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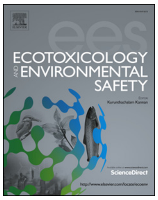

Phytotoxicity of polymetallic mine wastes from southern Tuscany and Saxony[☆]

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ABSTRACT

Restoration potential of mine wastes or approaches to improve soil conditions and to ameliorate phytotoxicity on these sites may be simulated in standardized greenhouse experiments. Plants can be cultivated side by side on materials from different origins in dilution series with defined admixtures of certain aggregates. Mine wastes used in the present study originated from Fenice Capanne (FC, Tuscany, Italy) and Altenberg (ALT, Saxony, Germany). Tailings of the Italian site contain high concentrations of lead, zinc, arsenic and sulphur while tin, wolfram, molybdenum and lithium are highly elevated in the German mine waste. We tested growth responses of five crop species and analyzed concentrations of various metals and nutrients in the shoot to evaluate the toxicity of the FC mine waste and found oilseed rape being the most and corn the least resistant crop. Interestingly, oilseed rape accumulated seven times higher levels of lead than corn without showing adverse effects on productivity. In a subsequent comparison of FC and ALT mine waste, we cultivated different species of buckwheat (*Fagopyrum* spec.), a fast growing genus that evolved in mountain areas and that has been shown to be tolerant to low pH and high concentrations of metals. We found that the FC mine waste was more toxic than the ALT substrate in *F. tataricum* and *F. esculentum*. However, lower admixtures of FC material (10%) resulted in stronger growth reductions than higher proportions (25%) of the mine waste which was primarily related to the slightly lower pH and higher availability of essential metals due to the admixture of sand. These results confirm the importance of managing the soil chemical and physical characteristics of wastelands and call for the development of assisted reclamation to prepare sites for regular biomass production.

1. Introduction

In many regions of Europe historical metal extraction and smelting activities left behind large deposits of mine wastes and slags, which over the time became re-vegetated by grassy and shrubby pioneer vegetation and secondary forests without human intervention. Today, only few mines and smelters remain active due to economic and environmental constraints and the operation of these facilities as well as the controlled flooding of underground mines are highly regulated using best available technologies. Adverse mining and smelting impacts in modern times are mostly locally restricted, while historical activities affected larger areas by the deposition of airborne particles and unmanaged discharges of metal sludge into the rivers (Ernst et al., 2009). Furthermore, the long-term and partly continued use of metal slags as liming materials and fertilizers in agriculture and as road construction materials have added up to the geogenic metal levels Europe wide. Repeated fine-scale, pan-European geochemical mapping projects will enable us to identify pollution hotspots and to assess the enrichment of toxic metals in soils and sediments over time (e.g. Fauth, 1985; Salminen et al., 2005; Reimann et al., 2014; Tóth et al., 2016; Birke et al., 2017).

Historical mining sites are an often neglected cultural and industrial heritage and knowledge about their geochemistry, geomorphology and ecology should not fall into oblivion. Since heavy metals will not degrade in the soils, ancient mining sites may be useful outdoor laboratories for the study of long-term effects of these pollutants on biota

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(Camizuli et al., 2018). While information on the geographical distribution of mines is available for sites that continued to produce until modern times, cadasters of long abandoned ancient mines will be necessary for environmental impact studies as well as for assessing their potential re-use or re-mining of strategic metals. Some of the places may be prone to ground collapses and the subsequent leaching of acid mine drainage (AMD) and toxic metals (e.g. Environment Agency, 2008). Erosion of the deposited material will be more pronounced when vegetation is removed or damaged e.g. by severe weather events and fires. Recent examples for ecological studies on ancient mine wastes in Wales and Spain are presented by Davies et al. (2016), Rossini-Oliva et al. (2016) and Fernández et al. (2017). The increased chemical weathering under climatic change (higher temperatures and precipitation) will probably lead to higher releases of AMD and metals in the future. On the other hand, former mining sites may offer chances as a readily available, pre-processed substrate for re-mining e.g. for strategic and rare earth metals. In nature conservation they may be used for the creation of wealthy secondary habitats, i.e. calaminarian and serpentine grasslands hosting highly adapted and endemic plants and insects (Baumbach et al., 2007). In the EU, these open semi-natural grasslands (habitat code 6130) have been protected under the habitats directive and the Natura2000 network. While the establishment of secondary nature should be restricted to outcrops with high metal pollution, flat basins of moderately polluted former mine sites may offer some potential for the cultivation of bioenergy crops and short rotation coppices.

Since plants are the first component of the food chain and metals can be both essential and non-essential for plant growth, it is important to know how these metals will interact with the physiology and ecology of plants and why some of the plant taxa were able to develop metal tolerant lines (metallophytes). These ecotypes are able to persist on former mine sites and have developed mechanisms to detoxify or exclude metals. The presence of and the metal concentrations in certain plant species can be used for the environmental monitoring at abandoned mines, but the involved taxa can also be used in vegetation assisted clean-up and remediation approaches, often referred to as phytoremediation and phytostabilization (Mahar et al., 2016). However, such plants are rather unproductive and are adapted to the harsh conditions and nutrient poor conditions in metal enriched soils. In order to reduce the stress created from a low availability of nutrients and essential elements, fertilization of such sites and soil amendments can be an option to improve the growth conditions and productivity locally with changes in plant composition (Chiarucci et al., 1998).

