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Potential risks of metal toxicity in contaminated sediments of Deûle river in Northern France

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ABSTRACT

The aim of this paper was to evaluate the potential sediment cumulative damage and toxicity due to metal contamination in a polluted zone of Deûle river (in northern France) from nearby two smelters. Metal-enrichment factors and geoaccumulation indices measured with sediment depth revealed that ─ compared to background levels either in local reference soils or in world rivers sediments / suspended particulate matter ─ Cd contributed to the highest pollution levels, followed by Zn, Pb and to a much lesser extent Cu and Ni. A comparison of the vertical distribution of AVS (Acid Volatile Sulfides), SEM (Simultaneously Extracted Metals), TMC (Total Metal Concentrations), TOC (Total Organic Carbon) and interstitial water-metal concentrations in the sediment allowed us to highlight the extent of toxicity caused by Cd, Pb, Zn, Ni and Cu and to raise the possibility of their association with certain geochemical phases. To assess the actual environmental impacts of these metals in Deûle river, numerical sediment quality guidelines were further used in the present work. Sedimentary Pb, Zn, and Cd contents largely exceeded PEC (Probable Effect Concentration) values reported as consensus-based sediment quality guidelines for freshwater ecosystems. As for risks of toxicity from pore waters, metal concentrations reached their maxima at the surficial layers of the sediment (1-3 cm) and IWCTU (Interstitial Water Criteria Toxicity Unit) observed for Pb and to a lesser extent Cd, violated the corresponding water quality data recommended by USEPA.

KEYWORDS

Sediment; pore water; trace metal; pollution; water quality; toxicity

1. INTRODUCTION

Large uncontrolled metal inputs from industrial sources have contributed to increase pollution in rivers [1-6]. Depending on hydrodynamics and environmental conditions, metals tend to accumulate in sediments at the bottom of the water column; and if toxic levels are reached, metals can affect benthic organisms and food chain, raising the possibility of a threat of human health for local population. To obtain a realistic estimate of the actual environmental impact of metals in an aquatic medium, their chemical nature or potential mobility / availability must be addressed. Trace-metals global determination including the characteristics of metals in water and the identification of the geochemical phases of metals in sediments as well as quantification by carrying out chemical speciation is crucial to evaluate the ecological risks of these contaminants in the study area [1, 3, 4, 7-9]. In recent works, vertical sediment and/or pore water profiles were often used to examine the contamination history of different aquatic systems [10-14]; Metal distribution / enrichment / accumulation in sediment layers were studied and data constituted valuable tools for assessing both the extent of metal pollution and sediment quality [9, 14, 15].

On this view, we examine in the present work a river, Deûle, that is a major drinking-water source for the population living in the "Nord-Pas de Calais" region (in northern France), however, with severe metallic pollution, particularly, in a 3-km zone from nearby two smelters (Metaleurop and Umicore) near Douai city. Metaleurop factory was in activity for more than a century and was closed in January 2003. Umicore factory has still been in activity since 1869. The behaviour of trace metals in waters and sediments of Deûle river had been extensively by our research group [16-21]. For this reason, only data obtained with a series of sediment cores that are considered as the most representative ones of the polluted site of Deûle river, is presented in this paper. Speciation analysis of the different sedimentary compartments has been used to provide information of mobility/availability of anthropogenic metals with depth; And to predict sediment toxicity, metal concentration levels in sediment

layers have been compared with those of potential concern (by using water and sediment quality guidelines for freshwater ecosystems [22-26]), that might cause or contribute to adverse effects on sediment-dwelling organisms.

The present study has been initiated with the following objectives: (i) to determine the levels of contamination in Deûle river in relation to primary sources of pollution; (ii) to perform water and sediment quality assessments; (iii) to evaluate potential ecological risks due to metal pollution in a populated area; and (iv) to maximize the scientific basis for management decisions and restorations. Regarding this last point, the results of this investigation would have implications for a rational management of Deûle river and should be used for comparison with future sediment quality data. In addition, such a scientific and preventive approach based on better understanding of the source, fate and effects of metallic contaminants in an aquatic system would also be of great interest for the development of pollution-control and sediment-remediation strategies in other polluted rivers in the world.

