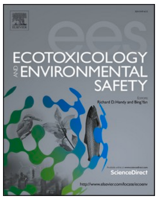
Ecotoxicology and Environmental Safety 281 (2024) 116614

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv



Comparison of sediment bioavailable methods to assess the potential risk of metal(loid)s for river ecosystems

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ARTICLE INFO

Edited by: Dr G Liu

Keywords:
River sediments
Trace elements
Acetic acid extraction
DGT
Pore water

ABSTRACT

A heavily impacted river basin (Caudal River, NW Spain) by Hg and Cu mining activities, abandoned decades ago, was used to evaluate the environmental quality of their river sediments. The obtained results compared with reference values established by the US EPA and the Canadian Council of Ministers of the Environment for river sediments, have shown that the main elements of environmental concern are arsenic (As), mercury (Hg) and, to a lesser extent, copper (Cu), which reach concentrations up to 1080, 80 and 54 mg kg^{-1}, respectively. To understand the role that river sediments play in terms of risk to ecosystem health, a comparison has been made between the total content of metal(oid)s in the sediments and the bioavailable contents of the same elements in pore water, passive DGT (Diffusive Gradients in Thin films) samplers and the sediment extractant using acetic acid. A good correlation between the As and Cu contents in the DGTs and the pore water was found, resulting in a transfer from the pore water to the DGT of at least 47 % of the Cu and more than 75 % of the As when the concentrations were low, with a deployment time of 4 days. When As and Cu concentrations were higher, their transfer was not so high (above 23.6 % for As and 19.3 % for Cu). The transfer of Hg from the pore water to the DGT was practically nil and does not seem to depend on the content of this metal. The fraction extracted with acetic acid, conventionally accepted as bioavailable, was clearly lower than that captured by DGTs for As and Cu ($\leq$5 % and $\leq$8.5 % of the total amount, respectively), while it was similar for Hg (0.2 %).

1. Introduction

River sediments constitute the main source of food and habitat for many organisms and therefore, this environmental compartment plays an important role in the transmission of pollutants along the food chain (Banaee et al., 2024; Eyong, 2008; US EPA, 1988). Although the assessment of freshwater ecosystems has traditionally focused on the quality of the water column (Ejigu, 2021), this is not sufficient for a complete evaluation, since contaminated sediments can cause direct adverse effects on aquatic life, even constituting uninhabitable areas for benthic organisms (Jiwarungrueangkul et al., 2024; US EPA, 2002, 1987). By acting as sinks, sediments can accumulate metals in water over time, even if their concentrations are very low and long after the original sources of contamination have been removed (Soares et al., 1999). In addition, this accumulation can become a source of pollutants when the physico-chemical conditions of the environment change naturally or anthropically (García-Ordiales et al., 2020; Kim et al., 2006).

The harmful effects of metals in aquatic environments depend on their specific chemical forms, so sediment analysis in environmental studies have been often relied on leaching or extraction procedures, trying to find the 'bioavailable' elemental forms (Okoro et al., 2012; Quevauviller, 1998). Several analytical procedures have been developed to obtain information on the potential risk to aquatic ecosystems, particularly by assessing the different fractions of metals in the water column, given the established relationship between chemical speciation of metals in water and their toxicity (Batley et al., 2004). The bioavailability of toxic metals indicates their potential to be taken up by organisms, leading to harmful health effects, so identifying the most bioavailable fractions helps to evaluate environmental risks and prioritize remediation work (Ali et al., 2024). ISO/TC190/Soil Quality has developed an international standard for measuring the bioavailable

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https://doi.org/10.1016/j.ecoenv.2024.116614
Received 19 February 2024; Received in revised form 30 May 2024; Accepted 16 June 2024

fraction of organic chemicals in soil materials (Van Vark et al., 2018), but there is a need for further knowledge on how to determine the bioavailable fraction of metals in sediments. It is considered essential to deepen the knowledge of the different ways of quantifying the bioavailable fraction in metals in sediments and the critical analysis of these techniques.

This article focuses on the procedures commonly used by the scientific community to assess metal contamination in river sediments and how to determine the potentially bioavailable fraction to estimate associated ecological risk. The aim of this research is to compare several methodologies by applying them to an anthropised river basin. This requires sampling the sediments and analytically determining their pseudo-total (i.e. aqua regia extractable) and acetic acid-extractable metal concentrations, as well as analyzing the sediment pore water. In addition, to be more independent of concentration fluctuations, the Diffusive Gradients in Thin-films (DGT) technique, a passive in situ sampling technique developed by Zhang and Davison (1995), based on Diffusive Equilibration in Thin Films (DET), can be used to estimate the time-weighted average concentration of labile metals with high spatial resolution (Huang et al., 2019; Uher et al., 2011).

Sequential chemical extraction protocols have classically been considered as useful tools to estimate chemical speciation/mobility and, indirectly, bioavailability of metal(loid)s. These procedures use different extracting agents (typically $MgCl_2$/$CaCl_2$, H_2O_2, CH_3COOH/CH_3COONH_4, $Na_2P_2O_7$, NH_2OH, HNO_3/HF) so that it is possible to assign each fraction with a chemical or physico-chemical form of the metal(loid) in the sample. In most of the commonly applied sequential chemical extraction protocols (among others, the one proposed by the Standards, Measurements and Testing Programme -formerly BCR- of the European Commission; Ure et al., 1993), 0.11 M acetic acid is used as extractant agent in the first step. The fraction thus extracted is ideally assimilated to the sum of the exchangeable+water soluble+acid soluble forms, which in turn is accepted as equivalent to the bioavailable fraction.

Fluvial sediments are formed by sedimentation of mineral particles from the overlying water column. In this process, water is trapped in the sediment interstitium, forming pore water, and the chemical species in the water column tend to equilibrate between the pore water and the solid phase. Knowing the pore water concentrations is useful for assessing the contribution of the sediment to the contamination of the overlying water column (Bufflap and Allen, 1995).

