Diffusive Gradients in Thin Films (DGT) as an Aid to Risk Assessment in Watercourses Affected by Mine Drainage

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Abstract

This study evaluates the environmental quality of river water and sediments in the Caudal River basin (NW Spain), historically affected by Hg and Cu mining. Initial sampling revealed high metal(oid) concentrations, especially downstream of former Hg mines. A second campaign used DGT (Diffusive Gradients in Thin Films) passive samplers to assess bioavailable fractions at selected points. Results showed a strong correlation between As and Cu in DGT and pore water, with As showing up to 75% transfer at low concentrations, indicating its nearly fully bioavailable chemical form. This highlights the usefulness of DGT samplers for determining bioavailability.

Keywords: Bioavailability, DGT, Ecological Risk, River Sediments, Trace Elements

Introduction

River sediments are essential components of aquatic ecosystems, serving as both habitats and food sources for a variety of organisms. However, their ability to act as sinks for pollutants, including trace metals and metalloids, can lead to considerable ecological risks. These risks are particularly pronounced in regions affected by historical mining activities, where sediments continue to harbour contaminants long after the cessation of mining operations. Such contamination can severely affect benthic organisms and the broader ecosystem by influencing the bioavailability of harmful elements (Banaee *et al.* 2024; Eyong 2008).

Traditionally, environmental assessments have concentrated on water column quality, but this approach often overlooks the potential for sediments to act as reservoirs and sources of pollutants. Changes in physicochemical conditions, whether natural or anthropogenic, can trigger the remobilization of contaminants from sediments into the overlying water, amplifying ecological hazards (García-Ordiales *et al.* 2020; Kim *et al.* 2006). Given these dynamics, sediment assessments that account for bioavailability, i.e. the fraction of contaminants available for biological uptake, are critical for accurately evaluating environmental risks (Ali *et al.* 2024).

Bioavailability is influenced by the chemical forms of contaminants and their interactions with sediment matrices and pore water. Therefore, various analytical methods have been developed to estimate bioavailable fractions, ranging from leaching and extraction methods to advanced in situ technologies. Sequential extraction techniques using weak acids, such as acetic acid, have been widely adopted to target exchangeable, water-soluble, and acid-soluble fractions of metals, which are presumed to represent bioavailable forms (Rauret *et al.* 1999). However, these traditional methods may fall short in capturing the dynamic interactions between contaminants and their surrounding environment.

Diffusive Gradients in Thin Films (DGT) technology has emerged as a powerful alternative, offering dynamic and time-integrated measurements of bioavailable contaminants. This technique not only provides insights into the mobility and speciation of metals in sediments but also minimizes sample handling and potential contamination (Davison & Zhang 2012). DGT's ability to quantify labile metal fractions with high spatial resolution has made it a preferred tool in environmental monitoring (Huang *et al.* 2019; Taylor *et al.* 2020).

The primary objective of this research is to compare methodologies for evaluating the bioavailability of key contaminants in river sediments. By integrating traditional extraction techniques and advanced DGT-based assessments, this work aims to identify the most effective approaches for estimating ecological risks. The study's findings will contribute to the ongoing discourse on sediment contamination, with implications for risk management in mining-affected aquatic systems. Specifically, this work explores the dynamic interplay between sediment-bound and dissolved contaminants, highlighting the advantages and limitations of different analytical approaches in characterizing bioavailable fractions.

Methods

Study Area

The research was conducted in the Caudal River basin, located in Asturias, northwest Spain. This area has a long history of mining activities, particularly mercury (Hg) and copper (Cu) extraction, which have left a lasting environmental legacy (mining waste still remains in uncovered spoil heaps, exposed to mechanical and chemical weathering). The basin's geological substrate primarily comprises Carboniferous sedimentary rocks, including sandstones, shales, and graywackes, interspersed with calcareous outcrops. These rocks exhibit low permeability, which, combined with the region's humid climate and high annual rainfall exceeding 1,000 mm, results in predominantly surface runoff-dominated hydrology.

