Science of the Total Environment 468–469 (2014) 598–608

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Elements uptake by metal accumulator species grown on mine tailings amended with three types of biochar

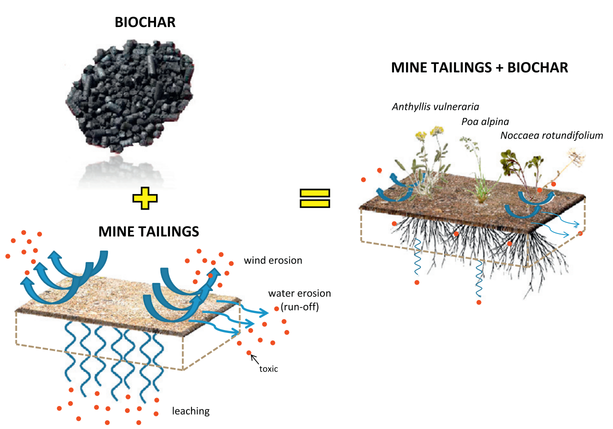
G. Fellet [a,*], M. Marmiroli [b], L. Marchiol [a]

[a] Department of Agriculture and Environmental Sciences, University of Udine, Via delle Scienze 208, I-33100 Udine, Italy
[b] Department of Environmental Sciences, Section of Genetics and Biotechnologies, University of Parma, 43100 Parma, Italy

HIGHLIGHTS

- Biochar from manure pellets and prune residues reduces Cd and Pb plant accumulation.
- Biochar increases the biomass of the facultative metallophytes *Anthyllis vulneraria* and *Poa alpina*.
- Biochar affects the bioavailability and leachability of the inorganic pollutants.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 January 2013
Received in revised form 5 August 2013
Accepted 23 August 2013
Available online xxxx

Editor: F.M. Tack

Keywords:
Biochar
Mine tailings
Heavy metals
Phytostabilization
SEM/EDX

ABSTRACT

Mine tailings are of great concern due to the risk their toxic inorganic elements pose to the environment. The application of biochar as an amendment may be a solution to reduce the risk of pollutant diffusion. The main purpose of the research was to verify the effects of different types of biochar produced from different feedstocks (pruning residues, fir tree pellets and manure pellets) on changing the substrate conditions to promote plant growth for the phytostabilization of mine tailings. The SEM/EDX characterization showed different structures in terms of porosity and granulosity as well as the element composition.

The plants used in the pot experiment were *Anthyllis vulneraria* subsp. *polyphylla* (Dc.) Nyman, *Noccaea rotundifolium* (L.) Moench subsp. *cepaeifolium* and *Poa alpina* L. subsp. *alpina*. The biochars were applied at three doses: 0, 1.5 and $3\%_{dw}$. Although to different extents, the biochars induced significant changes of the substrates in terms of pH, EC, CEC and bioavailability of the metals. The biochar from manure pellets and pruning residues reduced shoot Cd and Pb accumulations. The former also led to a higher biomass production that peaked at the1.5% dose.

Biochar has great potential as an amendment for phytoremediation but its effects depend on the type of feedstock it derives from. The characteristics of the substrate to be treated are crucial for the biochar selection.

1. Introduction

Mine wastes are of great concern due to their high metal concentrations and subsequent contamination of the environment and the risk

* Corresponding author. Tel.: +39 432 558608; fax: +39 432 558603.
E-mail address: guido.fellet@uniud.it (G. Fellet).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.08.072

posed to human health (Cobb et al., 2000). In the past, large amounts of mining and industrial wastes were dumped in the vicinity of the sites where they were produced and no further precautions were taken to avoid contamination of the surroundings. The European Environmental Agency (2007) estimates that at least 250,000 polluted sites in member states require urgent remediation. Phytotechnologies potentially offer a series of cost-effective in situ alternatives to conventional technologies for remediation of low to medium contaminated matrices (Mench et al., 2010).

The term phytostabilization refers to a type of phytotechnology that belongs to the general process of site treatment called phytoremediation. Phytostabilization aims at immobilizing the pollutants in a contaminated substrate by establishing vegetation on top of the polluted material. This green cover avoids the diffusion of the pollutants by physically reducing wind erosion and water run-off. Through water uptake, plants can directly and indirectly lower the mobility of pollutants hindering groundwater contamination. Phytostabilization can thus be considered as a temporary or even long-term solution for the containment of xenobiotics in areas such as mine dumping sites. In these sites, the application of biochar (a biomass derived black carbon) to mine wastes may be a solution to reduce leaching of pollutants. In fact, the application of biochar as an amendment has proven to be effective in improving soil physical and chemical characteristics: biochar can increase nutrient retention and avoid leaching losses, hence increasing the cation exchange capacity (CEC) (Glaser et al., 2002; Lehmann et al., 2003; Major et al., 2010a); it improves the water retention capacity (Glaser et al., 2002); it affects the pH (Hossain et al., 2010; Uchimiya et al., 2010) and soil respiration (Smith et al., 2010).

The application of biochar as an amendment has recently captured the attention of the scientific community because it increases carbon sequestration, hence decreasing the amounts of CO_2 (Spokas et al., 2009) that enter the atmosphere. Its influence on the soil properties also extends to the mobility of inorganic elements such as Cd, Cu, Pb and Zn (Karami et al., 2011; Park et al., 2011) or organic compounds like polychlorinated biphenyls (PCBs) or polyaromatic hydrocarbons (PAHs) and pesticides (Denyes et al., 2012). The biochar influence and its performance as a soil conditioner depend on its properties that derive from the material used to produce it (feedstock) and the pyrolysis process (Lehmann, 2007).