Conventional techniques for chemical analysis generally measure the total concentration of the extract, often including inert organic matter and large colloidal particles with low bioavailability. While continuous extraction methods can isolate labile components from soil or sediment, the transport processes of analytes in solution are not well understood, so there is a need to focus on understanding the kinetic processes of the labile fraction of target analytes within both the solid phase of sediment and in solution (Liu et al., 2024). Passive sampling technology effectively integrates sampling, isolation, and analyte preconcentration during field deployment and maintains the chemical integrity of the analyte at its original site, minimizing environmental interference, and thus stands out as a superior alternative to conventional active sampling techniques (Taylor et al., 2020; Huang et al., 2019). The use of DGT in natural aquatic environments clarifies the equilibrium between river water and sediments in terms of metal exchange and has shown good performance in detecting labile metal speciation, so this technique has gained widespread recognition for its effectiveness in quantifying and representing latent bioavailable fractions (Huangfu et al., 2024; Liu et al., 2024). This technique has the advantage of performing an in-situ measurement, which avoids the risks associated with sample handling and contamination. In addition, the diffusion process is independent of the flow rate, so the uncertainty associated to sampling rates is eliminated, which significantly improves measurement accuracy (Wang et al., 2024). DGT technique allows representative measurements to be obtained over a period of time (time-averaged concentration), assessing with high resolution the elemental distribution in microenvironments, such as the sediment-water interface (Zhang et al., 2014). In the last few years, DGT are increasingly used to determine changeable concentrations in order to assess and predict the toxicity and bioavailability of metals to aquatic biota (Gu et al., 2023a,b, 2022a, 2022b; Chaudhary et al., 2020). In most of the published works, the DGT technique proved to be superior to conventional procedures for predicting the bioavailability of toxic elements and compounds in various environmental compartments (Senila and Kovacs, 2024; Ji et al., 2022), which justifies future work in this line.

As already mentioned, the bioavailable fraction of metals in sediments is a key factor for risk assessment, which in turn helps in the characterization of contaminated sites and ecosystems. Therefore, the main objective of this work is to explore and compare the different techniques that are commonly used to evaluate this fraction and for this purpose an area affected by former metallic mining where high concentrations are to be expected is chosen. To the best knowledge of the authors, there are no works in the literature that study samples from the same points in which metal and metalloid concentrations in sediment, pore water, acetic acid extracts and passive samplers are analyzed and compared, and therein lies the main novelty of this work.

2. Area of study

The area studied is located in Asturias (NW Spain), a region with a long mining tradition, where numerous metal and coal mines, now closed, are located. In particular, mercury (Hg) mining was quite prevalent in the Mieres and Lena districts (Loredo et al., 2003), which are located in the Caudal River basin, a tributary of the main river of the region, the Nalón River (Fig. 1).

The geological substrate of the Caudal River basin is constituted of Carboniferous detrital sedimentary rocks (sandstones, graywackes, shales) and some calcareous outcrops, both in the highest and lowest parts of the basin. Since most of these rocks have very low permeability, runoff is dominant rather than infiltration. This, together with the fact that it is a humid area with a temperate climate, where it rains more than 1000 mm $year^{-1}$, means that the watercourses are perennial and have high flow rates. Hg is usually found in the Mieres and Lena mining districts in the form of sulphide (cinnabar) and rarely as native Hg. In these deposits, arsenic (As) is also found in the form of sulphides such as realgar, arsenopyrite and As-rich pyrite, together with other minor metals. These elements are still being released to the aquatic environment since, although the Hg mines were closed in the 1970s, in most cases no restoration actions have been undertaken and the old facilities and spoil heaps storing large quantities of metallurgical wastes and low-grade ore continue to be exposed to the environment.

3. Methodology

3.1. Sampling location

For this study, eight sediment sampling points were selected in areas affected by Hg and copper (Cu) mining (Fig. 1). Sampling point 1 was located at the Muñón stream, which drains the most affected area of the Lena Hg mining district (La Soterraña mine and others) and point 2 was located at the Lena River, right after receiving the waters of the Muñón stream. The Lena River is a tributary of the Caudal River and point 3 was located at the latter, downstream of the mentioned Lena Hg mines and also downstream of an area intensely exploited for coal. Sampling points 4 and 5 were located in the San Juan and San Tirso Rivers, respectively, which drain the most relevant mining sites of the Mieres Hg district: Los Rueldos and El Terronal mines, respectively (Ordóñez et al., 2013). These two rivers are also tributaries of the Caudal River and point 6 was located downstream of their mouth. Sampling point 7 was located in the Llamo River, downstream of the closed Cu-Co-Ni Texeo mine. Finally, point 8 was placed in the Caudal River, after receiving the waters of the

Fig. 1. Area of study: Location of the main mine sites, watercourses and sampling points (red dots).

Llamo River and close to its mouth into the major Nalón River. Duplicates were sampled at points 4 and 5 (which were suspected to be affected by old Hg mining), so 10 sampling points were selected in total. The sampling campaign was undertaken in June 2023.

3.2. *Bulk sediment*

Sediment samples (1 kg approx.) were taken manually below the sediment-water interface with plastic tools, near the banks of the rivers. Each sediment sample agglutinates 4 sampling increments of about 250 g each, which were taken from a total bank length of less than 2 m. They were transported in labelled plastic bags to the laboratory at the University of Oviedo. They were air-dried until constant weight and sieved, and the fraction below 63 μm was sent for pseudo-total concentration analysis to the ALS Life Science laboratory. This was undertaken by ICP-OES following the U.S. EPA Method 200.7 (U.S. EPA, 1994). Quality Assurance and Quality Control (QC/QA) included the analysis of laboratory of duplicates (20 % of the total number of samples) and control standards (also 20 % of the total samples), with recovery ratios between 94.7 % and 102 %. The results of the analysis of laboratory blanks were always below the limits of reporting (LOR).

