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Determining the influence of the physicochemical parameters of urban soils on As availability using chemometric methods: A preliminary study

Christophe Waterlot, Aurélie Pelfrêne, Francis Douay*

Civil and geo-Environmental Engineering Laboratory (LGCgE), ISA Lille, 48 boulevard Vauban, 59046 Lille cedex, France

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ABSTRACT

An initial exploration was conducted using mathematical and statistical methods to obtain relevant information about the determination of the physicochemical parameters capable of controlling As uptake by ryegrass grown on contaminated topsoils. Concentrations of As in the soils were from 10 to 47 mg/kg, mainly in the As(V) form (57%–73%). Concentrations of As in water extracts were very low (61–700 μg/kg). It was suggested that As(III) was mainly in the uncharged species and As(V) in the charged species. Chemometric methods revealed that the values of the ratio As(III)/As(V) depended on the assimilated-phosphorus, the pseudo-total and water-extractable Fe contents and the soil pH. Arsenic concentrations measured in ryegrass shoots ranged from 119 to 1602 μg/kg. Positive linear correlations were obtained between As in ryegrass shoots and water extractable-As. The transfer coefficient of As correlated well with the ratio assimilated-phosphorus/Fe-oxides. As(III) uptake by the shoot of ryegrass was controlled by the organic matter and Fe-oxide contents.

Introduction

Arsenic (As) is a metalloid which is mainly found in the environment combined to other elements such as chloride, iron and sulphurs to form inorganic compounds and to a lesser extent organic species including monomethyl and dimethyl arsenic acid, trimethylarsine oxide and a variety of other organic compounds in soils (Smith et al., 1998). Among its four oxidation states (−3, 0, +3, +5), the most important As species found in the environment include arsenite (As(III)) and arsenate (As(V)) (Smith et al., 1999). Depending on pH, redox potential and the physicochemical parameters of soils, As(V) is mainly sorbed onto clays, iron, manganese and aluminium oxides/hydroxides and organic matter while in iron-rich soils, As(III) is usually associated to iron oxides/hydroxides (Smith et al., 1998; Dixit and Hering, 2003; Drahota and Filippi, 2009; Komárek et al., 2013). Because the environmental availability and the toxicological effects of As depend on its speciation (Cullen and Reimer, 1989), the knowledge of the oxidation state of As in soils is essential for the risk assessment. Generally, As(III) is more mobile and toxic than As(V) but both arsenic species are soluble in water (Masscheleyn et al., 1991; Manning et al., 2002). Under reducing conditions, As(III) is predominant while under oxidizing conditions, As(V) is dominant. Their presence depends on the soil pH. They form oxyanions such as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} for arsenates and H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-} for arsenites. Among these species, arsenious acid (H_3AsO_3), oxyanions $H_2AsO_4^-$, and $HAsO_4^{2-}$ are the main inorganic species in soils with pH values ranging from 5 to 8 (Sadiq et al., 1983). These may contribute to the larger solubility of As(III) in soils under a

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* *Corresponding author*. E-mail: christophe.waterlot@isa-lille.fr (Christophe Waterlot).

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neutral pH and around a potential value of 100 mV in comparison with As(V) for which electrostatic interactions between negatively charged As(V) species and the charged hydroxide surface can occur (Goldberg, 2002).

Arsenic accumulation in the aerial parts of plants is generally low (O'Neill, 1995). This is attributed to the low As uptake by plant roots and to the limited translocation of As from roots to shoots. However, phytotoxicity effects of As have been reported in many studies. These depended on the soil texture, chemical parameters (organic matter, phosphates, Fe-, Mn- and Al-oxides/hydroxides), physical parameters (pH and redox potential), concentrations of As in soils but also on the ability of a plant to take up As and to translocate it to the target organs (Marin et al., 1993; Smith et al., 1998; Hartley and Lepp, 2008a; Koo et al., 2011; Huang et al., 2012). Regarding the complex chemical behaviour of As, various mechanisms including the physicochemical parameters of soils and the plant physiological traits that affect As plant uptake and the mechanisms of its phytotoxicity were proposed (Fitz and Wenzel, 2002; Meharg and Jardine, 2003; Briat, 2010; Koo et al., 2011). The plant uptake is mainly influenced by the As source and its solubility (Smith et al., 1998, 2009).

