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Research article

Non-destructive soil amendment application techniques on heavy metal-contaminated grassland: Success and long-term immobilising efficiency

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ABSTRACT

Extensive contamination of grassland with cadmium (Cd), lead (Pb) and zinc (Zn) is a typical problem close to Pb/Zn smelter sites. The entry of Cd or Pb into the food chain is very likely, as are toxicity effects of Zn in plants. Previous promising results from pot and field experiments showed the high potential of using amendments for immobilisation to reduce metal input into the food chain via crops grown on smelter-contaminated soils at Arnoldstein (Austria) (Friesl et al., 2006). The aim of this study was to find a practical solution for large-scale contaminations in hilly regions that avoids erosion. Field application of amendments without destroying the vegetation cover (grassland) involved two approaches: (a) slurrying (Slu) the amendments into cut gaps in the vegetation cover and (b) injecting (Inj) the amendments through the vegetation cover. Here, we investigate the immobilising and long-term efficiency of treatments [gravel sludge (2.5%) + red mud (0.5%) (GS + RM)]. Risk assessment was based on soil, plant and water samples taken over a period of 10 years. Ammonium-nitrate-extractable Cd was reduced up to 50%, Pb up to 90%, and Zn over 90%. Plant uptake into the grass mixture and narrow leaf plantain was significantly reduced for Cd, Pb, and Zn. Harvesting early in vegetation period can further reduce uptake and meet the threshold for fodder crops. The reduction of these elements in the seepage water in 24 samplings within these 10 years reached 40%, 45% and 50%, respectively. Immobilisation increased microbial biomass and decreased human bioaccessibility for Pb. Our investigation of the long-term efficiency of GS + RM in all treatments shows that the Slu and Inj amendment application techniques have promising potential as a realistic and practical method for extensively contaminated hilly land. Slurrying performed best. We conclude that grassland remediation methods involving tillage are counterproductive from the viewpoint of bioaccessibility and soil protection and therefore should be avoided.

1. Introduction

Mining and smelting is a key source of heavy metal deposition onto surrounding areas. Besides industrial areas, also garden soils (Douay et al., 2008), arable soils (Neugschwandtner et al., 2008) and grassland (Vogel-Mikus et al., 2005) are affected. Friesl-Hanl et al. (2009) provide an overview of "famous" smelter sites all over the world, and in many cases hilly grassland is affected, e.g. in Austria (Friesl et al., 2006) or Slovenia (Vogel-Mikus et al., 2005). Hilly regions additionally frequently suffer from soil erosion due to tillage or other invasive surface treatments if the protecting vegetation cover is destroyed. One potential consequence is wind and water erosion along with further dispersion of trace elements (TE). Areas with a permanent vegetation cover (e.g. grassland) are characterised by soil losses that are generally more than an order of magnitude lower than those on arable land. Cerdan et al. (2010) estimate an erosion rate of 3.6 t per hectare and year for arable areas in Europe. For Austria, Strauss and Klaghofer (2006) reported erosion rates between 8 and 72 t per hectare and year for ploughed plots where soil losses were influenced solely by one weather

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event. One extreme event in a different watershed was responsible for the highest soil loss: one field had a total soil loss of almost 300 t per hectare arable land. Heavy metal distribution is also based on the fact that the smallest particles, which contain the highest heavy metal concentration, are eroded most. Negative effects of erosion include organic matter loss, reduction in water storage capacity and water pollution by nutrients and, in the present context, contaminants.

The traditional option for applying soil amendments to immobilise heavy metals is surface application combined with or followed by tillage. Applying amendments on the surface without tillage, however, fails to reach the required efficiency. A homogeneous mixture cannot be gained without destroying the vegetation cover. In the latter case, erosion is the consequence. This calls for approaches that avoid erosion despite applying soil amendments and improve grassland use. To our knowledge the hilly region of Arnoldstein is the only example where different application techniques were tested with respect to heavy metal immobilisation. Non-invasive techniques for applying liquid manure were investigated by Chen et al. (2001). Those authors compared the use of a soil aerator, a sleighfoot applicator and an injector for the incorporation of liquid manure. Their aim was to avoid ammonia volatilisation, so that the method is not directly applicable for immobilising amendments.

The efficiency of every remediation technique must be assessed. For experiments in field soils, plant and water samples that consider both mobile and bioavailable metal fractions are suitable indicators for risk assessments (Wahle and Kördel, 1997). In this study, we assess the plant uptake in different species (grass mixture and narrow leaf plantain) and compare the values with legal compliance levels. Some vascular plants are known to concentrate trace metals and to be suitable indicators of contaminated sites. Narrow leaf plantain (*Plantago lanceolata* L.) is one indicator for metal uptake from contaminated sites (Kos et al., 1996). Using different plants with differing uptake mechanisms (monocots vs. dicots) as well as different time points in the vegetation period may provide even better insights into efficacy.