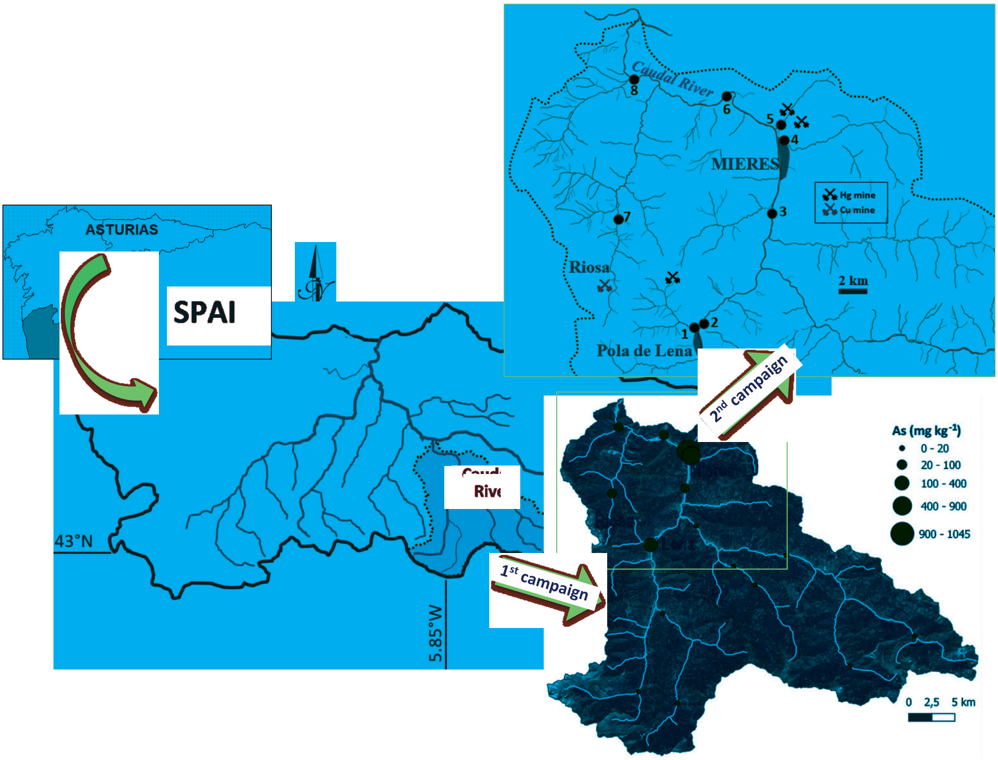

Figure 1 Caudal River basin; As concentrations found in the first sediment sampling campaign; Location of sampling points of the second campaign (mod. Escudero et al., 2024; Alvarez et al. 2024).

Mining operations in the basin ceased decades ago; however, residual contamination persists. Spoil heaps and unremediated mine facilities continue to release pollutants, including arsenic (As), mercury (Hg), and copper (Cu), into the river system. These elements are originally present in various mineral forms, such as cinnabar (HgS) for Hg, arsenopyrite (FeAsS) for As and Chalcopyrite ($CuFeS_2$) for Cu, which contribute to the complex contamination profile. The Hydrological Planning Office reports that the Caudal River is in poor ecological condition, especially in its lower section. Macroinvertebrate studies show low biodiversity, suggesting that old mine sites are negatively affecting aquatic life (Escudero *et al*. 2024). Sampling points were strategically located downstream of the Hg mining sites in Mieres and Pola de Lena and the Cu mine at Riosa (Fig. 1) to identify the extent of contamination and its ecological implications.

Sampling and Analysis

In a first campaign, water and bulk sediment samples were collected on the banks of the main watercourses of the basin (Fig. 1), using plastic tools. The area where the highest concentrations of elements of concern (Hg, As and, to a lesser extent, Cu) were found (see next section), was selected for the second sampling campaign (Fig. 1). This second phase includes the bioavailability study, so eight sediment sampling points were critically selected in the most affected areas (Fig. 1), including 2 field duplicates (samples 4 & 5). Each sampling event involved the collection of bulk sediments, pore water, and in situ deployment of DGT devices.