2. EXPERIMENTAL

2.1. Location and sampling

Smelting activities are well-known to be responsible for significant metallic pollution in soils around Deûle river [27-29]. Taking into consideration recent analytical data obtained at different stations along Deûle river [16-18, 20], we had chosen in the present work a sampling site located in a part of Deûle river that was considered as its most polluted zone (Figure 1). Sediment samplings were carried out on May 2007. Undisturbed sediments cores were collected together with their overlying water using 35-cm long Perpex tubes. One was used to assess directly in the field the profiles *versus* depth of redox potential and pH, and another one was employed to determine *in situ* the vertical concentration profile of dissolved sedimentary oxygen. In the laboratory, one core was used for the analysis of trace metal total

concentrations in pore waters and sediment particles, and another one was dedicated to the analysis of acid volatile sulfides (AVS) and simultaneously extracted metals (SEM) concentrations.

Under a nitrogen atmosphere inside a glove box, the cores were sliced in 2-cm thick slices. A part of these sliced sediments was kept in plastic bags previously purged with N_2 for solid analyses and the remaining part was centrifuged (2500 rpm for 30 min) in order to recover supernatant waters. The centrifuged tubes were returned to the N_2 flushed glove box, where pore waters were filtered with 0.45 µm Alltech filters (cellulose acetate membrane) and immediately acidified with ultra-pure nitric acid (100 µL in 10 mL of pore water).

2.2. Chemical analyses

AVS contents were measured according to the method described by Allen and his coworkers [30]. Shortly, approximately 2 g of wet (anoxic) sediment were mixed under nitrogen with a 6M HCl solution during one hour at 25°C. H_2S gas was generated and trapped inside a 1M NaOH solution to form dissolved sulfide, and its concentration was subsequently measured with a sulfide specific electrode composed of a Ag_2S polycrystal membrane (Orion). For a couple of sediment samples, AVS concentrations were measured in triplicate, and results were found to be reproducible with an analytical precision ≤ 15 %.

Simultaneously Extracted Metals (SEM) were extracted from 1 g of raw sediment with 20 mL of a 1M HCl solution [31-34]. The mixture was shacked at room temperature during 24 hours, and afterwards filtrated through a 0.45 µm Alltech filter (cellulose acetate membrane). SEM concentrations present in the filtrate were determined using ICP-AES (Vista Pro, Varian). Total analytical errors made on SEM measurements in all the SEM extraction procedure used were ≤ 10 % [35].

The contents of total organic carbon (TOC) in Deûle-river sediments at different depths were determined first by drying samples at 60°C during 1 day, and second by heating them to 450 °C for 12 hours in order to assess the ignition loss: at each step of this heating procedure, carbon was measured using an elemental CHNS analyser (model 932 LECO). Mean error percentage on TOC was ± 10 %.

After filtration and acidification, pore waters were analyzed by means of ICP-MS [Thermo Scientific, Finnigan Element II (in the Norwegian University of Science and Technology, Norway) and Thermo Elemental X7 (in the University of Lille 1, France)] to determine the concentrations of dissolved metals (Fe, Mn, Cd, Cu, Ni, Pb and Zn). For pore water element analysis, the analytical quality was assured by analysing a riverine water standard reference material (SLRS-4) provided by the National Research Council of Canada. Overall, trace-metal concentrations were found to be within 80-100 % of the certified values [18]. After an acid digestion of sedimentary solids with concentrated acids (according to two steps: firstly with HF and secondly with aqua regia), total concentrations of sedimentary metals (Fe, Mn, Cd, Cu, Ni, Pb and Zn) were determined using ICP-MS. For total sediment element analysis, analytical quality was assured by analysing the selected Canadian International Sediment Standards HISS-1, MESS-3 and PACS-2. The concentrations obtained were generally found to be within 90-100 % of the certified ones [18].