Soil pore water samples have also been collected. They indicate that the mobile fraction of heavy metals, as total or pseudo-total concentration, are poor eco- and human toxicology indicators (Clemente et al., 2008). Moreno-Jiménez et al. (2011) proposed that in situ pore water sampling could enhance the realism of risk assessment on contaminated sites. To assess the remediation impact on microorganisms, phospholipid fatty acid extractions (PLFA) to determine microbial community structure (Frostegard et al., 1996) have been applied.

Many batch or pot experiments were conducted on the immobilising of TE by several amendments (Rinklebe et al., 2016; Shaheen and Rinklebe, 2015a; Shaheen et al., 2015b, 2015c, Karer et al., 2015) but looking at short-term effects.

Long-term effectiveness of the applied amendments is an important factor determining the application of the immobilising technique. Long-term monitoring of contaminants should be part of any successful management scheme for in-situ remediated areas (Vangronsveld et al., 2009). Nonetheless, until now only few successful long-term field experiments have been reported (Kennen and Kirkwood, 2015).

The hypothesis for this study is that non-destructive application techniques of soil amendments for TE immobilisation are as effective as destructive tillage. The novelty of this study is on the one hand the comparison of application techniques and on the other hand the long-term monitoring, which is still very seldom available for applied gentle remediation options (GRO).

The objectives of the present study were (i) to compare methods for the application of soil amendments in the upper soil horizon while maintaining the vegetation cover to prevent erosion and (ii) to assess the long-term effect of amendments on the mobilisation of heavy metals, on microorganisms, plants and simulated human toxicological effects of the contaminants.

2. Materials and methods

2.1. Site description

The site is situated in the southern part of Austria, close to the border to Italy and Slovenia. In 1992 the Pb/Zn smelter at Arnoldstein (Austria) closed and emissions ceased. Approximately five hundred years of emissions (Pb, Zn, Cd, and to a lesser extent Cu, As) were dispersed over the surrounding area, which is used for housing (playgrounds), horticulture, forestry, and agriculture. More data are given in Friesl et al. (2006), Drasch et al. (2000), Kasperowski (1993) and Halbwachs et al. (1982) about emission data, contamination levels, intoxication of horses and investigations of human blood and urine. Recent emissions from the industrial area (e.g. recycling of Pb accumulators, incineration of hazardous waste and household waste, production of polymers) are lower than former emissions but explain the ongoing elevated Pb and Cd depositions (Luftgütesituation im Raum Arnoldstein, 2014).

The experimental site was chosen 300 m west of the smelter stalk in Arnoldstein, Carinthia, Austria (latitude: 46°33′13.74″; longitude: 13°41′23.70″) (Soil D). In this glacially influenced region a Leptosol developed on lime-free sandy loam (Table 1) (IUSS Working Group WRB, 2007) and is used as grassland. Investigations of agricultural soils in this area of the Gail valley showed significant contaminations with Pb (<5870 $mgkg^{-1}$), Zn (<3480 $mgkg^{-1}$), Cd (<24.4 $mgkg^{-1}$), Cu (<188 $mgkg^{-1}$), and As (<65.9 $mgkg^{-1}$) (Horak, 2001). Heavy metals of geological origin are also present in the subsoil (Friesl et al., 2006). Nevertheless, heavy metal contents in the soil profile on the field site decrease for Cd from 16 $mgkg^{-1}$, for Pb from 1500 $mgkg^{-1}$ and for Zn from 2000 $mgkg^{-1}$ in the upper horizon (0–10 cm) to 10 (Cd), 1000 (Pb), 1500 $mgkg^{-1}$ Zn in the next horizon (10–30 cm) and to 5 (Cd), 700 (Pb) and 900 $mgkg^{-1}$ (Zn) below 30 cm. Further characteristics are given in Tables 1 and 2.

The microclimate of the Gail valley is influenced by its east-west direction. In autumn and winter, stable inversions occur, while during the rest of the year the wind direction alternates between west and east. Yearly precipitation is about 1300 to 1400 mm with two maxima, one in summer and the other in autumn.

2.2. Amendments

In the field experiment we used a mixture of 2.5% gravel sludge (GS) (pH = 8.2) and 0.5% red mud (RM). Gravel sludge is a fine-grained waste product of the gravel industry and consists of 40–65% SiO_2, 10–14% Al_2O_3 3–7% Fe_2O_3, 5–12% CaO, and 4–6% MgO and content of Pb is 37.4 $mgkg^{-1}$, of Cd is 0.34 $mgkg^{-1}$, and of Zn is 103 $mgkg^{-1}$. Red mud (pH = 10.4) is a by-product of bauxite processing (alumina industry) and originated from Hungary. It consists of about 15–17% Al_2O_3, 12–14% SiO_2, 39–43% Fe_2O_3, and 8–10% Na_2O, and content of Pb 158 $mgkg^{-1}$, of Cd is 4.1 $mgkg^{-1}$, and of Zn is 334 $mgkg^{-1}$. These amendments were used because of their promising results (Friesl et al., 2006) in pre-experiments and their availability in large quantities.

2.3. Set-up of the field experiment

Four different application treatments were applied in May 2004 parallel to the set-up of the field experiments on arable land (Friesl et al., 2006). The mixture was applied to replicated (n = 4) 2 × 2 m