1. Bulk Sediments: Approximately 1 kg of sediment was manually collected from the uppermost layer (≤3 cm depth) using plastic tools to minimize contamination. Samples were air-dried, sieved to isolate the fine fraction (<63 µm), and subjected to pseudo-total digestion using aqua regia. Metal(loid) concentrations were analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES).
2. Pore Water: Sediment pore water was extracted through centrifugation under anoxic conditions to prevent oxidation. The extracted water was filtered, acidified to pH 2 with nitric acid, and stored at 4 °C until analysis. Trace metals were quantified using inductively coupled plasma mass spectrometry (ICP-MS).
3. DGT Deployment: DGT devices were deployed at the sediment-water interface for a period of four days. The DGT units contained binding gels tailored to capture specific contaminants, including Chelex-100 for trace metals and ferrihydrite for arsenic. After retrieval, the binding gels were eluted, and the accumulated contaminants were quantified to determine time-averaged bioavailable concentrations.
4. Acetic Acid Extraction: A subset of samples from the bulk sediments underwent a selective extraction using 0.11 M acetic acid to isolate exchangeable and acid-soluble fractions. This method simulates conditions conducive to bioavailability and provides a comparative benchmark against DGT measurements.

Results and discussion

The results of the first campaign revealed that stream waters downstream the mine sites (with up to 0.76 mg L^{-1} As) exceed concentrations established by the US Environmental Protection Agency (EPA) and Spanish regulations for the protection of human health and the environment. Hg and As concentrations in sediments (up to 195 and 1045 mg kg^{-1}, respectively) exceeded the thresholds set by the Canadian Sediment Quality Guidelines (CCME 2023) and the US Environmental Protection Agency (US EPA 2022) guidelines, indicating possible adverse and chronic effects on aquatic life (Escudero *et al.* 2024). In addition, the concentrations found downstream the mines are high above the background values found for the whole basin: 14.7 mg kg^{-1} As, 0.23 mg kg^{-1} Hg and 16.65 mg kg^{-1} Cu (Barrio-Parra *et al.* 2025). The Hydrological Planning Office reports that the Caudal River is in poor ecological condition, especially in its lower section. Macroinvertebrate studies show low biodiversity, suggesting that old mine sites are negatively affecting aquatic life, despite being inactive for decades (Escudero *et al.* 2024).

Table 1 Analytical results (after Álvarez et al. 2024)

	Sediment (mg kg^{-1})			Acetic acid extract (mg kg^{-1})			Pore water (µg L^{-1})			DGT (µg L^{-1})		
Sample	**As**	**Hg**	**Cu**	**As**	**Hg**	**Cu**	**As**	**Hg**	**Cu**	**As**	**Hg**	**Cu**
1	313	8.76	28.5	15.8	0.0011	0.52	221	0.043	2	75	0.013	1.6
2	218	7.72	25.7	6.72	0.0009	0.61	144	0.074	4	34	0.018	0.9
3	34.5	1.57	26.4	<0.20	<0.0004	1.20	<5	0.063	2	5.6	0.004	1.0
4	39.7	1.88	24.6	0.22	0.0007	0.35	14	0.080	2	4.7	0.002	0.9
4dup	16.1	<0.20	12.8	<0.20	<0.0004	0.33	10	0.105	3	<2.9	0.005	1.8
5	1080	80.7	22.5	33.9	0.0205	1.17	746	0.263	2	580	0.059	1.7
5dup	921	78.0	21.2	24.7	0.0029	1.07	649	0.255	4	220	0.034	1.0
6	38.4	1.31	27.3	0.40	<0.0004	0.52	13	0.069	2	11	0.006	1.1
7	17.9	<0.20	54.3	<0.20	<0.0004	4.64	6.0	0.032	14	7.6	0.007	2.7
8	34.9	3.76	25.4	0.28	<0.0004	1.59	10	0.071	2	7.5	0.006	1.2

In sediments sampled in the second campaign, As and Hg levels surpassed Probable Effect Levels (PELs), with concentrations up to 1080 mg/kg for As and 80 mg/kg for Hg. These findings underscore the critical need to evaluate not only the total contaminant load but also the bioavailable fractions that directly influence ecological risks.

