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Flocculation of sewage sludge with $FeCl_3$ modifies the bioavailability of potentially toxic elements when added to different soils

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ABSTRACT

Land application of sewage sludge (SS) is a convenient way of disposal compared to incineration or landfill, but can result in accumulation of potentially toxic elements (PTE) in agricultural soils. The environmental risk associated with PTE accumulation in soils that received several SS applications depends mainly on soil pH and SS treatments. We studied the effects of addition to soil of SS treated and untreated with $FeCl_3$ on the biological availability of Zn, Ni, Cd and Cu to oilseed rape (*Brassica napus*). The plants were grown on an acid and a neutral soil in a greenhouse incubation experiment. The following treatments were carried out: (i) unamended control soil, (ii) sewage sludge amended soils kept bare throughout the experiment and (iii) sewage sludge amended soil planted with oilseed rape. Amended soils received either untreated SS or $FeCl_3$ treated SS at a rate equivalent to 75 t d.w. $ha^{-1} y^{-1}$.

Plant growth was enhanced by addition of both untreated SS and $FeCl_3$ treated SS, but the latter produced a lower shoot dry matter than untreated SS, particularly in the acid soil. Evaluation of biological availability of PTE was performed by three different methods: plant shoot analysis, single DTPA-extraction, and sequential fractionation procedure (SEP) in soil. After 50 days, accumulation of PTE was considerably larger in plant shoots grown on the acid soil and amended with $FeCl_3$ treated sludge. Conversely, the $FeCl_3$ treated SS reduced Cd, Ni and Zn accumulation in shoots in the neutral soil in comparison to untreated SS. Copper was generally unaffected by SS treatment in both soils. Plants significantly decreased the DTPA-extractability of Cd, Ni and Zn in both soils that received $FeCl_3$ treated SS, but they did not change it in soils that received untreated SS.

These different behaviors may be explained by the different mechanism involved in metals stabilization in the two soils: adsorption on Fe and Mn oxides in the neutral soil, precipitation and organic complexation in the acid soil.

The chemical flocculation treatment of waste water with $FeCl_3$ and addition to soils reduces PTE availability in neutral soils amended with SS, but markedly increases their solubility and bio-availability in acid soils. Therefore, the application of SS obtained from flocculation with $FeCl_3$ should be restricted to neutral or calcareous soils.

1. Introduction

After the implementation of EU Directive 91/271/EEC in 2005 regarding wastewater treatment, the production of sewage sludge (SS) in Europe was expected to increase (Egiarte et al., 2008; Kelessidis and Stasinakis, 2012). Sustainable disposal of this waste product is therefore of growing concern in wastewater management. Land application of SS as amendment to agricultural soils is an economically effective alternative to disposal through landfill, composting or incineration (Hall, 1995; Latare et al., 2014).

Generally, SS have large organic matter as well as plant macro- and micro-nutrient contents and can therefore potentially improve soil productivity (Silveira et al., 2003; Singh and Agrawal, 2008). In fact, SS has been shown to increase the dry matter yield of many crops (Bozkurt and Yarilgaç, 2003; Antolin et al., 2005). However, application to soil may result in nitrate leaching and contamination with potentially toxic elements (PTE) or toxic organic compounds posing risk to human health and environment. Long-term applications can cause PTE accumulation in soil and their transfer to the food chain as well as to groundwater compartments (Dai et al., 2006; Pathak et al., 2009). Furthermore,

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soil amended with contaminated SS can result in PTE build up in plant tissues inducing physiological or metabolic alterations impairing plant growth, development and yield (Gascó and Lobo, 2007; Jamali et al., 2009).

The release, mobility and plant uptake of PTE associated with SS is influenced by several factors such as soil pH, soil organic matter, soil texture, redox potential, Fe oxides content, plant species and metals speciation (Fuentes et al., 2004; McBride, 2003). For example, mobility of PTE in alkaline soils is usually expected to be very low due to their poor solubility, whereas in acidic soils several studies showed contrasting trends with only minor PTE migration in some cases (Camobreco et al., 1996; Dowdy et al., 1991) but significant percolation of Zn, Cr, Cu and Cd in others (Frenkel et al., 1997; Karathanasis et al., 2005; Toribio and Romanyá, 2006).

Dewatering of SS is essential for an efficient management of waste water treatment and coagulants are sometimes added at different treatment steps to speed up thickening operations. Iron chloride ($FeCl_3{\cdot}7H_2O$) is widely used for this purpose during both secondary aerobic/anaerobic treatments to improve water clarification or during tertiary flocculation to remove phosphorous or trace elements and to facilitate dewatering (Buzier et al., 2006; Georgantas and Grigoropoulou, 2005). At neutral to alkaline pH, ferric ions precipitate as amorphous Fe hydrated oxides or oxy-hydroxides, which have relatively stable and reproducible surface properties and can be efficient sinks for many cations and anions (McBride, 1994). Several divalent metals can be sorbed on the surface or incorporated (immobilised) into the oxide structure, decreasing in this way their bioavailability (Contin et al., 2007, 2008; Schwertmann and Taylor, 1989). In recent years, several attempts have been made to decontaminate sludge prior to its disposal on land. Use of different chemicals such as ferric and ferrous salts, chelating agents and inorganic or organic acids have been reported for extraction of metals (i.e., Cu, Zn, Pb and As) from sludge (Brunori et al., 2005; Codling et al., 2000; Friesl et al., 2004; Ito et al., 2000; Moore et al., 2000; Pathak et al., 2009). The most commonly used products for immobilising contaminants include Fe oxides, ferrous/ferric sulphates and chlorides, and ferrihydrite (Udeigwe et al., 2011).

