Research article

Arsenic adsorption and plant availability in an agricultural soil irrigated with As-rich water: Effects of Fe-rich amendments and organic and inorganic fertilisers

Elena Arco-Lázaro, Tania Pardo[*], Rafael Clemente, Mª Pilar Bernal

Department of Soil and Water Conservation and Organic Waste Management, CEBAS-CSIC, PO Box 164, 30100 Murcia, Spain

ARTICLE INFO

ABSTRACT

The use of As-rich water for irrigation in agricultural soils may result in As accumulation in soil and crops, with the consequent risk of its entry into the food chain. The effectiveness of three different Fe-based materials (a commercial iron oxide (Bayoxide®), lamination slag (a by-product of the hot rolling of steel) and a commercial red mud derivative (ViroBind™)) used as soil amendments to minimise the impact of irrigation with As-rich water in an agricultural soil-plant system was evaluated in a pot experiment. Simultaneously, the influence of organic and inorganic fertilisation (olive oil mill waste compost versus NPK fertiliser) on the effectiveness of iron oxide in As adsorption processes was also assessed. The As adsorption capacity of the amendments was determined in a preliminary batch experiment using sorption isotherms. Then, a pot experiment was carried out in a growth chamber using an agricultural soil (arenosol) from Segovia province (central Spain), amended with the different materials, in which *Lactuca sativa* (lettuce) was grown for two months. The As adsorption capacity was higher in the commercial iron oxide and in the red mud derivative, which fitted the Freundlich model (no saturation), than in the lamination slag, which fitted the Langmuir model (limited adsorption). All the materials decreased the pore water As concentration compared to the control (by 29–80%), but only iron oxide reduced As availability in the soil, and none of the amendments decreased the As concentration in plant leaves. The combination of iron oxide and compost did not significantly improve plant growth, but increased nutrients (N, K, Ca, Na and Mg) concentrations and availability in the soil and their concentration in the plants, relative to the other treatments and the control. Therefore, this seems to be a viable option to prevent As leaching and improve the plant nutritional status.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Arsenic contamination originating from geogenic sources occurs in many regions of the world, such as Bangladesh and India (Hossain, 2006; Chowdhury et al., 2000), where the elevated concentration of As in crops is mainly due to the irrigation of agricultural soil with As-contaminated groundwater (Dahal et al., 2008; Brammer and Ravenscroft, 2009). The use of As-rich water for the irrigation of agricultural land can result in the accumulation of As in the soil (Moyano et al., 2009; Gillispie et al., 2015) and in the plants, reducing crop productivity and increasing the risk of As entering

the food chain (Alam et al., 2003; Cubadda et al., 2010; Mayorga et al., 2013). Elevated levels of As in both deep and shallow groundwater (slightly above the limit for drinking water of 10 μg As l^{-1}; WHO, 2011) with a geological origin have been detected in the south-western part of the Tertiary Duero Basin, in the Valladolid and Segovia provinces (Spain) (García-Sánchez et al., 2005; Gómez et al., 2006; Moyano et al., 2009; de la Fuente et al., 2010). Calvo-Revuelta et al. (2003) reported that more than 88% of the waters that they sampled within this area showed concentrations above 10 μg As l^{-1}, 10% had values above 100 μg As l^{-1} and the maximum values were close to 200 μg As l^{-1}. The As background and soil parent material concentrations in this region are low (>16 mg kg^{-1}, Moyano et al., 2009). However, elevated As levels have been found in agricultural soils of this area (Moyano et al., 2009; de la Fuente et al., 2009, 2010). In addition, high As concentrations (near or above the limits for foodstuff; Moyano et al., 2009) have been

reported in crop plants like potato (*Solanum tuberosum*), sugar beet (*Beta vulgaris*), carrot (*Daucus carota*) or wheat (*Triticum aestivum*), which represents a serious threat to food safety (Mayorga et al., 2013). The intense exploitation of As-rich aquifers and the leaching processes facilitated by the sandy characteristics of the soil have been proposed as the key factors that have provoked the contamination of groundwater with As in this area (García-Sánchez et al., 2005; Vega et al., 2008).

Arsenic mobility and phytoavailability in soil are majorly controlled by adsorption-desorption processes (Wang and Mulligan, 2008), which are greatly affected by soil physico-chemical properties such as pH, redox potential, clay and organic matter (OM) content and the presence of metal (Fe, Mn and/or Al) oxides and/or competing ions such as phosphates (Calvo et al., 2006; Fayiga et al., 2007; Sharma et al., 2010; Caporale et al., 2013). In As-contaminated soils, the incorporation of amendments with high adsorption capacity has been proposed as an efficient approach to reduce the mobility of As through its *in situ* fixation (immobilisation) (Lombi et al., 2004; Kumpiene et al., 2008; Ascher et al., 2009; Komárek et al., 2013; Hwang and Neculita, 2013). However, studies evaluating the use of soil amendments to minimise the impact of As-rich water irrigation in agroecosystems are really scarce in the literature (de la Fuente et al., 2010).

