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Soil-to-plant transfer of arsenic and phosphorus along a contamination gradient in the mining-impacted Ogosta River floodplain

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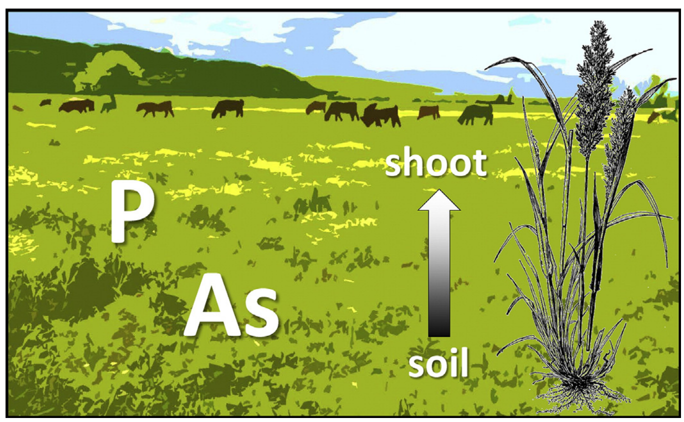
HIGHLIGHTS

- Soil-to-plant transfer of As and P was studied on As contaminated pastureland.
- As contents of *H. lanatus* and *T. repens* shoots reflected the As gradient in the soil.
- Low As transfer factors (mostly <0.07) indicated a restricted soil-to-shoot transfer.
- Intake via soil ingestion was estimated to dominate total As intake for grazing livestock.

GRAPHICAL ABSTRACT



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ABSTRACT

Riverine floodplains downstream of active or former metal sulfide mines are in many cases contaminated with trace metals and metalloids, including arsenic (As). Since decontamination of such floodplains on a large scale is unfeasible, management of contaminated land must focus on providing land use guidelines or even restrictions. This should be based on knowledge about how contaminants enter the food chain. For As, uptake by plants may be an important pathway, but the As soil-to-plant transfer under field conditions is poorly understood. Here, we investigated the soil-to-shoot transfer of As and phosphorus (P) in wild populations of herbaceous species growing along an As contamination gradient across an extensive pasture in the mining-impacted Ogosta River floodplain. The As concentrations in the shoots of *Trifolium repens* and *Holcus lanatus* reflected the soil contamination gradient. However, the soil-to-shoot transfer factors (TF) were fairly low, with values mostly below 0.07 (TF = As_{shoot}/As_{soil}). We found no evidence for interference of As with P uptake by plants, despite extremely high molar As:P ratios (up to 2.6) in Olsen soil extracts of the most contaminated topsoils (0–20 cm). Considering the restricted soil-to-shoot transfer, we estimated that for grazing livestock As intake via soil ingestion is likely more important than intake via pasture herbage.

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1. Introduction

Many riverine floodplains in industrialized countries accumulated high loads of potentially toxic trace elements which were carried along with the river from upstream sources such as mining and ore processing facilities (Byrne et al., 2012). The mining industry annually produces several Gt of tailings, a mixture of crushed rock and processing fluids (Kossoff et al., 2014). Tailings generated during processing of sulfidic ores are of environmental concern due to their elevated concentrations of potentially harmful metals (e.g. Cd, Cu, Pb, Hg, Zn) and metalloids (e.g. As, Sb). Furthermore, large amounts of acidity are generated when sulfidic tailings are oxidatively weathered. In the absence of carbonate minerals, this often results in low pH drainage water which is commonly referred to as acid mine drainage (Lindsay et al., 2015). The most common approach to handle mine tailings is to store them behind dammed impoundments, the so called 'tailings dams' (Kossoff et al., 2014). They are typically constructed from locally-derived soil, waste rock and the tailings themselves. Ideally the impoundments should isolate the tailings to prevent their potentially harmful constituents from entering ground and surface waters, and to protect them from wind erosion. Unfortunately, isolation is often not sufficient, allowing the tailings tips to be eroded and drainage to leave the impoundments. Moreover, around 200 tailings dam failures were reported over the last century with an unknown number remaining unreported (Azam and Li, 2010). These incidents often release huge quantities of tailings into river systems and contaminate downstream floodplains (Kossoff et al., 2014). In some cases, mine tailings or slurries have been disposed directly into rivers or wetlands, causing severe pollution (Vogt, 2013).

Arsenic (As) is one of the most concerning hazardous elements entering the environment with or from mine tailings; the non-essential and carcinogenic metalloid is frequently elevated in mining-impacted riverine floodplain soils, as reported e.g. by Marron (1992), Hudson-Edwards et al. (2003), Tighe et al. (2005), and Jordanova et al. (2013). Since soil decontamination in river floodplains on a large scale is usually unfeasible, management of As contaminated floodplains must focus on providing land use guidelines and implementing usage restrictions in order to reduce human exposure and to foster natural attenuation processes (Wang and Mulligan, 2006). Therefore, knowledge about the distribution, chemical forms, mobility and availability of As in the soils is required. Uptake by plants may represent an important pathway for As to enter the food chain. However, the relationship between soil As and uptake by plants is still poorly understood, especially under field conditions and for plants other than commodity crops.