Currently, there is a lack of data on prediction of effects of $FeCl_3$ treatment on PTE availability after soil application of SS. Our hypothesis is that the addition of $FeCl_3$ during SS flocculation could result in PTE adsorption and fixation on freshly precipitated Fe (hydr)oxides and therefore have a strong impact on plant availability.

In this work, we tested the effect of SS flocculation with $FeCl_3$ and its addition to soils on the biological availability of selected PTE (Zn, Ni, Cd and Cu) to oilseed rape (*Brassica napus*). A plant model integrated with chemical analyses such as plant analyses, sequential extraction procedure (SEP) and DTPA-extraction, were used to assess the changes in toxic metals bioavailability. The capability of the extraction methods to predict PTE availability to plants in two types of soil with different sludge amendment was also compared and discussed.

2. Materials and methods

2.1. Sewage sludge and soils

2.1.1. Origin and properties of sewage sludge

Sewage sludge was sampled from a water treatment station in San Giorgio di Nogaro (Udine, Italy). This treatment plant receives both urban and industrial sewage water (700 000 p.e.), and treats sewage by the conventional activated sludge process. The sludge produced from primary and secondary sewage treatment is anaerobically digested and then treated with flocculants to reduce phosphorous content and improve sludge dewatering (tertiary treatment). The SS used in this work was collected immediately at the end of secondary treatment phase and before any clari-flocculation process. Its main chemical properties and PTE content are presented in Table 1.

Half of the SS was re-suspended and flocculated with $FeCl_3$ at a rate of 40 g Fe kg^{-1} SS d.w. to simulate flocculation as performed in sewage treatment plants. Throughout the whole text we refer to this process as $FeCl_3$ chemical conditioning of water for sludge production (shortly $FeCl_3$ treatment). For the clarity of the manuscript both SS were denominated with respective abbreviations as follows: original untreated SS (O-SS) and $FeCl_3$-treated SS (Fe-SS).

After sludge settling, water was removed and the thickened SS air-dried. Addition of $FeCl_3$ produced a slight decrease in pH of SS and a significant increase in Fe content (Table 1).

Pseudo-total concentrations of metals in each SS were determined by ICP-AES after microwave digestion (USEPA 3051, 1995). Both SS (O-SS and Fe-SS) presented PTE contents below the maximum limits defined by the Council of the European Communities (1986) (86/278/EEC) with the exception of Zn that exceeded the limit defined for acid soils (Table 1).

2.1.2. Origin and properties of soils

The two soils used in this study differed mainly by their pH and were of acidic and neutral (calcareous) nature. The acid soil was sampled near Reana del Roiale (Udine, Italy) and classified as Cutani-Chromic Luvisol (WRB), while the neutral soil sample was collected in the experimental farm of the University of Udine (Udine, Italy) and classified as Calcari-Fluvic Cambisol. Multiple soil samples were collected from the top 25 cm layer, pooled together and sieved (<2 mm). All soils were stored at 5 °C for about a week before starting the pot experiment. A portion of sieved soil sample for both soils was air-dried at room temperature to be used for chemical analyses.

The main characteristics of the two soils are given in Table 2. Particle size analyses were determined by the pipette method (Gee and Dani, 2002). Soil pH was measured in water by a glass electrode (1:2.5 soil to water ratio) (Thomas, 1996), carbonates by calcimeter (Loeppert and Suarez, 1996), saturated paste extraction was used to determine electrical conductivity (EC) (Rohades, 1996), organic C and total N were determined by an automated flash combustion elemental analyser (Nelson and Sommers, 1996), and pseudo total metal concentration was determined by ICP-AES after microwave assisted digestion (USEPA 3051, 1995a).

Table 1
Composition and chemical characterisation of O-SS and Fe-SS.

Sewage sludge properties	O-SS[a]	Fe-SS[a]	Threshold limit[b] pH < 7	pH > 7
pH (H_2O)	6.8	6.1	–	–
Organic C (g kg^{-1})	304	290	>20	>20
Total N (g kg^{-1})	46	42	>15	>15
C/N ratio	6.7	6.9	–	–
Fe (mg kg^{-1})	10,988	30,319	–	–
Mn (mg kg^{-1})	339	368	–	–
Potentially toxic elements (PTE; $\mu g\, g^{-1}$)				
Cd	15.4 ± 0.4	16.6 ± 0.1	20	40
Ni	265 ± 13	252 ± 6.4	300	400
Zn	2.863 ± 74	3.021 ± 45	2.500	4000
Cu	621 ± 22	604 ± 11	1.000	1750
Cr	47.1 ± 3.2	56.4 ± 1.1	–	–
Hg	3.2 ± 0.5	2.9 ± 0.4	16	25
Pb	95.3 ± 8.5	88.1 ± 1.3	750	1200

[a] O-SS: original sewage sludge; Fe-SS: $FeCl_3$ treated sewage sludge.
[b] Land disposal limit acording to European Directive 86/278/EEC, 2015 as function of soil pH.