3. RESULTS AND DISCUSSION

3.1. Environmental quality assessment on undisturbed sediments of Deûle river

Geoaccumulation index (I_{geo}) — The level of pollution in sediment solids from this river can be evaluated by comparing current metal concentrations with preindustrial ones through the calculation of the geoaccumulation index, as pointed out previously [18, 36].

For that purpose, the geochemical background contents of the selected metals in the studied area were those found in Loessic and alluvial reference soils [28]. As a whole, the I_{geo} values determined for the selected metals (Cd, Cu, Ni, Pb and Zn) revealed that all along the cores studied sliced samples were characterized as very strongly polluted (class 6) for Cd (I_{geo}, 6.47-7.96), Pb (I_{geo}, 4.77-7.80) and Zn (I_{geo}, 5.30-6.02), moderately to strongly polluted (class 3 and 4) for Cu (I_{geo}, 2.73-3.37), and unpolluted (class 0) for Ni [I_{geo}, (-0.51)-(+0.86)] (see Figure 2).The averaged pollution degree of these metals decreased in the following order: Cd > Pb ~ Zn > Cu >> Ni, as shown in Figure 2.

Sediment enrichment factor (SEF) — To evaluate anthropogenic influences on studied solid sediments in Deûle river, as proposed recently [18], the SEF ratio can be used as a pollution index by referring selected-metals concentrations to background levels of metals either in world-rivers sediments/suspended particulate matters or in local soils [29, 37]. Overall Cd, Pb and Zn indicated the heaviest contamination with SEF values varying with depth between 258 and 499 for Cd, 56-514 for Pb and 56-157 for Zn. Deûle sediments were in contrast much less polluted in copper ($4.1 \leq SEF_{Cu} \leq 21$) and nearly unpolluted in nickel ($SEF_{Ni} \leq 1.8$). Note further that, at some depths (13, 19, 21 cm), maximum SEF values were detected in particular for anthropogenic metals (Cd, Pb and Zn), suggesting stronger inputs in some periods of industrial exploitation. From these data, a similar metallic pollution scale was found as that observed from I_{geo} values, i.e.: Cd ≥ Pb > Zn >Cu >> Ni.

3.2. AVS, SEM and total metal concentrations

Because the solubility product constants (Ksp) of MeS (with Me^{2+}: Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+}) are lower than those of FeS and MnS [38], sediment sulfides which are composed of FeS and MnS, can react with cationic metals (Me^{2+}) to generate more insoluble metal sulfides

[39]. Such a reaction scheme then reduces the availability of the metals, “Me”, for benthic organisms and thereby contributes to diminish the potential risk of metal toxicity in the sediment [39-45]. By treating sediment with cold hydrochloric acid, many sediment sulfides are liberated: amorphous and crystalline FeS, greigite Fe_3S_4 as well as MnS and other metal sulfides, organic-S phases, and even dissolved sulfide compounds and polysulfides [42, 46]. These are called Acid Volatile Sulfides (AVS), and are considered globally as a key distribution phase controlling trace-metals geochemistry [39, 43, 47, 48] . The vertical distribution of AVS in a sediment core sampled in Deûle river is presented in Figure 3. Overall, AVS contents increase gradually with depth, however, with some fluctuations. The vertical distribution of total organic carbon (TOC) is also shown in Figure 3. It is noticed that the profiles of AVS and TOC with depth differ somewhat each other, suggesting that: (i) the supply of organic carbon along the sediment core may be a factor less important for AVS generation than the SO_4^{2-} reduction process; and (ii) consequently sulphates should be rate limiting in Deûle-river sediments (as observed for instance in Waal-river sediments, The Netherlands [49]).

On the other hand, cationic metals (Cd^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+} and Zn^{2+}) extracted in a 1M hydrochloric acid solution (and called ∑SEM: Simultaneously Extracted Metals) are often considered to be potentially bioavailable in sediments under variable hydrological conditions [49, 50]. In this context, a comparison of the vertical distribution of AVS, SEM and total metal concentrations in the sediment can bring relevant information about metal partitioning between the pore water and the solid phase, and hence, on metal mobility in the sedimentary medium.