3.3. *Pore water*

In order to analyze the pore water, sediment samples were taken in plastic micro tubes at the same described sampling points in anoxic conditions to avoid oxidation. At the laboratory of the University of Oviedo, they were centrifuged at 7000 rpm for 10 minutes at 20 °C. The pore water was separated, filtrated and adjusted to pH 2 using trace analysis grade HNO_3, with 15 mL of sample refrigerated at 4°C until analysis. Metal(loid)s were determined by ICP-MS following the US EPA Method 200.8 and Hg by CVAFS, following US EPA Method 245.7 (U.S. EPA, 2005) at the ALS Life Science laboratory. QC/QA included the analysis of laboratory control standards (10 % of the total samples), with recovery ratios between 93.4 % and 104 %. The results of the analysis of laboratory blanks were always below the LOR.

3.4. *Diffusive Gradients in Thin Films (DGT)*

Diffusive Gradients in Thin Films establish a controlled diffusion gradient in a gel layer, so they can be used as passive samplers to investigate chemical and biological processes. DGT involves continuous diffusion of labile analyte through a gel matrix followed by rapid and irreversible absorption by the binding resin (Lui et al., 2024). It is a dynamic technique, as it continuously removes the analyte from the medium, so information can be acquired on speciation in solution, and solid phase transfer to solution in sediments due to the dynamic response of the medium to removal (Davison, 2016). DGT technology focuses on assessing the bioavailability of metals in sediments by measuring in situ time-averaged concentrations of their labile forms (Davison and Zhang, 2012). The DGT device uses a hydrogel binder layer impregnated with Chelex resin or other binding agents to accumulate ions, which must first diffuse through a diffusion layer (filter + diffusing gel) that coats the binder layer. The concentrations of elements in solution are measured on the basis that a constant concentration gradient is established in the diffusion layer. The application time is usually a few days (Zhang et al., 2014).

In this case, DGT devices were deployed at the same points where the sediments were sampled (in addition to two duplicates at points 4 and 5). Standard DGT sediment probe samplers (DGT® Research Ltd.) were selected. At each point, two samplers were deployed. Sampler LSPB-AP, with a 3-mercaptopropyl functionalized silica gel binding layer, was used for Hg and sampler LSPY-NP, with a Chelex-100 and ferrihydrite mixture-binding layer, used for metals and As (Fig. 2; supplementary material). The deployment was carried out following manufacturer's recommendations. At the site, each probe was removed from its oxygenfree environment and immediately smoothly pushed into the sediment, keeping it in vertical position. The deployment time was four days (it was precisely recorded for each DGT). The temperature in the sediment was accurately recorded during the deployment period by means of a data logger. After retrieving the DGT probe from the sediment, it was thoroughly rinsed with MQ water and placed in a plastic bag for transportation. At the laboratory, it was thoroughly rinsed again with MQ water and treated in a laminar flow hood: the resin gel (binding layer) was separated from the filter membrane and the diffusive gel and cut selecting only the part that was in contact with the sediment (the sediment-water interface was marked in situ in each DGT). The Hg content of the gel of sampler LSPB-AP was immediately analyzed at the University of Oviedo facilities, by means of a LUMEX RA-915+ analyzer, coupled with an RP-91 C pyrolizer, where the sample was heated at 800 °C, releasing the contained Hg in the form of vapor, which was measured. The resin gel of the other sampler (LSPY-NP) was measured, weighted and placed into a micro tube to which 15 mL of a 1.0 M solution of high purity HNO_3 (trace analysis grade) was added. It was allowed to stand for 24 h and the eluate was filtered (0.45 µm) and refrigerated at 4°C prior to analysis by ICP-MS following the US EPA Method 200.8 at the ALS Life Science laboratory. QC/QA included the analysis of laboratory control standards (18 % of the total number of samples), with recovery ratios between 94.1 % and 107 %. The results of the analysis of laboratory blanks were always below the LOR. For both types of DGT sampler a DGT blank (an unexposed DGT device carried through all steps of the measurement process, from extraction through analysis), was analyzed. According to the manufacturers, DGT measurements are very reproducible in standard solutions with relative standard deviation less than 10 %.

The accumulated mass of metal on the binding layer of the samplers *M* (mg) was deduced from metal concentration in the resin eluate, using the following equation (Davison, 2016):

$$M = \frac{C_e \quad (V_g + V_e)}{f_e} \qquad [1]$$

where C_e (mg L^{-1}) is the concentration of the ion in the elution solution, V_g (mL) is the volume of the gel, V_e is the volume of the elution solution (15 mL), and f_e is the elution efficiency (0.92).

The mass, M, from Eq. 1 was used to calculate the mean flux *F* (mg cm^{-2} s^{-1}) from the sediment through the window of the DGT probe (physical area of exposed gel that was measured), of area A_p (cm^2), for deployment time, *t* (s).

$$F = \frac{M}{A_p \cdot t} \qquad [2]$$

Fick's law of diffusion was used to calculate the in-situ concentration. The time-averaged concentration of each analyte in the deployment medium measured by DGT (the mean concentration at the surface of the probe during the deployment time, in mg mL^{-1}) was calculated as:

$$C_{DGT} = \frac{M \cdot \Delta_g}{D \cdot A_p \cdot t} \qquad [3]$$

where Δ_g is the total thickness of the materials in the diffusion layer (0.094 cm) and *D* (cm^2 s^{-1}) is the diffusion coefficient of analyte in the material diffusion layer at the average deployment temperature. The values of *D* were obtained from DGT Research (2023).

3.5. Acetic acid extraction

For this method, 1 g of dry sediment sample (fraction below 63 µm) was added to 40 mL of 0.11 M acetic acid, prepared using suprapur grade acid, in a centrifuge tube. All the tubes were shaken for 16 h at ambient temperature and then centrifuged at the same conditions as those given for the pore water, in order to separate the extract from the solid residue. The supernatant was decantated, filtered and 15 mL were refrigerated until analysis following the same method as that given for the DGTs.