Due to its resistance to degradation (Krull et al., 2006), its effects may last for a very long time. In addition, the reduction in terms of metals bioavailability and other modifications to the substrate induced by the application of biochar may be beneficial to the establishment of a green cover on top of the wastes to acquire long-term phytostabilization. Indeed, as regulators and stakeholders are currently focusing their attention on the bioavailability and mobility of contaminants and the consequent effects on the environment rather than considering just their total concentrations in soil (Beesley et al., 2011), new treatments for contaminating wastes that may have effects on these properties are of great interest.

Mine tailings are wastes stocked in areas where agriculture should not be practiced for safety reasons and in most cases they can only be considered as hazardous areas to be confined. In this context, biochar can be an interesting option to deal with such areas by combining C-sequestration with green approaches of remediation. Most studies so far have involved crops and crop plants as they are better known from the agronomic management point of view and produce high biomass. The latter is not so crucial, although important for limiting wind erosion and reducing pollutants leaching. When the aim of the green approach is phytostabilization plants are neither harvested, removing the metals from the site, nor is the plant material utilized as food or fodder. With regard to the choice of species for phytostabilization in areas such as dumping sites, it is more convenient to choose local species and potentially more likely to lead to a successful outcome because they are already adapted to the pedoclimatic conditions and, most importantly, are naturally capable of growing on a substrate with high contents of trace elements.

In this paper, we present and discuss the results from a pot experiment aimed at verifying the effects of different types of biochar produced from different feedstocks (pruning residues, fir tree pellets and manure pellets) when used as an amendment to improve the conditions of mine wastes collected from a real dumping site that requires urgent remedial measures due to the high content of inorganic pollutants and the risks these pose to the environment. The plants used in the experiment were obtained from seeds of three species (*Anthyllis vulneraria* subsp. *polyphylla* (Dc.) Nyman, *Noccaea rotundifolium* (L.) Moench subsp. *cepaeifolium* and *Poa alpina* L. subsp. *alpina*) collected on the dumping site and thus adapted to the extreme conditions in terms of concentrations of toxic inorganic elements.

2. Materials and methods

2.1. Origin of the mine tailings and biochars

The mine tailings used for this experiment were collected from the mining site at Cave del Predil (NE, Italy) (Fellet et al., 2011). About 200 kg were collected from the site and homogenized. Table 1 shows the pseudo-total element content of the mine tailings and biochars. The latter were produced using three feedstocks: (i) pruning residues from orchards (ROM); (ii) fir tree pellets (ABE); (iii) manure pellets (70%) mixed with fir tree pellets (30%) (MAN). The first type of biochar was produced at a discontinuous pyrolysis plant (Romagna Carbone Snc, Bagnacavallo, Italy); the highest treatment temperature (HTT) was 500 °C; the black carbon content was 23.1% and BET surface area was 141 $m^2\ g^{-1}$. The following element ratios were measured: 80.11 (C/N), 0.30 (H/C) and 0.12 (O/C). The second and third types of biochar (ABE and MAN) were produced at the University of Udine using the basic model of microgassificator LuciaStove without electric ventilation (©2009 World Stove) (350 °C < HTT < 400 °C). The reason for mixing fir tree pellets with manure pellets was that the LuciaStove would not work with only manure pellets. Tests showed that a minimum of 30% of fir tree pellets were enough to obtain complete pyrolysis. The element ratios for ABE and MAN were 408 (C/N), 0.04 (H/C), 0.22 (O/C) and 35.0 (C/N), 0.05 (H/C) and 0.39 (O/C), respectively. The ash contents were: 1.4%, 36% and 46% for ABE, MAN and ROM, respectively.

The biochars were crushed and sieved to less than 2 mm prior to applying to the mine tailings. Since the yield of the LuciaStove was usually low and its feedstock capacity was limited (<1 kg), several cycles were necessary to reach the required quantity of biochar to perform the whole experiment. All the biochar produced from the same feedstock was mixed together and the whole amount was sampled for laboratory analysis.

2.2. Biochar SEM/EDX analysis

The three biochars were analyzed utilizing a scanning electron microscopy with X-ray microanalysis.

Sample preparation for SEM/EDX analysis consisted of drying the biochar at 75 °C for a week then grinding with a ceramic mortar and pestle. The resulting powder was attached on a microscope slide with a double adhesive carbon tape. The slides were produced in triplicate and covered with colloidal graphite under vacuum to ensure electron conductivity. Each slide was analyzed singly to avoid cross-contamination in the microscope sample chamber. A Jeol 6400 SEM (Jeol, Osaka, Japan) was used equipped with an Oxford X-ray detector managed by the INCA software (version 4.0) (Oxford Instruments, Oxford, UK). The operating parameters were set as follows: Electron beam energy at 20 keV, working distance 13 mm, dead-time of X-ray acquisition between 15 and 20%, the magnification varied according to needs. Line-scan analyses were performed to analyze the morphology and content of the three types of biochar. Dot maps of each element present in the samples were acquired through a series of scans (up to 5000) of the whole sample, each lasting 30 s, in order to acquire reliable maps.