In the present work, ∑SEM represents the sum of all the SEM_{Me} contents (with Me = Cd, Cu, Ni, Pb and Zn) determined in mmol of metal per kg of sediment. The evolution of ∑SEM with depth in Deûle-river sediments is compared to that of AVS (Figure 3) because the potential

availability /toxicity of trace metals is intimately related to the AVS and ∑SEM contents in the sediment [39, 51-53]. It can be seen that the molar concentration of ∑SEM is greater than that of AVS in the first centimetres of the surface sediment (*i.e.* with ∑SEM/AVS ratios > 1); indicating that the toxicity to aquatic organisms in terms of "heavy" metals is likely certain in the top layers. On the contrary, at lower depths, ∑SEM becomes closer to AVS, suggesting that metal toxicity tends to decrease somewhat with depth. Indeed, it is assumed that: (i) when SEM is in excess with reference to AVS, trace metals can exist substantially in pore waters and thereby affect benthic organisms [43, 54, 55], and consequently, sediment is considered to be potentially toxic [39, 56-59]; and (ii) conversely when there is sufficient AVS in the sediment to scavenge all the available trace metals, metal toxicity to benthic animals should not take place in the sedimentary medium, and sediment is then non-toxic [55, 57]. However, such interpretations had often been criticized because there are many other metal-binding phases such as organic matter, carbonates and oxides able to cause increased toxicity in the sediment [54, 57, 60-63]. In this context, to assess the additional binding distribution of Cd, Cu, Ni, Pb and Zn among various geochemical phases other than AVS, the sequential extraction procedure [64-67] was previously applied by our research group to anoxic sediments of Deûle river [19]. It was found that the key binding fractions are: (i) sulfides/organic matter for copper (82%-84%), and to a lesser extent for cadmium (35%-70%) and nickel (26%-30%); (ii) Fe and Mn oxides/hydroxides for cadmium (26%-62%), zinc (38%-42%) and to a lesser extent for nickel (23%-24%); and (iii) exchangeable ions and carbonates for Ni (7%-9%) and Zn (2%-6%). All these findings do reveal that, in addition to AVS, a part of ∑SEM is likely to be bound to the variable matrices contained in the sediment, mainly: organic matter, Fe and Mn oxides/hydroxides and exchangeable ions and carbonates. As for lead, we believe that this metal is in fact preferentially associated with sulfides in the

crystalline form of galena which was in the past deposited in this area, as previously evidenced [19].

Furthermore, the profiles of SEM_{Me} and total metal concentrations (TMC) measured with depth along a Deûle-river sediment core revealed both similar trends (Figure 4), with peak values recorded around the depths of 13 cm and 19 cm, indicating a more significant metal contamination at these depths, which correspond to certain time periods (not yet dated in the past) of industrial exploitation in this area. Note that the appearance of these peaks is more pronounced for Cd, Zn and Pb than for Cu and Ni, confirming their anthropogenic origins [18].

It is also found that SEM_{Me} contents determined for these metals in Deûle-river sediments account for a relatively large percentage of the total metal concentrations according to the following order: 23-32 % for cadmium; 20-26 % for zinc; 13-22 % for lead; and to a lesser extent: 11-15 % for nickel and 2-15 % for copper. As a whole, these proportions indicate close associations of these metals with sulfides in the sediment. It is worth noting that, as ∑SEM exceeds slightly AVS in most cases, the remaining metals (corresponding to the difference: ∑SEM – AVS) are either selectively bound with other compositions of sediments (including carbonates, oxides/hydroxides and organic matter) or are remobilized into the pore water. Based on [SEM-AVS] contents in sediments, several authors made reliable predictions on potential risks of trace metals in aquatic media [39, 40, 68-70]. On this view, the evolution of both [SEM_{Me} – AVS] and ∑SEM versus interstitial water concentrations of metals measured at different sediment depths in Deûle river (Figure 5) reveal several features: (i) dissolved metal concentrations in pore waters are clearly controlled by the parameter [SEM-AVS] for each metal through the effects of AVS on the metal distribution in the sedimentary medium; (ii) [SEM-AVS] values found for the studied metals are all negative, except partially for zinc in surface sediments; and (iii) the most available metal able to cause any medium

