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Research article

Exchangeable Sodium Percentage decrease in saline sodic soil after Basic Oxygen Furnace Slag application in a lysimeter trial

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ABSTRACT

The Basic Oxygen Furnace Slag results from the conversion of hot metal into steel. Some properties of this slag, such as the high pH or calcium and magnesium content, makes it suitable for agricultural use as a soil amendment. Slag application to agricultural soils is allowed in some European countries, but to date there is no common regulation in the European Union.

In Italy soils in coastal areas are often affected by excess sodium, which has several detrimental effects on the soil structure and crop production. In this study, carried out within an European project, the ability of the Basic Oxygen Furnace Slag to decrease the soil Exchangeable Sodium Percentage of a sodic soil was evaluated. A three-year lysimeter trial with wheat and tomato crops was carried out to assess the effects of two slag doses (D1, 3.5 g $kg^{-1}year^{-1}$ and D, 2, 7 g $kg^{-1}year^{-1}$) on exchangeable cations in comparison with unamended soil. In addition, the accumulation in the topsoil of vanadium and chromium, the two main trace metals present in the Basic Oxygen Furnace Slag, was assessed. After two years, the soil Exchangeable Sodium Percentage was reduced by 40% in D1 and 45% in D2 compared to the control. A concomitant increase in exchangeable bivalent cations (Ca^{++} and Mg^{++}) was observed. We concluded that bivalent cations supplied with the slag competed with sodium for the sorption sites in the soil. The slag treatments also had a positive effect on tomato yields, which were higher than the control. Conversely the wheat yield was lower in the slag-amended soil, possibly because of the toxicity of vanadium added with the slag. This study showed that Basic Oxygen Furnace Slag decreased the Exchangeable Sodium Percentage, but precautions are needed to avoid the build up of toxic concentrations of trace metals in the soil, especially vanadium.

1. Introduction

Secondary soil salinization, i.e. the salinization caused by human activities, is a widespread phenomenon. Irrigation with saline water, poor drainage conditions and over-pumping leading to seawater intrusion are among the most important causes of secondary salinization worldwide (Daliakopoulos et al., 2016). Soil salinization is considered to be a major factor limiting crop production in arid coastal areas (Li et al., 2012; Sparks, 2003) and a driving factor for desertification (Geeson et al., 2003; Abu Hammad and Tumeizi, 2012).

Moderate to severe secondary salinization affects between 3.8 (Stanners and Bourdeau, 1995) and 4 Mha in Europe (Van-Camp et al., 2004). In the Mediterranean region, 25% of irrigated agricultural land is significantly affected (Mateo-Sagasta and Burke, 2012). In the coming years, salinization-related issues are expected to be exacerbated by climate change, for example due to the increase in ground water pumping in coastal areas (Daliakopoulos et al., 2016).

Saline, sodic and alkaline soils are included within the category of saline soils (Van Beek et al., 2010). Soil sodicity consists of an excess of exchangeable sodium (Na^{+}) compared to other soil cations such as calcium (Ca^{++}) and magnesium (Mg^{++}). In Italy, as well as in other Mediterranean countries, the main cause of soil sodicity

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is saline intrusion in coastal aquifers and irrigation with saline water (Cucci et al., 2003), the most affected being the coastal areas of southern regions, e.g. Apulia, Campania and Sicily.

The excess of exchangeable sodium can significantly affect plant growth via direct and indirect mechanisms including: sodium (Na^+) or chloride toxicity, competition or interference due to uptake of other cations and micronutrients (Rengasamy et al., 2003) and the osmotic effect on water uptake (Grewal, 2010).

Sodicity is expressed by of the Sodium Adsorption Ratio (SAR) or the Exchangeable Sodium Percentage (ESP). ESP is calculated as the percentage of exchangeable sodium respect to Cation Exchange Capacity (CEC) and is used to describe the risk associated with the level of sodium in the soil. If the ESP equals or is >15%, the soil is sodic (Richards, 1954). Above this threshold, many soils show a sharp deterioration in physical properties, i.e. dispersion of aggregates (Abrol et al., 1978) and consequent deterioration of water and air movement (Acharya and Abrol, 1978; Gardner et al., 1959).

Leaching of exchangeable sodium by the replacement with calcium ions is the most efficient way to reduce ESP in the rooting area (Qadir et al., 2001). Thus, for sodic soil reclamation, different categories of chemical amendments can be used, such as soluble calcium salts (e.g. gypsum, calcium chloride), acids or acid forming substances (e.g. sulphuric acid, iron sulphate, aluminium sulphate, pyrite), and calcium salts of a low solubility (e.g. ground limestone).

Gypsum is the most commonly used product for sodic soil reclamation in agriculture. However, it is expensive, as the production entails high costs for extraction, material purchase, and transport from the site of generation to the site of use (Ghafoor et al., 2001; Iho and Laukkanen, 2012). Thus, the use of alternative and cheaper materials, such as industrial by-products, would be more suitable from the perspective of a circular economy strategy. The large content of calcium and magnesium oxides makes Basic Oxygen Furnace Slag (BOFS) a potential alternative material for sodic soil reclamation.

