environments, but it is strongly associated with natural organic matter (Kleja et al., 2022). Additionally, Sn is considered to have a very low toxicity (Rüdel, 2003), and due to the very low solubility of mineral phases such as cassiterite SnO<sub>2</sub>, the mobility of Sn is limited (Dill et al., 2006; Lottermoser and Ashley, 2006).

Using European standardized techniques, studying the mobility of trace elements from these sediments would aid in material classification.

However, the lack of ecological threshold values for U is currently limiting. To better assess the impact of dredging operations and inland disposal of trace element-enriched sediments, ecotoxicological tests for instance should be carried out to confirm the absence of environmental risks.

#### 4. Environmental implications

The analysis of Lake Saint-Clément's sediments revealed two main influences: (i) the transportation of Charrier TE-rich tailings particles, indicated by the presence of Fe-rich chamosite, Cu and Bi-rich residual sulfide minerals and cassiterite and, (ii) natural and mining inputs for U. Additionally, Cu, U and Bi were primarily found as extractable fractions, likely controlled by their sorption onto mineral phases and/or natural organic matter. These results are consistent with numerous studies that have identified the prevalence of sorbed metal species in soils and sediments affected by mining (Dewey et al., 2021) and dredging (Cervi et al., 2021; Manceau and Matynia, 2010). Specifically, the possible control of Bi as sorbed species in sediments confirmed the pioneering study of Kleja et al. (2022) where strong Bi complexation with dissolved and particulate organic matter was identified. However, the stability of the available TE fraction was confirmed by the low TCLP values obtained. This indicates that there is a limited risk of mobilization of Cu, Zn, U, Sn, and Bi associated with the dredging and inland storage of sediments from Lake Saint-Clément.

This study emphasizes the importance of utilizing both mineralogical and chemical methods to characterize trace element speciation and availability in lake sediments. The characterization of mine tailings,



which act as one of the sources of TE in the sediments of Lake Saint-Clément, contributes to the understanding of their stability.

The Cu-bearing phases in Charrier tailings were found to be more diverse and oxidized compared to the inherited phases from the initial ore, indicating partial weathering. Given the increasing occurrence of extreme climatic events (e.g., floods, storms) caused by climate change, it is necessary to assess sediment management strategies to quantify particulate and dissolved transport under these conditions (Schiedek et al., 2007).

#### CRediT authorship contribution statement

**Louise Darricau:** Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Arnaud Mangeret:** Conceptualization, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing. **Josselin Gorny:** Conceptualization, Methodology, Supervision, Validation, Writing – review & editing. **Emmanuel Joussein:** Investigation, Methodology. **Sebastian Schoeder:** Investigation, Methodology, Resources. **Jean-Louis Reyss:** Methodology, Resources. **Antoine Thouvenot:** Methodology, Resources. **Alexandra Courtin:** Conceptualization, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing.

#### 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.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2024.105995>.

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