toxicity is zinc, followed by lead. Note further that in this aquatic medium the potential risk of metal toxicity should prevail predominantly in the first centimetres of the surface sediment; Thus, according to the USEPA (United States Environmental Protection Agency), Deûle river sediments belong to **Tier 2** at 3-23 cm depths with [∑SEM-AVS] values varying from -0.91 to 3.51 µmol g^{-1}, whereas they belong to **Tier 1** at surface depths with [∑SEM-AVS] values reaching up to 8.75 µmol g^{-1}, with probable associated adverse effects on aquatic life [53].

The organic carbon-normalized excess SEM (i.e.: when SEM exceeds AVS) that is defined as: $(\sum SEM\text{-}AVS)/f_{oc}$ (where f_{oc} represents the fraction of organic carbon in the sediment), is also used in the present work to predict the occurrence of sediment toxicity caused by metals, as proposed previously [70, 71]. The variation of $(\sum SEM\text{-}AVS)/f_{oc}$ calculated at different sediment depths in Deûle river is illustrated in Figure 3. Overall, we found values ranging from -17 to 592, suggesting that the risk of metal toxicity is uncertain in surface sediment (at 1-5 cm depths) and no toxic at depths lower than 5 cm (according to the guidelines of USEPA [72]), because of higher AVS contents detected in buried sediments.

To summarize, SEM, AVS, TMC, TOC and interstitial water-metal concentration relationships were used in this paragraph in order to highlight the extent of toxicity caused by metals in undisturbed sediments of Deûle river. However, to improve our diagnosis of water quality in Deûle river, numerical sediment quality guidelines reported in the literature are necessary to be used in the present work as an empirical approach in the interpretation of our results and in the predictions of possible environmental impacts.

3.3. Risks of toxicity from sedimentary metals

In recent development in sediment quality guidelines [22], the reliability in predicting toxicity in sediments were assessed from consensus-based values for individual contaminants.

These Consensus-Based Sediment Quality Guidelines (CBSQGs) have only considered effects to benthic macro-invertebrate species (and not the potential with time for bioaccumulation in aquatic organisms and subsequent food chain transfers). In this context, PEC (Probable Effect Concentration [73]) has been defined as the upper effect level at which toxicity to benthic-dwelling organisms are predicted to be probable. In doing assessments of sediment quality, recommended sediment quality guideline values for metals and associated levels of concern (PEC) to be used were previously reported [22, 73].

An index of toxicity risk, PEQ (probable-effect quotient), was evaluated in this work for each studied metal by dividing its total sedimentary concentration by the probable effect concentration (PEC) [22]. The PEQ variations with depth obtained for Cd, Cu, Ni, Pb and Zn are shown in Figure 6. Overall, it was found that, whatever sediment depths, the metal concentrations of sedimentary Pb, Zn and Cd largely exceeded PEC values with PEQ values ≥ 10, suggesting a potential toxicity of these metals in Deûle sediments. Conversely, it was shown that the toxicity risks were much lower for Cu and Ni, with PEQ values ≤ 1.3 (Figure 6).

To estimate more globally the toxicity risk resulting from metal mixtures, the individual PEQ_{Me} for the selected metals (Cd, Cu, Ni, Pb and Zn) were summed, $\sum PEQ_{Me}$, and considered as toxic units (TU) [25]. This toxicity index was plotted against sediment depth (Figure 6). As a whole, excepted for Cu and Ni (with PEQ_{Me} values lower than 1.3), $\sum PEQ_{Me}$ values are somewhat higher in buried sediments with a toxicity profile similar to those shown in Figure 4, suggesting that metal contamination decreased slightly in surface sediments since Metaleurop smelter was closed in 2003.