BOFS is a by-product of the steel industry, produced in BOF steelmaking where hot metal is refined with oxygen and scrap is added in order to balance the heat. BOFS is usually subjected to iron removal, which is recycled back into the steelmaking processes. The inert BOFS can be used in road pavements, bottom ballast and aggregates in asphaltic concrete and for quarry filling and CO_2 sequestration (Polettini et al., 2016). Slags have been successfully used to remove various organic pollutants from wastewater (Ali et al., 2012) or as physical stabilizers, to reduce the mobility and availability of some metals (Lee et al., 2014).

Among the various uses, in Europe about 3% of steel slags are used as fertilisers or soil amendments (Euroslag, 2010). In northern Europe steel slag is used most commonly as a liming agent to increase soil pH (Lopez et al., 1995). There is evidence that slags improve phosphate availability, due to their soluble silicate content, which can increase phosphate desorption from solid phases (Branca and Colla, 2012). Slags can also be used as a silicon source for high demanding crops such as rice (Pereira et al., 2004), or to provide plants with major elements, such as calcium and magnesium (Peregrina et al., 2008) or micronutrients, such as iron, zinc, boron and cobalt (Wang and Cai, 2006).

However, the feasibly of slag application to agricultural soils depends on several factors, and lack of knowledge regarding the bioavailability of trace metals in the slag, especially the most abundant, chromium (Cr) and vanadium (V), is one of the main concerns (Mäkelä et al., 2012). Recent investigations have highlighted the possibility of removing V from BOFS using different microorganisms (Mirazimi et al., 2015). Anion exchange resins in both batch and column tests are also efficient in removing and recovering V from steel slag leachate (Gomes et al., 2017). Nevertheless, these trace metals still represent a critical issue for slag application to agricultural soils (Larsson et al., 2015). During the aging of slags, for example, the proportion of the more soluble vanadium species can increase (Chaurand et al., 2007), leading to potentially higher bioavailability once applied to the soil. Although the biological importance of vanadium as a minor nutrient for plants has been debated (Venkataraman and Sudha, 2005), it is widely accepted that a high concentration of this element in soil can be harmful to a variety of organisms (Imtiaz et al., 2015). Little is known about vanadium phytotoxicity. Ranges of effective toxic concentrations (EC_{50}) vary from 18 to 510 mg V kg^{-1} soil (Larsson et al., 2013) for barley and tomato plants or 21–180 mg V kg^{-1} soil for a set of selected crops and wild species (Smith et al., 2013). Chromium in its hexavalent oxidation state is highly toxic, as it is a strong oxidising agent, and free radicals are formed during the reduction of Cr(VI) to Cr(III) (Mathur et al., 2016). However, only a small amount of Cr in the BOFS is in the hexavalent form (Chaurand et al., 2007). The other stable form of chromium, Cr(III), can inhibit root and shoot growth in selected species at concentrations as low as 100 mg kg^{-1} soil (Lopez-Luna et al., 2009).

In Italy the application of slags to agricultural soils is forbidden, since they are classified as waste (Italian Ministerial Decree, 1998; Italian Ministerial Decree, 2006). Overall the use of BOFS as a soil amendment is also limited by a lack of knowledge regarding its potential benefits for crop cultivation, which also depends on the different soil characteristics. Although the use of BOFS for agricultural purposes is not new, its application to alkaline or saline/sodic soils, related to the possible beneficial effects due to the calcium/magnesium supply, have not been investigated to date. In fact, several studies have focused on the use of slags as a liming material (Ali and Shahram, 2007). However, few studies have investigated the following: the fertilizing or amending properties; the possible risks associated with the presence of trace elements (Kühn et al., 2006) in the slags applied to neutral and alkaline soils in Mediterranean regions (Branca et al., 2013); the effects of BOFS on neutral, alkaline, well drained soils (Wang and Cai, 2006), typical of Mediterranean regions; and the interactions with salty irrigation water on sodic soil and the behavior of trace elements have not been studied until now. To the best of our knowledge, there are no studies that have assessed the effects of slag applications to these kinds of soil conditions. Previous studies on the leaching behavior of slags have been carried out only with laboratory tests (Motz and Geiseler, 2001) or through column tests (Pistocchi et al., 2012), while in this study the lysimeter test was performed, which was close to the field conditions. The SLAGFERTILISER project, the “Impact of long-term application of blast furnace and steel slags as liming materials on soil fertility, crop yields and plant health” (RFSR-CT-2011-00037), funded by the Research Fund for Coal and Steel, contributed to filling this knowledge gap through the assessment of fertilizing and liming properties of iron and steel slags, such as BFS, BOFS and LFS (Ladle Furnace Slag) under different soil conditions in Europe (Morillon et al., 2015).

Our Italian case study dealt with the application of BOFS from ILVA Steelworks in Taranto (Italy) to alkaline soils affected by excess sodium. According to a previous study and the achieved preliminary results (Branca et al., 2013), new experimental tests were planned. The objectives of the experimental trial described in this paper were to evaluate:

1) the potential of two different BOFS doses in decreasing the exchangeable sodium content of saline sodic soil irrigated with saline water;
2) the effects on tomato and durum wheat growth and productivity in comparison with untreated controls;
3) the accumulation of Cr and V in the soil after three years of slag application and their uptake by plants.