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Modulation of hexavalent chromium toxicity on *Origanum vulgare* in an acidic soil amended with peat, lime, and zeolite

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HIGHLIGHTS

- Addition of Cr(VI) to an acidic soil increased Cr(VI) and Cr(III) in soil and plant.
- Amendment of peat to a Cr(VI) contaminated soil decreased toxicity in plant.
- Cr(VI) and Cr(III) increased in soil and plant at higher pH in the lime-amended soil.
- Oregano has a certain potential to be used as an accumulator for Cr.

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ABSTRACT

Dynamics of chromate (Cr(VI)) in contaminated soils may be modulated by decreasing its phytoavailability via the addition of organic matter-rich amendments, which might accelerate Cr(VI) reduction to inert chromite (Cr(III)) or high-cation exchange capacity amendments. We studied Cr(VI) phytoavailability of oregano in a Cr(VI)-spiked acidic soil non-treated (S) and treated with peat (SP), lime (SL), and zeolite (SZ). The addition of Cr(VI) increased the concentrations of Cr(VI) and Cr(III) in soils and plants, especially in the lime-amended soil. The plant biomass decreased in the lime-amended soil compared to the un-spiked soil (control) due to decreased plant phosphorus concentrations and high Cr(VI) concentrations in root at that treatment. Oregano in the peat-amended soil exhibited significantly less toxic effects, due to the role of organic matter in reducing toxic Cr(VI) to Cr(III) and boosted plant vigour in this treatment. In the lime-amended soil, the parameters of soil Cr(VI), soil Cr(III), and root Cr(III) increased significantly compared to the non-amended soil, indicating that Cr(VI) reduction to Cr(III) was accelerated at high pH. Added zeolite failed to decreased Cr(VI) level to soil and plant. Oregano achieved a total uptake of Cr(III) and Cr(VI) of 0.275 mg in plant kg^{-1} soil in a pot in the non-amended soil. We conclude that peat as soil amendment might be considered as a suitable option for decreasing Cr(VI) toxicity in soil and plant, and that oregano as tolerant plant species has a certain potential to be used as a Cr accumulator.

1. Introduction

Hexavalent chromium (Cr(VI)) is well-known for its severe toxic effects to plants, animals and humans alike (Choppala et al., 2013a; Kwak et al., 2018). Although geogenic occurence is not impossible, most soil Cr(VI) has anthropogenic origin, with global fluxes

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ranging from 0.43 × 10^6 to 1.18 × 10^6 Mg (Choppala et al., 2017). Its prevalent form in the soil solution is the monochromate (CrO_4^{2-} and $HCrO_4^-$) and the dichromate ($Cr_2O_7^{2-}$ and $HCrO_7^-$) ions, all of which are anionic species. The nature of Cr species which dominate in soil solution depends on pH; $HCrO_4^-$ is dominant at pH 1–6, and CrO_4^{2-} at pH > 6 (Rani et al., 2017). Acidic soils typically have lower ratio of cation-over-anion exchange capacity than neutral-alkaline soils. This is because in acidic soils prevailing minerals are more progressed in weathering and bear higher amount of positive charge per unit mass of clay. Also, they typically have a higher degree of variable charge minerals, and this tends to decrease their usual negative charge at lower soil solution pH values (Khawmee et al., 2013). Hence, acidic soils have the ability to retain higher amounts of anions and lower amounts of cations compared to neutral-alkaline soils (Shaheen and Tsadilas, 2013). This is why lower pH values lead to higher phytoavailability of cations (reported for Cd and Zn by Yang et al. (2017)) and lower of anions (for As in a sorption test reported by Vitkova et al., 2017). Therefore it may be expected that Cr(VI) in acidic soils is strongly retained. There is the risk that if an acidic Cr(VI)-contaminated soil is limed, toxicity may be induced. However, there is no such evidence in the literature. The reason is that in limed soils growth conditions improve considerably (Nascimentode et al., 2016), and thus it is not known which of the following two possibilities will prevail: (a) enhanced Cr(VI) mobility or (b) improved plant growth. If (a) prevails, Cr(VI) plant toxicity will be severe. If (b), boosted plant growth may increase nutrient uptake, thereby decreasing Cr(VI) concentration in plant.