The acetic acid extracts were analyzed at the ALS Life Science laboratory. QC/QA included the analysis of laboratory control standards (20 % of the total number of samples), with recovery ratios between 93.2 % and 108 %. The results of the analysis of laboratory blanks were always below the LOR.

The statistical analysis of the analytical results included the calculation of Pearson's bivariate correlation coefficient between all the elements considered, in all the types of samples analyzed, as well as the calculation of the coefficient of variation (standard deviation divided by the arithmetic mean) for the purpose of comparing duplicate samples. The IBM SPSS Statistics v. 27 software was used.

4. Results and discussion

Information from the local Hydrological Planning Office stablished that the Caudal River was not in a good ecological condition in its lower basin (the area affected by the old mining sites), and the study of macroinvertebrates shows that the species richness (number of families) was low and the dominance (the relative abundance of the most abundant group) was high downstream of the source, which mean a reduction in biodiversity (Escudero et al., 2024). This could be due to the metallic load coming from the old mines, which still silently persists in the sediments despite the fact that they have been closed for several decades.

Although concentrations of 12 elements (As, Cd, Co, Cr, C, Hg, Mn, Ni, Pb, Sb, V and Zn) were initially considered, only six of them (As, Cu, Hg, Mn, Ni and Zn) were found in all types of samples above the analytical detection limit. The comparison of the different sampling and analytical techniques used in this work, therefore focuses on these elements, particularly on the first three, which reach remarkably high concentrations at some points.

4.1. Bulk sediment

In Table 1 the results of the sediment analysis shows that Hg concentrations were particularly elevated downstream of the old Hg mines of the Mieres district (samples 5 and 5a), followed by those taken downstream of the Lena district (samples 1 and 2). This was also the case of As, which is present in the mineral paragenesis of the Hg deposits. On the other hand, the highest Cu concentration was found in sample 7, downstream of the Texeo Cu mine. The Canadian Sediment Quality Guidelines (CCME, 2023) for the Protection of Aquatic Life establish Threshold Effect Levels (TELs) and Probable Effect Levels (PELs) for metals as a means of assessing whether adverse biological effects are likely to occur as a result of exposure to these contaminants in sediments. In this case, all the samples exceed the PEL for As (17 mg kg^{-1}) and most of them exceed the PEL for Hg (0.486 mg kg^{-1}), so they fit in the range within which adverse effects frequently occur, and negative effects on aquatic life should be expected. The Cu concentration in sample 7 was between both thresholds (the possible effect range within which adverse effects occasionally occur). The contents of all other elements in the samples are below their respective TELs (minimal effect range within which adverse effects rarely occur). In addition, all the samples far exceeded the U.S. Environmental Protection Agency Freshwater Sediment Screening Benchmark (FSSB; US EPA, 2022) for As (9.8 mg kg^{-1}), most of them are above the Hg level (0.18 mg kg^{-1}) and only sample 7 exceeded the threshold for Cu (31.6 mg kg^{-1}). The driving element appears to be As, as its concentrations are in some cases 1–2 orders of magnitude above the thresholds considered. Once released, As enters the biogeochemical cycle with no chance of degradation (Zhang et al., 2022). Arsenic contamination of aquatic systems is considered a major environmental problem affecting more than 115 countries worldwide (Hussain et al., 2021), so it might be useful to compare sediment bioavailability methods to assess the risk of As and other contaminants to fluvial ecosystems.

Table 1

Analytical results of the sediment samples (concentrations in mg kg^{-1}). Cd concentrations are below the analytical detection limit (0.4 mg kg^{-1}) in all samples.

Sample	As	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sb	V	Zn
1	313	12.7	15.4	28.5	8.76	564	29,1	23.6	<0.5	18.3	95.0
2	218	12.5	13.4	25.7	7.72	462	27,7	22.6	<0.5	15.9	89.8
3	34.5	10.6	15.6	26.4	1.57	273	25,3	22.1	<0.5	15.6	79.6
4a	39.7	8.62	8.84	24.6	1.88	640	17,2	24.2	<0.5	8.56	71.5
4b	16.1	5.2	7.68	12.8	<0.20	607	11,4	11.6	<0.5	6.21	46.6
5a	921	13.2	10.3	21.2	78.0	436	22,5	18.2	1.08	16.2	71.8
5b	1080	14.9	10.2	22.5	80.7	515	24,3	20.2	<0.5	17.3	78.9
6	38.4	11.1	15.6	27.3	1.31	597	24,8	24.2	<0.5	15.6	100
7	17.9	14.0	15.3	54.3	<0.20	446	29,9	15.2	<0.5	17.4	71.8
8	34.9	11	15.6	25.4	3.76	353	24,7	21.0	<0.5	16.2	80.8

4.2. Pore water

Table 2 shows the concentrations of the pore water samples that were collected in this work. Concentrations are undetectable for most metals, but Hg and As contents are high downstream of the Hg mines in Mieres (samples 4 and 5) and Lena Hg mining districts (samples 1 and 2). Cu concentration in sample 7 is one order of magnitude above those of the rest of the samples.

4.3. Diffusive Gradients in Thin Films (DGT)

The temperature registered during the course of deployment of the DGTs varied from 14.4 to 20.6°C, with an average of 17.1°C. Table 3 shows the values of the mass of analyte accumulated in the binding layer (M), the mean flux (F) and the mean concentration of analyte measurable by DGT in the pore water adjacent to the surface of the DGT device, averaged over the total deployment time (C_{DGT}) obtained for the ten samples and the blank, using Eqs. 1 to 3. The concentrations obtained in the blank were below the detection limit or were one order of magnitude lower than those measured in the samples, and, therefore, cross-contamination can be ruled out during sample preparation and analysis. Since the DGT continuously removes the analyte from the sediments, its concentration on the DGT surface may decrease during the course of deployment. If the analyte is continuously replenished into solution from the solid phase, the measured $\mathrm{C_{DGT}}$ approaches the concentration in pore waters and the spatially resolved maximum concentrations in the pore water are closely represented by DGT (Sochaczewski et al., 2009). In this case, the distribution of metal content in pore waters and DGTs is in the same order of magnitude, except for Hg (Fig. 3). As and Cu content in the pore water is of the same order or one order of magnitude higher than that in the DGT. However, the Hg content in the pore water is 3–4 orders of magnitude higher than that in the DGT. This might be influenced by the fact that Hg has a larger atomic radius and/or smaller charge than the other two elements.

