



## Aided phytostabilization of a trace element-contaminated technosol developed on steel mill wastes



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### HIGHLIGHTS

- A technosol developed on steel mill wastes displayed high soluble Cr and Mo levels.
- Input of ramial chipped wood and composted sewage sludge reduced soluble Cr in soil.
- *Festuca pratensis* best developed on the composted sewage sludge-amended soil.
- Its shoot Cr, Ni and Mo concentrations were lowest for the compost-amended soil.
- Shoot Mo concentration exceeded the maximum permitted concentration in forage.

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### ABSTRACT

Aided phytostabilization of a barren, alkaline metal(loid)-contaminated technosol developed on steel mill wastes, with high soluble Cr and Mo concentrations, was assessed in a pot experiment using (1) Ni/Cd-tolerant populations of *Festuca pratensis* Huds., *Holcus lanatus* L., and *Plantago lanceolata* L. sowed in mixed stand and (2) six soil treatments: untreated soil (UNT), ramial chipped wood (RCW, 500 m<sup>3</sup> ha<sup>-1</sup>), composted sewage sludge (CSS, 120 t DW ha<sup>-1</sup>), UNT soil amended with compost (5% w/w) and either vermiculite (5%, VOM) or iron grit (1%, OMZ), and an uncontaminated soil (CTRL). In the CSS soil, pH and soluble Cr decreased whereas soluble Cu, K, Fe, Mn, Mg, Ni and P increased. The RCW treatment enhanced soluble Fe, Mn, and Mg concentrations. After 15 weeks, shoot DW yield and shoot Cd, Cu, Fe, Mn, Mo, Zn, and Mg removals peaked for *F. pratensis* grown on the CSS soil, with lowest shoot Cr, Ni and Mo concentrations. *Holcus lanatus* only grew on the CTRL, UNT, and CSS soils and *P. lanceolata* on the CTRL soil. Best treatment, *F. pratensis* grown on the CSS soil, led to a dense grass cover but its shoot Mo concentration exceeded the maximum permitted concentration in forage.

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### 1. Introduction

Soil contaminations by trace elements (TE), here metal(loid)s with common concentrations in living organisms below 100 mg kg<sup>-1</sup> [1], are often legacies of long term industrial activities [2]. Several smelting activities are located in eastern

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France [3]. In particular, a large steel mill (30 ha) located at Chateauneuf, nearby Rive-de-Gier (Loire, France) has produced and dumped a huge amount (100 000 m<sup>3</sup>) of foundry wastes, slags, fire-bricks, and other by-products such as more or less hydrated lime in an internal landfill [4]. A technosol, i.e. with properties and pedogenesis dominated by artificial or transported materials [5], has developed on these old on-site tailings [6]. Its total TE concentrations exceed the background values for French sandy soils [7,8]. Such TE-contaminated technosols may pose a danger to human health and the environment [9]. For the Chateauneuf tailings, windblown dust, TE leaching beneath the technosol, and topsoil ecotoxicity were evidenced and this diffuse contamination may generate pollutant linkages nearby [4,6].

Among remediation techniques for TE-contaminated soils, aided phytostabilization is an alternative to physico-chemical methods [10]. This environmentally friendly, low cost option combines soil conditioners with the use of excluder's plants and their associated microorganisms. It aims at minimizing pollutant linkages such as TE transfer through natural agencies to the environmental compartments and into the food chain. Soil conditioners and vegetation cover must sustainably improve soil structure and fertility parameters, reduce labile contaminant pools and their migration, and limit detrimental effects on living organisms, notably in the root zone [11]. Accordingly, a field-scale aided phytostabilization program, named PHYSAFIMM, was developed to remediate the Chateaufort TE-contaminated technosol [6]. It aims at evaluating the efficiency of organic amendments combined with TE-tolerant plant species to alleviate pollutant linkages and create ecosystem services for this technosol. This one is contaminated by Fe, Mn, and various TE present in alloys such as Cr, Mo, As, Cu, Pb and Zn [6,8]. The amendment choice generally depends on soil pH and TE contamination, nutrient and organic matter (OM) contents, and sorbing phases such as Fe, Mn and Al hydr(oxides) and clays in the soil [12]. Input of OM such as compost, sewage sludge and ramial chipped wood (RCW) can (1) form immobilized complexes between organic ligands and TE, (2) improve soil texture and structure, (3) increase nutrient status and water retention and (4) change soil pH [12]. Their effects on TE bioavailability depend on the OM type, its microbial degradability, the salt content, soil pH and Eh, soil type, and TE of concern [8]. In 2009, the Chateaufort trial was divided into nine plots, either amended with RCW, composted sewage sludge (CSS) or non-amended (UNT) [6]. Just after their set up, topsoils of the RCW, CSS and UNT plots were collected for further pot experiments. As clays and Fe/Mn hydrous oxides can immobilize several TE [10,12], two additional treatments were constituted by incorporating vermiculite plus compost (VOM) and iron grit plus compost (OMZ) into potted UNT soil samples.

The choice of plant species is pivotal for a sustainable aided phytostabilization of such TE-contaminated technosol. One prerequisite is to select plant species and cultivars (1) tolerant to TE excess, (2) producing a dense, perennial and sustainable vegetation cover, (3) accumulating TE in their roots and (4) with low root-to-shoot TE transfer limiting TE inputs into the food chain, (5) able to stabilise TE in the root zone and (6) to decrease TE concentrations in the soil pore water (SPW), and (7) tolerant to other abiotic and biotic stress such as drought [10,11,13]. Based on previous findings, TE-tolerant populations of *Festuca pratensis* Huds., *Holcus lanatus* L., and *Plantago lanceolata* L. were relevant candidates [10,11].

