Divergent effects of PVC-microplastics on arsenic and mercury dynamics in a contaminated soil-plant system

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INTRODUCCIÓN

Microplastics (MPs) have emerged as contaminants of global concern, with an expanding body of literature documenting their pervasive occurrence across multiple environmental compartments, including the atmosphere, soils, sediments, and aquatic systems (Vieira et al., 2024). The inter-compartmental transport of MPs is now well established, with terrestrial ecosystems, and soils in particular, recognized as major sinks for these emerging pollutants. A further dimension of complexity arises from the frequent co-occurrence of MPs with other contaminants, notably metals and metalloids, a phenomenon that has attracted considerable scientific scrutiny in recent years. This co-occurrence has prompted investigation into the so-called "Trojan horse" hypothesis, which posits that MPs may function as preferential vectors for metal(loid) transport by adsorbing these elements onto their surfaces, potentially facilitating their translocation and bioavailability in ways that differ markedly from those of the free ionic forms.

Notwithstanding this growing interest, the mechanistic understanding of metal(loid)–MP interactions and the underlying sorption processes remains incomplete. The available evidence, derived predominantly from controlled laboratory experiments, points to polymer type as a key determinant of metal(loid) sorption capacity. However, such controlled conditions inherently fail to capture the full complexity of natural environmental settings. Of particular relevance is the progressive surface degradation of MPs driven by environmental stressors, including solar radiation, thermal fluctuations, and mechanical abrasion, which leads to the formation of oxygen-bearing functional groups capable of engaging in electrostatic and complexation interactions with both metal(loid)s and soil constituents. Beyond abiotic factors, the role of soil biota in mediating these interactions warrants explicit consideration, as organisms such as earthworms and plants are known to alter MP distribution, surface properties, and associated contaminant dynamics. Nevertheless, knowledge of MP behavior within the soil–plant continuum, and especially under conditions of concurrent metal(loid) contamination, remains critically limited, representing a significant gap in our current understanding of MP-driven risks in terrestrial ecosystems.

In this study, we investigate the influence of polyvinyl chloride microplastics (PVC-MPs), one of the most abundant polymer types detected in natural environments, on the soil–plant system of birch (*Betula pubescens*) grown in a historically contaminated mining soil with elevated As and Hg concentrations in northern Asturias, Spain. Specifically, we aim to evaluate whether the presence of PVC-MPs modifies the accumulation of these metalloids by the plant, and to advance the mechanistic understanding of MP–contaminant interactions within the soil–plant continuum.

METHODOLOGY

A field experiment was conducted at a legacy Hg mining site in Asturias, Spain, using a historically contaminated soil with elevated concentrations of As and Hg. The soil exhibited near-neutral pH, high clay content, and a mineralogical assemblage dominated by quartz, calcite, and clay minerals. PVC-MPs were incorporated into the soil at a concentration of 1% (w/w). Birch (*Betula pubescens*), previously validated as a phytoremediation species at this site for its capacity to immobilize As and Hg (Ranđelović et al., 2025; Sánchez et al., 2024), was selected as the test plant. A parallel control plot without PVC-MP amendment was established under otherwise identical conditions. After one year of growth, plant and soil samples were collected. Plant material was separated into roots and leaves, and total metal(loid) concentrations were determined by ICP-MS and atomic mercury analysis (AMA). To elucidate the underlying geochemical interactions, As and Hg speciation was investigated by X-ray absorption spectroscopy (XAS) at the CLAESS beamline (ALBA Synchrotron, Spain). As K-edge XANES was used to determine the relative proportions of As(V) and As(III), while Hg L-edge XANES combined with linear combination fitting (LCF) was applied to identify Hg-bearing phases. The reference dataset used for LCF included HgO, cinnabar (α-HgS), metacinnabar (β-HgS), $HgCl_2$, $HgSO_4$, corderoite ($Hg_3S_2Cl_2$), Hg complexed to humic acid, and Hg adsorbed onto goethite.

RESULTS AND DISCUSSION

Total concentrations of As and Hg in the experimental soil were 800 and 8 mg kg^{-1}, respectively. As K-edge XANES analysis revealed that As occurred exclusively as arsenate, As(V), consistent with the oxidizing conditions prevailing in the soil. Hg speciation, as determined by LCF, was dominated by cinnabar, metacinnabar, and Hg bound to goethite, a mineralogical assemblage that accounts for the inherently low mobility of Hg in this system.

Notwithstanding this low mobility, birch plants growing in the control soil showed substantial accumulation of both elements, with concentrations of 27 mg kg^{-1} As and 2 mg kg^{-1} Hg in leaves, and 84 mg kg^{-1} As and 0.6 mg kg^{-1} Hg in roots. The introduction of PVC-MPs induced divergent responses for the two contaminants. Hg accumulation decreased markedly across all plant tissues, declining to 1.3 mg kg^{-1} in leaves and 0.3 mg kg^{-1} in roots. Conversely, As concentrations increased in both compartments, reaching 32 mg kg^{-1} in leaves and 101 mg kg^{-1} in roots.

These contrasting responses suggest distinct interaction mechanisms for each element. The observed reduction in plant Hg uptake is consistent with immobilization of Hg onto PVC-MP surfaces, facilitated by the affinity of Hg^{2+} for chlorine-bearing functional groups characteristic of PVC. This hypothesis will be tested in a forthcoming synchrotron session, where shifts in Hg speciation, specifically, an increase in Hg–Cl phase contributions, will be evaluated. The enhanced As accumulation in PVC-MP-treated soils may reflect PVC-induced modifications of soil redox conditions, potentially promoting the reductive dissolution of Fe-(oxy)hydroxides and the concomitant mobilization of As(V) to the more bioavailable As(III) form. This mechanism will likewise be assessed by XAS analysis of As speciation in treated versus control soils.

CONCLUSIONS

These preliminary results demonstrate that MPs in soils can act as reactive geochemical interfaces that alter metal(loid) partitioning and, consequently, their bioavailability and accumulation within the soil–plant system. The contrasting behavior observed for As and Hg underscores the element-specific nature of MP–contaminant interactions and highlights the inadequacy of generalizing MP effects across different metal(loid)s. Ongoing synchrotron-based speciation work will be critical to resolving the mechanistic basis of these observations. Taken together, these findings call for a more comprehensive evaluation of how MPs modify biogeochemical cycles in contaminated terrestrial systems, not only in relation to metals and metalloids, but also in their interplay with other soil constituents and phases.

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