While metallophytes and the associated vegetation and mechanisms for metal accumulation on polymetallic sites were first addressed by Ernst (1974) and Baker (1981), many studies thereafter dealt with the effects of heavy metals on plants in laboratory and field studies. When addressing growth responses to heavy metals, native soils from metal sites are better suited than artificial substrates and the addition of rapidly soluble metal salts. Combining field and lab approaches gives a realistic impression of the toxicity and restoration potentials of post-mining substrates (Tesnerová et al., 2017). Using solid substrates with near-natural soil properties and relevant plant species should be preferred over using hydroponic cultures and cell cultures of model plants, which will not be able to mimic the conditions that drive the phytoavailability of elements in the infertile polymetallic sites. However, lab-based approaches and the use of defined metal solutions may help to investigate the involved biochemical and molecular biological mechanisms. Besides phytotoxicity studies, classical OECD acute toxicity tests can simulate whether soil biota would also be affected at such sites (Finngean et al., 2018). Before going into the field, the amendments with fertilizers, chelators, sorbents, organic matter as well as pH stabilizers and the improvement of the soil texture of mine wastes can all first be studied on the lab scale.

In present study we performed pot experiments with dilution series using a standard growth medium and wastes from an Italian and a German polymetallic mining site. The objective of the investigation was to develop a standard phytotoxicity testing scheme for mine wastes using crop plants. Since these plants produce more biomass than the metallicolous species naturally invading former mine sites, a combined approach based on soil improvement (fertilization and substrate loosening) of the mine waste and a directed cultivation of crop and bioenergy plants may favor the stabilization and carbon accumulation of those substrates. Provided that heavy metals are retained in the root zone, shoot mass can be subjected to bioenergectic uses, while accumulation of heavy metals and certain strategic elements in the hyperaccumulating shoot would be a prerequisite in phytomining.

2. Materials and methods

2.1. Mine waste materials used in the study

The **Fenice Capanne (FC)** sulphide deposit belongs to the Tuscan Colline Metallifere and the extraction and smelting of metals (Zn, Cu, Pb, Fe, Ag) dates back to the Etruscan times. Activities at the site were given up in 1985 and the flotation tailings and roasting piles remained untreated ever since. Environmental pollution at the site has been studied extensively by Benvenuti et al. (1997) and Mascaro et al. (2001) and studies related to the heavy metal tolerance of a metallicolous ecotype of *Silene paradoxa* L. and other species present in FC, were performed by Gonnelli et al. (2001), Arnetoli et al. (2008), Marchand et al. (2014) and Colzi et al. (2014). While these investigations focused on sulphidic substrates and plants adapted to rather acidic soils, the Italian researchers Angelone et al. (1993), Bini et al. (2017) and Selvi et al. (2017) focused on serpentine soils close to the study site and often addressed the nickel accumulator *Alyssum bertolonii* L.

A composite sample of 50 kg was obtained in April 2017 from tailing basin no. 1 (see photo in Mascaro et al., 2001) at the former mine at FC. The material had been deposited between 1957 and 1964 and contains high concentrations of heavy metals (Table 1). Soil cores of the yellowish to reddish sandy-silty material were taken at 20 vegetation-free positions from the upper layer (0–20 cm). A list of the few plant species present at the site is given in the results section.

After the transfer of the FC material sample to Germany, it was homogenized with a concrete mixer, air dried for a few days and sieved to 2 mm. Then the material was blended with washed river sand and a standard fertilized growth substrate (LD80) at defined proportions to generate five treatments ranging from 0% of FC material (the control) to the highest treatment containing 25% of the FC material. Every treatment was made up with 50% of the LD80 material to guarantee a basic supply of nutrients. Although the percentage of sand varied between 25% and 50%, we assume that differences in soil texture did not largely affect the outcome of the experiment. Fruhstorfer LD80 (Gebr. Patzer GmbH & Co. KG, Sinntal Jossa) is a standard plant growth medium. It is composed of peat, volcanic clay, bark humus and is enriched with a slow-release fertilizer. Having a pH of 5.9, the substrate contains 35% organic matter and has a salt content of 1 g L^{-1} KCl. Plant available nutrient concentrations are 150 mg L^{-1} each for N and P and 250 mg L^{-1} of K. The high share of the standard earth in each of the treatments guaranteed an adequate and similar supply of nutrients during the experiments. While LD80 and sand are free from heavy metals, we assumed sand and the FC substrate had low nutrient concentrations.

We addressed the chemical composition (heavy metals and nutrients) of the material used in present study and compared these results to published data (Table 1). However, we determined the HNO_3 extractable pseudo-total concentrations and did not include other extraction methods. In the study of Pignattelli et al. (2012) only low amounts of these metals proved to be phytoavailable after an extraction with 0.01 M $CaCl_2$ solution. When comparing the heavy metal loads of the diluted FC material to the precautionary values of the German soil protection and contaminated sites ordinance (BBSchV, 1999), we may