Table 2

Analytical results of the pore water samples (concentrations in mg L^{-1}, except for Hg, which are expressed in μg L^{-1}). The concentrations of Co, Cr, Pb, Sb and V are below their analytical detection limit (0.002, 0.001, 0.005, 0.01 and 0.001 mg L^{-1}, respectively) in all samples.

Sample	As	Cd	Cu	Hg	Mn	Ni	Zn
1	0.221	<0.0004	0.002	0.043	0.010	0.003	0.004
2	0.144	<0.0004	0.004	0.074	0.186	0.005	0.008
3	<0.005	<0.0004	0.002	0.063	0.086	0.005	0.011
4a	0.014	<0.0004	0.002	0.080	0.675	0.003	0.007
4b	0.010	<0.0004	0.003	0.105	0.168	0.004	0.008
5a	0.649	<0.0004	0.004	0.255	0.993	0.008	0.028
5b	0.746	<0.0004	0.002	0.263	0.963	0.005	0.005
6	0.013	<0.0004	0.002	0.069	0.923	0.003	0.010
7	0.006	<0.0004	0.014	0.032	0.218	0.006	0.023
8	0.010	0.001	0.002	0.071	1.240	0.005	0.008

4.4. Acetic acid extraction

There is a wide variety of extraction procedures, but extraction with weak acids, in particular with acetic acid, is one of the most widely used protocols in studies on the mobility of trace metals in sediments (Quevauviller, 1998; Rosado et al., 2023). Table 4 includes the acetic acid extractable metal concentrations found in the studied samples, after relating the contents of each extract to the original sediment mass. The average labile fraction of the analyzed metals with respect to the pseudo-total followed a decreasing order of Mn (49.9 %) > Co (21.4 %) > Zn (19.4 %) > Ni (14.0 %) > Cu (4.0 %) > Pb (2.1 %) > As (1.9 %) > Cr (0.5 %). The average ratio of labile/total Hg concentration in the sediments was 0.06 %. These percentages give an idea of the relative bioavailability of the above elements. As can be seen, except for manganese, for the remaining trace elements approximately less than one fifth of the total concentration is estimated to be bioavailable. Moreover, the elements of greatest concern and that exceeded the reference values for sediment quality (i.e. As, Cu, Hg) in this study area are associated with the residual and less available fractions. This shows that although the concentrations are in theory excessively high according to reference limits, the potential transfer to aquatic organisms is expected to be relatively limited, especially in the case of Hg.

4.5. Comparison of methods

Like the previous Tables, Table 4 shows the relatively high concentrations of Hg and As in points 1, 2, 4 and 5 and the elevated Cu content in point 7. Therefore, the methods used are consistent and comparable, at least for the pollutants of most concern. Fig. 3 shows a comparison of the results obtained for As, Hg and Cu. The uncertainty interval of the analysis for each element in each method, which ranged from 10 % to 20 %, is shown, although due to the scale it is not very well-defined in the graph. As expected, the results of the DGTs are similar to those of the pore water (except for Hg), since the passive sampler, once is deployed, is in direct contact with the pore water (Ma et al., 2024). On the other hand, the results of the acetic acid extraction and the total sediment contents are comparable to each other (Cappuyns, 2012).

The linear correlation between the studied elements has been studied in each of the four types of samples. Only significant correlations at the 0.01 level (bilateral) will be discussed:

In the case of As, the concentrations found in all types of analysis present high Pearson correlation coefficients with each other (>0.9). The correlation of the concentrations of this element in the sediment and in the acetic acid extract is high, with a coefficient of 0.98, and the correlation coefficient between the As content of the pore water and the DGT is 0.91. The concentration of As also appears to be highly correlated with that of Hg. The correlation coefficient between the As and Hg contents in the sediment is 0.98, and between the contents of both elements in the pore water and DTG is, respectively, 0.92 and 0.97. The correlation coefficient between Hg contents in sediment and acetic acid extract is 0.76, while that between Hg contents in pore water and DGT is 0.87.

Table 3
Results of the DGT analysis (M in mg, F in mg cm^{-2} s^{-1} and C_{DGT} in mg L^{-1}). The concentrations of Cd, Co, Cr, Sb and V in the DGT eluates are below their analytical detection limits (0.004, 0.02, 0.01, 0.005, 0.1 and 0.01 mg L^{-1}, respectively) in all samples.