Moreover, it is well documented that Cr(VI) has the ability to be reduced to the relatively inert Cr(III) species in soil. Reduction to Cr(III) is related to soil pH in the sense that it is a known proton consuming reaction, as follows:

Reduction half-reaction: $Cr^{VI}O_4^{2-} + 3e^- + 8H^+ \rightarrow Cr^{3+} + 4H_2O$

Oxidation half-reaction (in case H_2O is the electron donor): $2H_2O^{-II} \rightarrow O^0{}_2 + 4e^- + 4H^+$

Yielding: $Cr^{VI}O_4^{2-} + 5H^+ \rightarrow Cr^{3+} + 0.75O_2 + 2.5H_2O$

Thus the reduction is more favourable at higher pH values. As a consequence, liming an acidic soil would cause a higher rate of Cr(VI) reduction to Cr(III), which would thereby decrease Cr(VI) availability when the reduction procedure is complete. The reduction may also be accelerated when soils are flooded and reducing conditions abound in soil (Xiao et al., 2015); this occurs due to the concurrent oxidation of H_2O^{-II} to $O^0{}_2$, as shown earlier. Also, consecutive flooding/aeration soil conditions affect the dynamics of Cr species, with hexavalent increasing under oxidation conditions in pore water and decreasing under reducing conditions (Shaheen et al., 2014; Rinklebe et al., 2016a). The reduction of Cr(VI) to Cr(III) is also affected by the presence of soil organic matter: it occurs in the expense of organic C (C^0_{org}) oxidizing to $C^{IV}O_4$ (Antoniadis et al., 2017a). An additional factor affecting Cr species dynamics is redox potential (E_H): decreased E_H in acidic soils results in pH increase (Rinklebe et al., 2016b). This is important because added organic matter may cause a decrease in E_H, and thus it could accelerate Cr(VI) reduction to Cr(III) (Bolan et al., 2003a). Other soil factors may also have an important role in the distribution of Cr among its geochemical fractions and in the Cr(III)/Cr(VI) dynamics, such as the presence of amorphous and crystalline forms of Fe-Mn oxides (Langlois and James, 2005; Shaheen et al., 2017).

In soil contaminated with Cr(VI), its toxicity may be mitigated with: (a) stabilization, e.g., by adding to soil a high-CEC sorptive material, such as zeolite, and (b) reduction to inert Cr(III), e.g, by adding organic matter to soil. As for (a), various materials have been used with success, especially in batch sorption tests, mainly positive-charge minerals, such as oxides (Jo et al., 2008; Choppala et al., 2013a) and surfactant-modified zeolites (SMZ) (Song et al., 2015). However, these materials are difficult to be used in plant growth experiments, due to the development of hydrophobic surface (this concerns the use of SMZ) or due to high costs (this concerns use in field experiments). Thus, other abundant and plant-friendly materials could be used instead, such as natural zeolite; being a porous material, zeolite could function as a means of physical entrapment of Cr(VI) (Rangasamy et al., 2014). As for (b), the addition of organic matter has been previously used with several plant species in Cr(VI)-contaminated soils (Rendina et al., 2011; Zhong and Yang, 2012). Organic matter enhances plant growth due to added nutrients and improved soil physical conditions (increased macroporosity, decreased bulk density etc.) apart from functioning as a reducing agent for Cr(VI) to Cr(III).

However, a higher Cr(VI) transfer from soil to plant must be achieved if hyperaccumulators are involved during soil phytoremediation. Such plants have developed mechanisms to accelerate Cr uptake; e.g., Garcia-Gonzalo et al. (2017) reported increased root exudation of soluble organic substances which are capable of binding Cr and transferring it into roots. Higher transfer from soil to plant could be achieved by liming a Cr(VI)-contaminated soil due to decreased Cr(VI) sorption. On the other hand, accelerated Cr(VI) reduction to Cr(III) with liming may result in Cr(VI) stabilization. It has not been recorded in the literature what the net effect of liming would be on Cr(VI) dynamics: desorption or stabilization. In order to study the possible effects, a tolerant plant species should be selected. Oregano (*Origanum vulgare* L.) is a species enduring harsh environmental conditions and could be an ideal species that would behave as an accumulator in a case of enhanced Cr(VI) availability. To our knowledge, oregano has never been tested in similar experimental conditions. The aim of this work was (a) to evaluate Cr(VI) phytoavailability to oregano in acidic and limed soils and (b) to study the effect of added zeolite and peat in Cr(VI) dynamics in soil and plant. We chose oregano, because it is a species with known tolerance in extreme environments, and thus we suspect that it would exhibit tolerance towards Cr(VI).

2. Materials and methods

2.1. Soil, amendments, mixture preparation, and chromium spiking

An acidic soil (sampling, analysis methods are reported in Antoniadis et al. (2016); properties are shown in Table 1) was chosen for the experiment. We created mixtures of soil with lime, with peat and with zeolite. Lime, obtained from a marble quarry

Table 1
Selected physico-chemical properties of the studied soil.

Property	Unit	
pH	–	5.7
Electrical conductivity	dS m^{-1}	0.66
Sand	%	37
Clay		32
Texture	–	Clay loam
Organic carbon	%	0.87
Fe[a]	mmol kg^{-1}	19.61
Al[a]		22.70
Mn[a]		0.77
Cation exchange capacity	$cmol_c$ kg^{-1}	23.46
Olsen-phosphorus	mg kg^{-1}	32.31
Aqua regia Cr		25.28

[a] amorphous oxides extracted with ammonium oxalate.