Iron-rich materials, like iron oxides or Fe-rich industrial by-products, have been considered as suitable soil amendments because of their potential for trace elements immobilisation in soils (Lombi et al., 2002; Clemente et al., 2015; Farrow et al., 2015). Madeira et al. (2012) reported that the use iron oxides significantly reduced As bioavailability in soil and avoided its accumulation in crops and transfer to the food chain. The large surface area and small particle size of iron oxides contribute to the reduction of As (phyto)availability through co-precipitation or formation of insoluble complexes (Kumpiene et al., 2008; Mikutta et al., 2014). Recently, a wide variety of wastes originating from different industrial processes have been also proposed as promising As immobilising agents (Lombi et al., 2002; Lee et al., 2011; Clemente et al., 2015). For example, the main by-product of the hot rolling of steel, known as lamination slag, contains mainly iron oxides and has been shown to be effective in reducing the solubility of As in soil (de la Fuente et al., 2010) and the As concentration in plant tissues (Mench et al., 1998). Red mud, an alkaline by-product of bauxite processing rich in Fe and Al oxides (Wang et al., 2008; Hua et al., 2017), and its derivatives have also shown a capacity to reduce the availability of As in the soil (Nadaroglu et al., 2010; Ahmaruzzaman, 2011) and its plant uptake (Lombi et al., 2004; Lee et al., 2011; Pardo et al., 2016, 2017). The affinity of Fe-rich materials for As will depend on amount, type and surface area of their iron oxides (Mohan and Pittman, 2007). Despite the predictable lower As immobilisation efficiency of waste materials compared to commercial iron oxides, their use would mean a sustainable management approach, as it would result in an eco-friendly way of recycling them (Nadaroglu et al., 2010; Clemente et al., 2015).

One of the disadvantages associated to the addition of iron-rich amendments to agricultural soils is that they may often decrease the availability of some nutrients such as Mn or P (Komárek et al., 2013), which may limit crop productivity. To prevent that nutrient deficiency in soil, they can be combined with fertilising materials (Suda et al., 2015). However, the effects of the latter on As solubility in soil have been found to be quite controversial. Some studies have reported a decrease in As solubility in soils after the addition of organic amendments, as a consequence of the formation of organic matter-metal complexes that may strongly bind As

anions through metal-bridging mechanisms (Redman et al., 2002). However, other authors have observed an increase in As leaching after compost addition to soil due to competition between As and soluble organic compounds for the sorption sites in the soil (Mench et al., 2003; Hartley et al., 2010; Pardo et al., 2011, 2014). Also, the application of P-rich inorganic fertilisers may alter the As adsorption capacity of the iron oxides provided by the amendments, as a consequence of the chemical and structural similarities between phosphate and arsenate anions (Fitz and Wenzel, 2002; Arco-Lázaro et al., 2016).

The main objective of this study was to evaluate the effectiveness of three materials rich in Fe-oxides with potential to immobilise As (a commercial iron oxide, a lamination slag and a commercial red mud derivative), with regard to minimising the impact of using As-rich water for irrigation in an agricultural soil. Simultaneously, the influence of organic and inorganic fertilisation on the effectiveness of iron oxide in As adsorption processes, which is often ignored in this type of experiments, was also studied. For this, firstly As adsorption capacity of the Fe-rich materials was determined through As adsorption isotherms, and their optimum soil application rate calculated. Then, a pot experiment was carried out in a growth chamber to test the effect of these materials on the soil physico-chemical properties affecting As bioavailability and on the growth and As accumulation of lettuce (*Lactuca sativa* L.) as a test crop (plantox test).

2. Materials and methods

2.1. Soil and amendments characterisation

The soil used in this experiment was collected in an agricultural area near the village of Chañe (Segovia province, central Spain 41°20′25.97″ N, 4°26′34.05″ W). Soils in this area have been exposed to irrigation with As-rich groundwater (46.5 µg As l^{-1}; de la Fuente et al., 2010) that exceeds the limit for As in drinking water (10 µg l^{-1}; WHO, 2011). It is a sandy soil (98.14% sand), classified as arenosol (according to FAO soil classification), with a nearly-neutral pH and very-low concentrations of metals and As (Table 1). Its mineral composition consists mostly of orthoclase (46%), anorthoclase (25.2%) and quartz (24.9%).

Three different iron-rich amendments were used in the experiment (Table 1): a commercial iron oxide (Bayoxide® E33) with a granular Fe$_2$O$_3$ content ≥70% (IO); lamination slag (LS), a waste material that consists mainly of a mixture of iron oxides (36% magnetite, 35% maghemite and 29% plustite; de la Fuente et al., 2010) originating from the hot rolling of steel; and a commercial

Table 1
Physico-chemical characteristics of the soil, compost, commercial iron oxide (Bayoxide® E33) (IO), lamination slag (LS) and commercial red mud derivative (ViroBindTM T40) (RM). Metal and As concentrations refer to aqua regia soluble elements.

	Soil	Compost	IO	LS	RM
pH	6.4	8.8	–	–	10.95
EC (dS m^{-1})	0.13	6.1	–	–	0.14
OM (%)	0.65	73.1	–	–	–
TOC (g kg^{-1})	3.8	439	–	–	7.17
TN (g kg^{-1})	0.32	31.7	–	–	0.15
Fe (g kg^{-1})	1.23	1.80	700	654	90.2
Mn (g kg^{-1})	0.06	0.1	≤3000	3.8	0.90
As (mg kg^{-1})	<0.01	1.7	≤20	<0.05	4.7
Cd (mg kg^{-1})	<0.01	<0.01	≤5	<0.05	0.27
Cu (mg kg^{-1})	6	45	≤100	143	55.7
Pb (mg kg^{-1})	6	39	≤3	<0.05	41.2
Zn (mg kg^{-1})	17	158	≤100	1.7	10.6

–: data not available.