		As	Cu	Hg	Mn	Ni	Pb	Zn
1	**M**	1.8E-02	4.5E-04	3.8E-06	4.6E-02	4.4E-04	<8.5E-04	4.1E-03
	F	3.5E-09	8.7E-11	9.1E-13	8.8E-09	8.5E-11	<1.6E-10	7.9E-10
	C_{DGT}	7.5E-02	1.6E-03	1.3E-05	1.8E-01	1.7E-03	<2.4E-03	1.5E-02
2	**M**	1.5E-02	4.4E-04	8.8E-06	2.3E-04	<3.5E-04	<8.7E-04	1.1E-03
	F	1.6E-09	4.8E-11	1.2E-12	2.4E-11	<3.8E-11	<9.5E-11	1.2E-10
	C_{DGT}	3.4E-02	9.0E-04	1.8E-05	4.9E-04	<7.7E-04	<1.4E-03	2.3E-03
3	**M**	1.8E-03	3.8E-04	1.2E-06	8.4E-02	<3.4E-04	<8.6E-04	8.0E-04
	F	2.6E-10	5.5E-11	2.4E-13	1.2E-08	<5.0E-11	<1.2E-10	1.2E-10
	C_{DGT}	5.6E-03	1.0E-03	3.5E-06	2.5E-01	<1.0E-03	<1.8E-03	2.2E-03
4a	**M**	1.1E-03	2.4E-04	9.6E-07	9.7E-04	4.4E-04	<8.5E-04	6.8E-04
	F	2.2E-10	5.0E-11	1.6E-13	2.0E-10	9.1E-11	<1.8E-10	1.4E-10
	C_{DGT}	4.7E-03	9.4E-04	2.4E-06	4.1E-03	1.9E-03	<2.6E-03	2.7E-03
4b	**M**	<8.6E-04	6.3E-04	2.1E-06	1.7E-02	4.3E-04	<8.6E-04	2.8E-02
	F	<1.3E-10	9.8E-11	3.4E-13	2.7E-09	6.7E-11	<1.3E-10	4.4E-09
	C_{DGT}	<2.9E-03	1.8E-03	5.1E-06	5.4E-02	1.4E-03	<2.0E-03	8.4E-02
5a	**M**	9.2E-02	4.8E-04	8.5E-06	6.0E-02	<3.5E-04	<8.7E-04	1.2E-02
	F	1.0E-08	5.3E-11	2.3E-12	6.6E-09	<3.8E-11	<9.6E-11	1.3E-09
	C_{DGT}	2.2E-01	1.0E-03	3.4E-05	1.3E-01	<7.8E-04	<1.4E-03	2.5E-02
5b	**M**	1.4E-01	4.5E-04	1.9E-05	7.7E-02	3.6E-04	3.7E-03	9.4E-04
	F	2.7E-08	8.7E-11	4.0E-12	1.5E-08	7.0E-11	7.2E-10	1.8E-10
	C_{DGT}	5.8E-01	1.7E-03	5.9E-05	3.0E-01	1.4E-03	1.1E-02	3.5E-03
6	**M**	3.2E-03	3.8E-04	2.9E-06	5.5E-02	3.5E-04	<8.5E-04	4.6E-03
	F	5.1E-10	6.0E-11	4.0E-13	8.7E-09	5.5E-11	<1.4E-10	7.3E-10
	C_{DGT}	1.1E-02	1.1E-03	5.9E-06	1.8E-01	1.1E-03	<2.0E-03	1.4E-02
7	**M**	3.0E-03	1.2E-03	3.6E-06	6.6E-02	<3.5E-04	<8.7E-04	2.5E-03
	F	3.6E-10	1.4E-10	4.8E-13	7.9E-09	<4.2E-11	<1.0E-10	3.0E-10
	C_{DGT}	7.6E-03	2.7E-03	7.1E-06	1.6E-01	<8.5E-04	<1.5E-03	5.8E-03
8	**M**	2.5E-03	4.3E-04	3.5E-06	6.5E-02	3.9E-04	<8.6E-04	1.3E-03
	F	3.5E-10	6.1E-11	4.1E-13	9.3E-09	5.6E-11	<1.2E-10	1.8E-10
	C_{DGT}	7.5E-03	1.2E-03	6.0E-06	1.9E-01	1.1E-03	<1.8E-03	3.5E-03
Blank	**M**	<8.2E-04	2.4E-04	2.6E-07	2.2E-04	3.6E-04	<8.2E-04	5.6E-04

The case of Cu is similar to that of Hg, with correlation coefficients sediment-acetic acid extract and pore water-DGT of 0.88 and 0.73, respectively. However, Cu concentrations do not show high correlations with those of the other elements considered, except Ni in the sediment (0.68) and Zn in pore water (0.65). This is due to the fact that its origin is mainly located in the Cu-Co-Ni mineralization of the Texeo mine, in whose complex mineral paragenesis the presence of Zn species has also been mentioned.

The only remarkable correlation in the case of Mn is that corresponding to its contents in the sediment and the acetic acid extract (0.65). As far as Ni is concerned, only correlations with As and Hg concentrations in the acetic acid extracts are noteworthy (>0.6). There is also a significant Ni-Zn correlation (both chalcophile elements) in sediment, acetic acid extract and pore water. Finally, there are no outstanding correlations between Zn contents in the different types of samples.

Regarding the field replicates (samples 4a-4b and 5a-5b), in the case of As, the calculated coefficients of variation (CV) are high, reaching 60 % in the sediment (sample 4) and in the DGT (sample 5) and low in the rest of the cases, where similar concentrations are obtained. The general trend of Cu is similar to that of As, with the highest CV in the sediment and the DGT. There are no large variations between replicates in the case of Ni, perhaps due to its generally low concentrations. In the cases of Mn and Zn, the largest deviations occur in the DGT and pore water samples. Although a larger number of duplicate samples would be desirable, the significant influence of the DGT placement point is apparent.