This pot experiment aimed at assessing the efficiency of Ni/Cd-tolerant plants in mixed stand and soil conditioners to aided phytostabilize a TE-contaminated technosol developed on steel mill tailings, while avoiding pollutant linkages such as herbivory exposure.

## 2. Material and methods

### 2.1. Site

The site (45°26'N, 4°17'E) is a part (15 ha) of a steel mill, located at Chateaufort–Rive de Gier, near Saint-Etienne (Loire, France). It has been used from 1850 to 2001 as an open-cast discharge for disposing of steel mill wastes. The technosol is derived from the progressive transformation of tailings from casting operations in the steel mill [5,14]. The sandy topsoil is mainly composed of quartz, calcite, and oxides of Fe (Magnetite, Wustite, and Hematite), Mg (Periclase and Brucite) and Mn, with a pH of 11.8. It is poor in OM and nutrients, with high total TE concentrations notably for As, Cr, Cu, Ni, Mo, Pb and Zn (Table 1) [6]. Risk-assessment is site-specific

in France, and Canadian and Dutch guideline values are only listed for the comparison purpose (Table 1). The EDTA-extractable Cu and Zn fractions are low, i.e. Cu:  $3.5\% \pm 0.1$  in the UNT and amended soils and Zn: 10% (CSS) to 14% (UNT) (Table 1). Based on 0.01 M CaCl<sub>2</sub>-extractable concentrations, Al, Mo, Ni and Cr are more mobile in the UNT soil than Cu and Zn, whereas As, Cd, Pb and V are below the (ICP-OES) detection limit, but all values remain very low compared to total soil contents (Table 1 and supplemental information S1). The climate is semi-continental with rainy summers and dry winters. Average annual temperature is 12 °C (min. 4 °C in January, max. 20 °C in July/August). Average annual rainfall is 741 mm. The selected untreated area was devoid of vegetation (median recovery rate: 0%).

### 2.2. Experimental set up

Topsoils (0–10 cm layer, 50 kg) used for the pot experiment were collected in field plots implemented at the site for testing in situ stabilization/phytostabilization, just after their set up during the winter 2009–2010 [6]. These nine randomized plots (50 m<sup>2</sup> each) consist in three soil treatments in triplicates: untreated soil (UNT, soil pH 11.8), ramial chipped wood (RCW, 500 m<sup>3</sup> ha<sup>-1</sup>, pH 9.4), and composted sewage sludge (CSS, 120 t DW ha<sup>-1</sup>, pH 9.3) (Table 1). Amendments were incorporated into the soil by a shallow ploughing (10–15 cm depth). An uncontaminated sandy topsoil (CTRL, pH 7.9, 0–20 cm), was collected in a kitchen garden, Gradignan, Gironde, France. Topsoils were air dried and sieved (<5 mm, nylon mesh).

In February 2011, to complete the experimental layout, aliquots (1 kg air-dried soil) of UNT soil were amended with either vermiculite (5% of air-dried soil weight, w/w) combined with compost (5%) made of pine bark and poultry manure (VOM) or zerovalent iron grit (1%) combined with compost (5%, OMZ) (in triplicates). These materials were previously described [15]. All soil aliquots were manually homogenized by rotation in 2-L plastic flasks. One kg of each soil was placed in plastic pots (11 cm × 11 cm × 11 cm, 1.3 L), in triplicates. Therefore, the pot experiment included six treatments, i.e. UNT, RCW, CSS, VOM, OMZ, and CTRL, in triplicates. One Rhizon MOM moister samplers (Eijkelkamp Agrisearch Equipment, The Netherlands) was inserted with a 45° angle into each potted soil.

Potted soils, with a bottom cup to avoid any leaching, were watered and maintained five times a week at 70% of water holding capacity (WHC, 10% of air-dried soil) with deionized water, and allowed to react for a 4-week period at 20 °C in the laboratory. Seeds of *F. pratensis*, *H. lanatus*, and *P. lanceolata* were collected in 2010 in a long-term Cd/Ni contaminated plot of the Louis Fargue field trial, Bordeaux, France [16,17]. A mixed stand, i.e. 0.5 g of *F. pratensis*, 0.1 g of *H. lanatus*, and 0.1 g of *P. lanceolata*, was sowed in all pots (February 2011) and cultivated (15 weeks after seed germination) in a greenhouse [1340–7200 μmol photons m<sup>-2</sup> s<sup>-1</sup>, night/day: 3.9/13.1 °C], in a fully randomized design. Pots were daily weighed and watered with deionized water when required without loss from drainage. NPK fertilizer (15-15-15, 11 g pot<sup>-1</sup>) was applied to avoid N and P deficiencies. Seven weeks after germination, visible symptoms on shoots were recorded. Then shoots (length >2 cm) were cut (Cut 1) 1 cm above the soil surface for both grasses and at the petiole (with 2 leaves left per rosette) for *P. lanceolata*, and sorted by plant species. Dwarf plants (shoot length <2 cm) were left for the second cut (Cut 2). Shoots were washed twice with deionized water, blotted with filter paper, placed in paper bags, oven dried at 60 °C to constant weight for 72 h, and then weighed for determining the shoot DW yield. Fifteen weeks after germination, shoots were cut (Cut 2), weighed, and managed on the same way.

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