Comparison of Methods

Pore water concentrations revealed remarkable spatial variability, particularly for As and Cu. The highest concentrations of As and Hg were detected downstream of Hg mining sites, while elevated Cu levels were identified downstream of the Cu mine. The dynamic interaction between pore water and sediment phases was evident, emphasizing the role of pore water as a critical reservoir for bioavailable contaminants (Bufflap & Allen 1995). Pore water analysis effectively captured the soluble metal fraction but was influenced by sampling conditions and temporal variability.

Acetic acid method, widely accepted as a proxy for bioavailable metal fractions, revealed that bioavailability varied notably among elements. For As, the acetic acid-extractable fraction represented up to 5% of the total sediment content in areas near mining activities, compared to less than 1% in less contaminated locations. Cu exhibited slightly higher mobility, with extractable fractions reaching up to 8.5% in the most affected areas. In contrast, Hg showed negligible extractable fractions (≤0.2%), reflecting its low mobility and bioavailability under the studied conditions. Acetic acid extraction provided a straightforward, cost-effective means to estimate the labile metal fraction. However, it underestimated bioavailability for elements like As and Cu when compared to DGT (i.e. the fractions of As and Cu extracted by acetic acid from the sediment are lower than the fractions of these elements retained from the pore water in the DGT).

DGT technique provided in situ, time-averaged measurements of bioavailable metal fractions, offering a dynamic perspective on contaminant exchange at the sediment-water interface. Strong correlations were observed between As and Cu concentrations in DGTs and pore water (≥75% transfer efficiency for As at low concentrations), indicating a substantial bioavailable fraction. Conversely, Hg transfer to DGTs was negligible, regardless of sediment concentrations, likely due to its limited mobility and strong association with sediment particles (Davison & Zhang 2012). DGTs emerged as the most robust tool for assessing bioavailability, particularly for As and Cu. By integrating diffusion and kinetic replenishment processes, DGTs offered a more comprehensive understanding of dynamic contaminant exchange between sediment and water phases (Gu *et al.* 2023). Fig. 2 shows a comparison of results for the 3 samples closest to the Hg mines in Lena and Mieres and to the Cu mine.

Element-Specific Observations

Arsenic exhibited a complex behaviour across methods. While total sediment concentrations were consistently high, the bioavailable fraction measured by DGT and pore water analysis was more pronounced at sites with low total As levels, suggesting a dynamic equilibrium between solid and liquid phases. This equilibrium appeared disrupted at highly contaminated sites, where particulate-bound As dominated.

Copper showed moderate mobility and bioavailability, with DGT and pore water measurements aligning closely. The acetic acid-extractable fraction was relatively consistent, highlighting Cu's moderate affinity for sediment binding sites. Elevated Cu concentrations near the Cu mine in Riosa were particularly concerning, given their potential ecological implications.

Mercury demonstrated minimal mobility and bioavailability across all methods. The negligible transfer to DGTs, despite high total concentrations in sediments, underscores Hg's tendency to form stable, non-labile complexes within the sediment matrix (Chaudhary *et al.* 2020). This limited bioavailability suggests that Hg poses less immediate risk to aquatic biota, although long-term risks associated with remobilization cannot be discounted.

For the field replicates, the calculated coefficients of variation for As and Cu are high, reaching up to 60% for As in the sediment and the DGT, while remaining low in other cases.