Despite being more costly and time-consuming, the use of DGT has advantages compared to conventional methods, as it is a dynamic technique that simultaneously considers the diffusion of solutes and their kinetic replenishment from solid phases. The quantitative difference between the concentrations of As, Cu and Hg found in the DGTs with respect to their pore water and sediment analogs indicates that the former is mostly conditioned by the pore water, due to the water-solid ion exchange. However, there is no evidence to completely rule out some direct sediment-DGT transfer. The As and Cu contents in the DGTs after four days of deployment were in the same order of magnitude as those in pore water. In the samples with lower As contents (3, 6, 7, 8), the ratio between the concentrations of As in the DGT and in pore water exceeds 75 %, indicating a certain equilibrium and an almost totally bioavailable chemical form. In contrast, in the rest of samples, the concentration of this metalloid in the DGT binding layer is between 23.6 % and 33.9 % of that in pore water, except in sample 5b, in which that proportion reaches 77.7 %. This difference may be due to the possible presence of fine mineral particulate matter that, carrying As, could have passed through the diffusion layer. There is also the possibility of its presence in dissolved but less bioavailable forms. Cu contents in pore water are very low (0.002–0.004 mg L^{-1}) in all samples except sample 7, whose concentration is an order of magnitude higher. Its behavior is similar to that discussed for As: in most samples, the Cu concentration in the DGT gel is 47–80 % of that determined in the pore water, whereas in the samples with higher Cu content (7, 2 and 5) this ratio is between 19.3 % and 25.0 %. The behavior of Hg is clearly different; the concentrations of this element retained in the DGT, specific for the analyte, are 3–4 orders of magnitude lower than their equivalents in the pore water, so it can be concluded that Hg in pore water is practically non-bioavailable.

It is of interest to analyze comparatively the total content of the elements of concern in the sediment and their fraction recovered by extraction with acetic acid (equivalent to the first extraction of the BCR method, see details in Rauret et al., 1999), in which ideally the exchangeable, water-soluble and weak acid-soluble forms are extracted. In relation to As, two groups of samples must be distinguished: when the As content is low, the amount of As extractable with 0.11 M acetic acid is 0.5–1.2 % of the total. However, in the sediment samples clearly affected by mining activities (1, 2, 5a and 5b) the percentage of extractable As ranges between 2.7 % and 5.0 %. This may be due to the fact that in the vicinity of the mines it is expected to find traces of

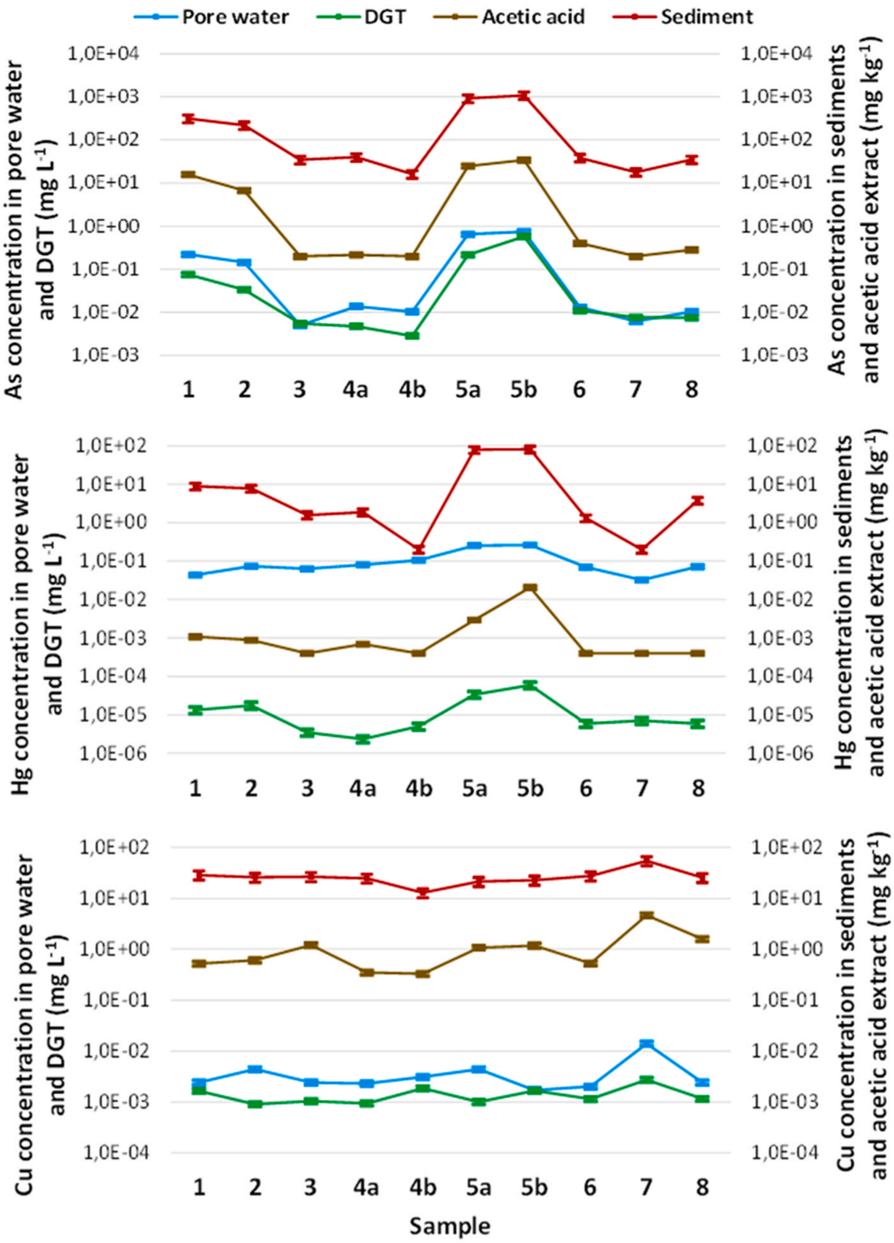

Fig. 3. Comparative graphical representation of the As, Hg and Cu concentrations in sediment, pore water, DGT and acetic acid extract. The uncertainty interval of the analysis is shown. Note logarithmic scale in both vertical axes.

Table 4
Acetic acid extractable contents (concentrations in mg kg^{-1}).