In this study, ryegrass (*Lolium perenne* L.) was selected due to its importance as a grazing crop and its use as a cover plant to prevent the entrainment of windblown contaminated dust and to create public open space/parkland. The objectives of this study were (1) to determine As concentrations in soils and plants, (2) to determine the concentrations of As in water extracts, (3) to estimate the speciation of As in terms of As(III) and As(V) in soils, plants and water extracting solutions, and (4) to determine the physicochemical parameters controlling the behaviour of As for a better understanding of As uptake by ryegrass using chemometric methods.

1. Materials and methods

1.1. Sampling, preparation and analysis of soils

Contaminated soils (CS; kitchen gardens and lawns) were collected in urban areas impacted by the past activities of two smelters located in the North of France. For each soil, about 10 elementary samples of the ploughed horizons (0–25 cm) were taken, homogenized and subsampled to constitute a representative topsoil sample which was then crushed to pass through a 10-mm stainless-steel. Then, the soil samples were air-dried, crushed to pass through a 2-mm stainless steel sieve before the determination of pedological and physicochemical parameters. Organic matter (OM) was determined by dry combustion according to the NF ISO 10694 standard after burning 50 mg samples at 1000°C in the presence of O_2 (Nelson and Sommers, 1982) and was performed by the INRA Soil Analysis Laboratory (Arras, France) accredited by COFRAC (French Accreditation Committee) according to the ISO 17025 standard. Soil pH was measured after adding 5 g sample to 25 mL of distilled water and mechanically shaking for 5 min. Then the mixture was allowed to settle for 2 hr and the pH was measured in triplicate in the supernatant. The carbonate content (expressed as $CaCO_3$) was determined by measuring the volume of CO_2 released by reaction with HCl, handling a Bernard calcimeter, as described in the NF ISO 10693 standard. Assimilated phosphorous (P) was extracted with ammonium oxalate solution (0.1 mol/L) extraction following the revised procedure of Joret and Hébert (1955) and was measured using a double beam spectrophotometer (UV-1800, Shimadzu, Tokyo, Japan) following the recommendation of the NF X 31-161 standard. Single extraction with a mix of solutions (sodium tricitrate, sodium bicarbonate and sodium dithionite) was performed to extract free Fe and Mn oxides/oxyhydroxides following the procedure described in Mehra and Jackson (1958).

Subsamples of each site were crushed with an ultra-centrifugal mill (Retsch type ZM 200, Haan, Germany) at less than 250-μm for pseudo-total As, Fe and Mn determinations. Sample digestion was conducted by a microwave assisted acid digestion (Berghof Speedwave MWS-2, Eningen, Germany; Waterlot et al., 2012). Briefly, subsample (300 mg) was transferred to a 100-mL digestion tube and a mixture of nitric acid (70% (*m*/*m*), 1.5 mL) and hydrochloric acid (37% (*m*/*m*), 4.5 mL) was added. After mineralization, digestion products were completed to 25 mL with ultra-pure water (resistivity 18.0 MΩ/cm) and stored in acid-washed plastic bottles at 4°C prior to analysis. Certified and standard reference materials hereafter were used to check the quality of the analytical procedures: BCR-141R (a calcareous loam soil from Pellegrino, Italy), BCR®-483 (a sewage-sludge amended soil from Great Billings Sewage Farm (Northampton, England) and NIST 2710a (a soil from the flood plain of the Silver Bow Creek, Montana). The accuracy of all methods comprised two components: precision and trueness (Sutherland, 2010). Precision was defined as (standard deviation / mean) × 100. Trueness was calculated following the relation: (measured concentration − certified or indicative concentration) / certified or indicative concentration) × 100. The residual moisture contents were measured by weighing soil samples in three replicates before and after drying at 105°C in an oven (Binder, Tuttlingen, Germany) until they reached a constant mass according to the NF ISO 11465 standard. A correction to dry mass was thus obtained and was applied to the reported analytical values.

1.2. Water extractable As

Three grams of each subsample were weighed into a 50-mL graduated polypropylene centrifuge tube and 30 mL of ultra-pure water was added. The tubes were shaken using a rotor disc (10 r/min) for 2 hr. The extract was separated from the solid residue by centrifugation at 4530 r/min (Rotanta 460 Hettich, Tuttlingen, Germany) for 20 min at room temperature. Afterwards, the solution was filtered over an acetate Millipore membrane (0.45 μm porosity, Sartorius, Goettingen, Germany) and was placed in a polypropylene container before analysis.

1.3. Growth conditions and analyses of ryegrass grown on the soils studied

Ryegrass seeds (1.5 g) were sowed in pots containing 2.9 kg of air-dry soil (from CS1 to CS6). Experiments were conducted in six replicates under glasshouse conditions (natural light,