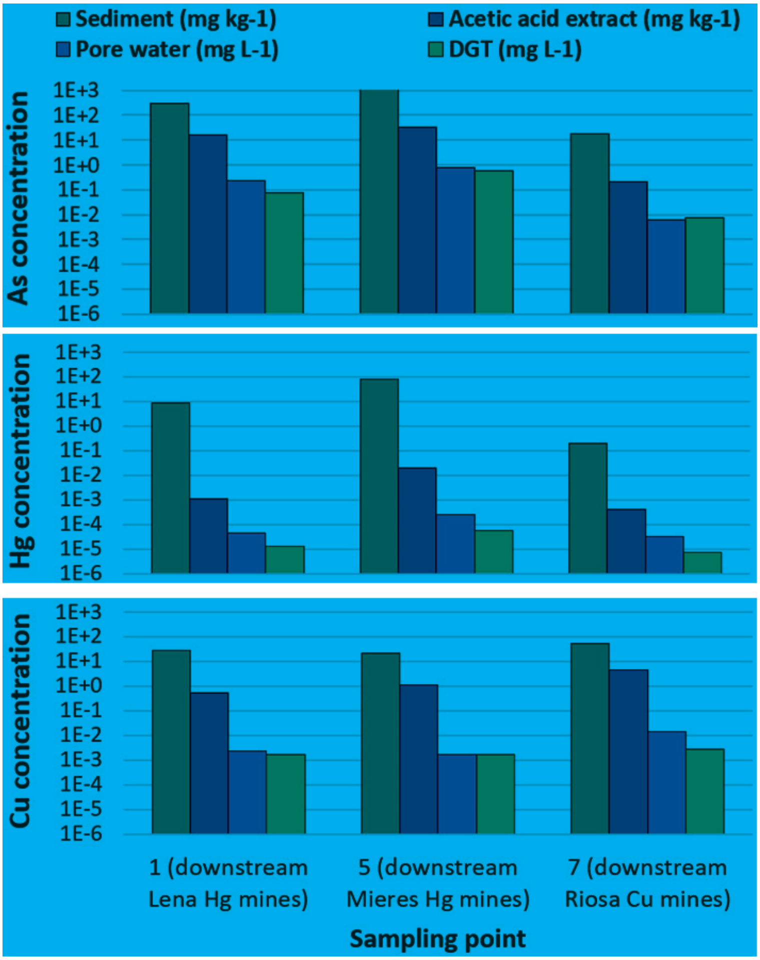

Figure 2 *As, Hg and Cu concentrations (same logarithmic scale) in sediment, pore water, DGT and acetic acid extract in three sampling points.*

Conclusion

The study highlights remarkable contamination levels of As, Hg and Cu in the Caudal River basin, a region heavily affected by historical mining activities. Total metal(loid) concentrations in sediments downstream of former Hg and Cu mining sites often exceed thresholds established by globally accepted guidelines, suggesting a high likelihood of adverse ecological effects.

These findings underscore the importance of integrating multiple methodologies to accurately assess ecological risks in mining environments. While total metal concentrations provide a baseline for contamination levels, bioavailability data are critical for understanding actual ecological effects. The superior performance of DGTs in capturing dynamic bioavailability highlights their potential as a standard tool in environmental monitoring and risk assessment frameworks.

The study demonstrates that dynamic techniques like DGTs offer substantial advantages over traditional methods, by allowing in situ and continuous measurements of available metal(loid) concentrations with high spatial resolution, enabling more accurate assessments of ecological risks posed by potentially toxic elements in river sediments, particularly in basins affected by mine drainage. The integration of these findings into environmental management strategies can aid in prioritizing remediation efforts and mitigating long-term influences on aquatic ecosystems.

Notwithstanding, the variability in field replicates, particularly for As, highlighted the influence of site-specific factors and methodological limitations. High coefficients of variation were found for some measurements, emphasizing the need for standardized deployment protocols and additional replicates to enhance reliability. Future research should focus on refining DGT calibration for elements like Hg and exploring correlations between DGT measurements and biological uptake in aquatic organisms.

Acknowledgements

The present study has been funded through the PID2020-115313RB-I00/AEI/10.13039/501100011033 research grant of the Spanish Ministry of Science and Innovation, and the CARESOIL-CM [TEC-2024/ECO-69] programme, funded by the regional government of the Community of Madrid (Spain).

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