3.4. Toxic unit analysis in pore waters

The levels of interstitial waters quality in Deûle sediments were examined in the present work by applying to each single metal, "Me", a water quality index named IWCTU (criteria toxicity unit of interstitial water) and defined as:

$$\mathrm{IWCTU}_{Me} = [\mathrm{Me}]_{\mathrm{i.w.}} / \mathrm{FCV}_{\mathrm{Me}} \quad (1)$$

Where $[\mathrm{Me}]_{\mathrm{i.w.}}$ represents the concentration of the dissolved metal "Me" and $\mathrm{FCV}_{\mathrm{Me}}$ is the hardness dependent final chronic value for each metal [24, 26, 74, 75]. Firstly, the FCV values of the selected metals (Cd, Cu, Ni, Pb and Zn) were determined with depth (Table 1) and, secondly, the IWCTU index was calculated from equation (3) for each metal at every sediment depth (see the data reported in Table 2). As a whole, it was shown that in surface sediments (*i.e.* at 1-3 cm depths), the IWCTU values observed for Pb and to a lesser extent for Cd violated the corresponding water quality data recommended by USEPA [24]. As often observed previously by several authors [76-80], metal pore water concentrations reached their maxima at the surficial layers of the sediment (~ 1-3 cm), suggesting a metal release from biogenic material during the aerobic degradation of organic matter [78]. In contrast, in deeper sediment layers (≤ 7 cm), the IWCTU values were found to be lower than 1, and no violations of the recommended USEPA water quality data were then detected. Furthermore, two indexes were used to estimate water quality based on the chemical response from multiple metals at a certain sediment depth [75]:

$\sum \mathrm{IWCTU}_{\mathrm{Me}}$, where $\mathrm{IWCTU}_{\mathrm{Me}}$ represents the individual toxicity level of each metal in the interstitial water;

and the Nemeraw Index (NI) defined as:

$$(\mathrm{NI}) = \left\{ \left[(\mathrm{IWCTU})^2_{\max} - (\mathrm{IWCTU})^2_{\mathrm{mean}} \right] / 2 \right\}^{1/2} \quad (2)$$

The $\sum \mathrm{IWCTU}_{\mathrm{Me}}$ and (NI) values listed in Table 2 did show that interstitial waters were seriously contaminated in the first centimetres of surface sediments and that this contamination significantly decreased at depths lower than 7 cm. The depletion of dissolved

metals observed with depth was indeed explained as follows. Firstly, the mineralization process of organic matter with the reduction of SO_4^{2-} involving in the sediment according to [81-83]:

$$53\ SO_4^{2-} + (CH_2O)_{106}(NH_3)_{16}H_3PO_4 \rightarrow 106\ HCO_3^- + 16\ NH_4^+ + 53\ HS^- + HPO_4^{2-} + 39\ H^+ \quad (3)$$

Secondly, sulfides and/or carbonates generated through reaction (3) interacted favourably with Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} and Ni^{2+} to form authigenic minerals in the buried sediment [19]. Likewise, the OWCTU values (overlying water criteria toxicity units) obtained for these metals in the overlying water were low under weak hydrodynamic conditions, and therefore did not indicate any violation of USEPA water quality data (Table 2). Consequently, our investigations did reveal that a potential metal toxicity occurred dangerously in the first centimetres of surface sediments (see the impact grade in Table 2) in which microorganisms used oxidants according to the following sequence: $O_2 \rightarrow NO_3^- \rightarrow$Mn (III, IV) $\rightarrow$ Fe(III) $\rightarrow$ SO_4^{2-} [84-86] to initiate anaerobic oxidation reactions for organic matter mineralization.