Sample	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sb	V	Zn
1	15.76	0.106	2.956	0.060	0.520	0.0011	322.8	4.000	0.284	<0.4	<0.04	15.20
2	6.720	0.102	3.276	0.052	0.608	0.0009	252.8	3.788	0.652	0.40	0.04	14.16
3	<0.2	0.092	1.800	0.072	1.204	<0.0004	106.0	2.124	0.404	<0.4	<0.04	12.20
4a	0.216	<0.055	<0.52	<0.04	0.348	0.0007	242.0	2.864	<0.2	<0.4	<0.04	11.68
4b	<0.2	0.030	0.132	<0.04	0.328	<0.0004	199.2	1.416	<0.2	<0.4	<0.04	7.480
5a	24.72	0.078	5.080	0.056	1.072	0.0029	272.4	5.200	0.396	<0.4	<0.04	23.44
5b	33.92	0.075	5.480	0.056	1.172	0.0205	313.6	5.480	0.380	<0.4	<0.04	24.08
6	0.400	0.108	2.624	0.064	0.524	<0.0004	395.6	3.064	0.792	<0.4	<0.04	23.16
7	<0.2	0.071	2.672	0.044	4.640	<0.0004	169.6	2.536	0.268	<0.4	<0.04	5.680
8	0.284	0.096	2.264	0.100	1.588	<0.0004	177.6	2.232	0.716	<0.4	<0.04	16.20

arsenical salts in the sediments, possibly as sulphates, which seem to be a greater contribution to the extractable fraction than that corresponding to the more distant samples, where presumably As has been fixed to a greater extent onto mineral surfaces (Fe-Mn oxides and clays). Cu shows, in general, a similar behavior; the extractable fractions with acetic acid in samples with contents below the threshold of 30 mg kg^{-1} Cu vary between 1.4 % and 6.3 % of the total, reaching 8.5 % in the only sample that exceeds these values. In the case of Hg, the amount extractable from the sediment with acetic acid is negligible, with a maximum value of 0.2 % in samples close to mining activities. In the rest of the samples, this element is undetectable in the extracts with acetic acid. Assuming that this is the bioavailable fraction, the bioavailability of these elements in the sediments would be medium-low for Cu, low for As and practically nil for Hg. For the rest of the elements three groups were found according to their bioavailability; Cr (<0.6 %) and Pb (<3.4 %) with very low bioavailability, while Co, Ni and Zn had medium bioavailability around 14–21 % and finally Mn, for which bioavailability exceeded 60 % in some samples.

5. Conclusions

In the studied area of the Caudal River basin (NW Spain) it has been found that As, Hg and, to a lesser extent, Cu in the sampled sediments can pose a threat to biota due to their elevated concentrations resulting from Hg and Cu mine sites, despite having been inactive for several decades. The methods used to estimate bioavailability allowed an assessment of the potential risk of these elements for aquatic ecosystems.

Among the procedures used, the advantages of the DGT, which considers the dynamics of analyte exchange between pore water and the solid phase and provides true information on the bioavailable forms of chemicals, are noteworthy. The concentrations of soluble elements such as Cu or As in the DGT are similar to those of pore water, which is considered the main source of what is retained in the DGT, so that an equilibrium is reached where the element is continuously replenished in solution from the solid phase, particularly in samples of low concentration. In contrast, less mobile elements, such as Hg, are not easily transferred from pore waters to DGT. The fractions usually considered as bioavailable are more significant in pore water for As and Cu, when the concentrations of these elements are low, while they reach their maximum in the sediments with high concentrations. However, in the case of Hg, this bioavailable fraction was negligible in quantitative terms.

The total concentration of contaminants in sediments is not the most appropriate indicator to determine their effect on ecosystems, since metal availability is influenced by the specific properties of the sediments and the fractions with which the trace elements are preferentially associated. Although expensive, DGT is a relatively new technique that has potential for applications in environmental monitoring, but further studies and guidelines are needed to correctly interpret the results. The study of field duplicates has shown significant uncertainty associated to the deployment point, with CV up to 60 % in the case of As. The differences between the methods are notable and, given the impact they have on risk analysis methodologies, it would be highly desirable to continue research to determine which one best matches bioavailability (e.g., by comparison to in vivo tests). The practical application of this work is helping in the decision making about the procedure to be used to estimate the bioavailable fraction in river sediments, depending on the expected metal(loid)s. The affection to fluvial environments by mining and industrial activities is a widespread problem, being, therefore, the potential cases of application of the results of this work very abundant. The methodology is particularly suitable in sedimentary basins which are the most frequent environments on the Earth's surface.

Author contribution statement

All authors contributed to the study conception and methodology design, in particular H. Serrano, M. Izquierdo. Material preparation, sampling and laboratory work were performed by R. Álvarez, E. García-Ordiales, F. Alberquilla, C. García and E. De Miguel. All the authors participated in the interpretation of data, particularly A. Ordóñez and F. Barrio. The first draft of the manuscript was written by A. Ordóñez, M. Izquierdo and R. Álvarez. All authors commented on previous versions of the manuscript, being E. De Miguel and S. Charlesworth the main supervisors. All authors read and approved the final manuscript.

Ethics approval

The work did not generate negative impacts on the environment. No current bioethical standards were violated.

Funding

This work was supported by the Spanish Ministry of Science and Innovation through the financing of the PID2020–115313RB-I00/AEI/10.13039/501100011033 project.

Almudena Ordóñez: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Rodrigo Álvarez**: Writing – original draft, Validation, Resources, Methodology, Conceptualization. **Miguel Izquierdo**: Writing – original draft, Methodology, Conceptualization. **Humberto Serrano**: Visualization, Methodology, Conceptualization. **Efrén García-Ordiales**: Resources, Methodology, Conceptualization. **Carmen García**: Visualization, Resources, Methodology, Conceptualization. **Fernando Alberquilla**: Visualization, Resources, Methodology, Conceptualization. **Fernando Barrio**: Methodology, Data curation, Conceptualization. **Eduardo De Miguel**: Writing – review & editing, Supervision, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **Susanne Charlesworth**: Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Almudena Ordoñez reports financial support was provided by Spanish Ministry of Science and Innovation. If there are other authors, they 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.

Acknowledgements

The authors acknowledge the Hydrological Planning Office of the Cantabrian Hydrographic Confederation for providing historical data.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2024.116614.

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