Numerous factors can affect the soil-to-plant transfer of As, including plant properties as well as environmental and soil chemical conditions, e.g., the chemical speciation of As in the rhizosphere (Moreno-Jiménez et al., 2012; Zhao et al., 2010). Under non-flooded, well-aerated conditions, As in soil is typically present as arsenate, which is the thermodynamically favorable form at high redox potentials. The oxyanion arsenate has similar sorption behavior as phosphate and the two molecules compete at various binding sites; the presence of phosphate can increase arsenate solubility in soil by competing for sorption sites on soil solid-phases (Bolan et al., 2013; Violante and Pigna, 2002). The two molecules also compete for uptake into plant roots. Both phosphate and arsenate enter the plant's root symplast via phosphate transporters (Zhao et al., 2009). Under flooded, anoxic conditions, arsenite dominates the soil solution phase (Parsons et al., 2013; Weber et al., 2010). In contrast to arsenate, arsenite enters plants as neutral $As(OH)_3$ via transporters belonging to the aquaglyceroporin membrane channel proteins which are involved in uptake of boric and orthosilicic acid (Mukhopadhyay et al., 2014; Zhao et al., 2009).

Detoxification of arsenite in plant cells includes complexation by –SH groups of glutathione or glutathione-derived phytochelatins, and active transport into vacuoles were it is stored. Moreover, arsenite efflux to the external medium – an important and well researched detoxification strategy in microbes (Bhattacharjee and Rosen, 2007) – was observed for the roots of several plant species (Zhao et al., 2009). In case of arsenate uptake, the reduction to arsenite by specific glutathione-dependent reductase enzymes precedes those detoxification mechanisms (Zhao et al., 2009). In most plants, the site of detoxification is largely the roots and the root-to-shoot transport is restricted. However, a fraction of the As entering the root will be translocated via the xylem to the shoot (Mendoza-Cózatl et al., 2011; Zhao et al., 2009); in the shoot it can be taken in by grazing livestock or wild animals.

Soil-to-shoot transfer factors (TF) from below 0.001, e.g. for *Rubus idaeus* L. (Otones et al., 2011), to higher than 10, e.g. for the As hyperaccumulating fern *Pteris vitata* L. (Ma et al., 2001), were reported ($TF = As_{shoot}/As_{soil}$, both in mg kg^{-1} dw). Vegetation surveys revealed that most terrestrial plants show TFs below 0.1 and that As (hyper)accumulation is a rare phenomenon (Baroni et al., 2004; Bergqvist and Greger, 2012; Tremlová et al., 2016). Intraspecies variation in soil-to-shoot TF can be considerable since, as mentioned earlier, many external factors determine how efficient plants transfer As from the soil to the shoot. Williams et al. (2007), e.g., surveyed commercially farmed temperate rice, wheat, and barley in Europe and the United States and found more than one order of magnitude variation in TF for these crops (0.05–3.84, 0.002–0.142, and 0.002–0.095, respectively). Today's knowledge does not allow satisfactory prediction of As TF for a given species and set of edaphic and environmental factors. In fact, we are just beginning to understand the mechanisms and factors controlling As soil-to-plant transfer. Pot experiments will be important to narrow the current gap of knowledge, but they must be accompanied by field studies in order to guide research towards ecologically relevant questions and experimental designs. A better understanding of As soil-to-plant transfer will allow to quantify the threat posed by the As burden of mining-affected floodplain soils to the ecosystem and the food chain via uptake by plants.

In this study, we investigated the soil-to-plant transfer of As for one leguminous (*Trifolium repens* L.) and two graminaceous plant species (*Holcus lanatus* L., *Apera spica-venti* L.) growing in an extensive pasture along a transect following a contamination gradient in the mining-impacted Ogosta River floodplain (Bulgaria). We aimed to elucidate whether As contamination gradients in the soils were reflected in the concentrations of As in the shoots of the three herbaceous species. In addition to total element concentration measurements, chemical soil extractions were conducted to obtain information on As and phosphorus (P) availability along the transect. Furthermore, the As soil-to-shoot TF were calculated for the wild plant populations investigated in this study and compared to findings from field surveys as well as pot, lysimeter, and field experiments reported in the literature.

2. Materials and methods

2.1. Study site

The study site is located in the floodplain of the Ogosta River, northwestern Bulgaria. The Ogosta River has its source in the West Balkan Mountains and drains into the Danube River. Large parts of its floodplain are used as pasture and arable fields. Due to mining activities the soils of the Ogosta River floodplain received large amounts of As and potentially hazardous metals. Historic gold mining in the Ogosta catchment began during Roman times, recent industrial metal exploration (Fe, Au, Pb, Ag) started in the early 1950s and ceased in the late 1990s. Over long periods, solid-loaded wastewater from two ore-dressing facilities was discharged into the river channels, contaminating the river sediments and the floodplain soils. Furthermore, after a tailings dam failure in 1964, large volumes of arsenopyrite-bearing, carbonate-rich sulfidic tailings sedimented in the floodplain and substantially contributed to the soil's contaminant burden (Jordanova et al., 2013; Stoyanova and Traykov, 2014). At present, the distributed arsenopyrite is, for the most part, oxidatively weathered and As is largely associated