4. CONCLUSION

In doing assessments of metallic pollution with sediment depth in Deûle river, it was shown that - from metal enrichment factors (SEF) and geoaccumulation indexes (I_{geo}) - Pb, Zn and Cd contents were above background levels in the studied cores, while those of Ni and Cu were generally around background concentration ranges. Overall, the relative importance of metal pollution in Deûle sediments showed the following order: Cd > Pb > Zn > Ni >> Cu. SEM_{Zn} predominated largely over all the other metals, and accounted for 83-90 % of the total amount of acid extractable metals, followed by SEM_{Pb} with 8-16%, whereas the total contribution of Cd, Cu and Ni to the ∑SEM value did not exceed 2%. By comparing AVS to SEM, the possibility of associations between trace metals and sulfides in anoxic sediments of Deûle river was raised, particularly, in deeper layers. The identification of potential additional

metal-binding phases competing with the AVS fraction was also done with: exchangeable ions and carbonates for Ni and Zn; Fe and Mn oxides/hydroxides for Cd, Zn, and to a lesser extent Ni; and probably organic matter for Cu and to a lesser extent Cd and Ni. Predictions of sediment toxicity were made using consensus based sediment quality guidelines for freshwater ecosystems: (i) potential risks of metal toxicity exist in this river with individual PEQ quotients reaching up to 10, and the toxicity sum, ΣPEQ, of all the selected metals (Cd, Cu, Ni, Pb and Zn) ranging from 21.9 to 147.0; (ii) interstitial waters were seriously contaminated in the first centimetres of surface sediments with the water quality index, IWCTU, reaching up to 29.5 and 20.9 for Pb and Cd respectively, and the sum, ΣIWCTU, calculated for Cd+Cu+Ni+Pb+Zn ranging from 0.3 to 52.5. This latter observation suggests that possible adverse environmental impacts should occur under sediment resuspension events. In this context, complementary studies are under way in the field and in the laboratory to better understand how sedimentary trace metals behave under strong hydrodynamic conditions and to assess the real implications of any physical disturbances on the water quality of Deûle river.

Figure Captions

Figure 1: Deûle-river map and location of the sediment sampling site, close to a former Pb-Zn smelter (Metaleurop).

Figure 2: Geoaccumulation indexes (I_{geo}) calculated for the trace metals Cd, Cu, Ni, Pb and Zn in polluted sediments of Deûle river. The histogram represents average I_{geo} values measured all along the sediment cores and deviation bars limit the minimum and maximum I_{geo} values observed for each metal. (a) Data published by Martin and Whitfield (1983) [37]; (b) averaged values published by Sterckeman et al. (2000, 2002) [27, 28].

Figure 3: Evolution with Deûle-river sediment depth of (a) SEM (simultaneously extracted metals in mmol kg^{-1}), AVS (acid volatile sulfides in mmol kg^{-1}), TOC (total organic carbon in mgC g^{-1}), and (b) the ratio (∑ SEM – AVS) / foc (where foc represents the sedimentary organic carbon fraction).

Figure 4: Variations with depth of total concentrations of Cd, Cu, Ni, Pb and Zn and corresponding SEM (simultaneously extracted metals) in Deûle-river sediments (mmol kg^{-1}).

Figure 5: (a) Dissolved concentrations of Cd, Cu, Ni, Pb and Zn (in µmol L^{-1}) plotted against the concentrations SEM_{Me} – AVS (in µmol g^{-1}) measured in a sediment core of Deûle-river. (b) Sum of dissolved metallic concentrations (in µmol L^{-1}) plotted against ∑ SEM – AVS (in µmol g^{-1}) measured in the same core.

Figure 6: Sum of the toxic units ($\sum PEQ_{Me}$) estimated for the trace metals Cd, Cu, Ni, Pb and Zn in suspended particulate matter (water column) and in Deûle river sediments. PEQ_{Cu} and PEQ_{Ni} represent individually less than 1.3 (not shown in this histogram).

Table captions

Table 1: Hardness-dependent final chronic values (FCV_{Me}) determined for Cd, Cu, Ni, Pb and Zn in the water column and in interstitial waters extracted at various depths of Deûle river sediments.

Table 2: Metal concentrations in interstitial waters extracted from Deûle-river sediments, and response indices for single metal (criteria toxicity of interstitial water, IWCTU, referred to final chronic values, FCVs) and for multiple metals [$\sum(IWCTU)_j$, with j varying from 1 to 5 and corresponding to the trace metals: Cd, Cu, Ni, Pb and Zn] with depth.

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