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

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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.

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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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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 O₂ (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 CaCO₃) was determined by measuring

the volume of CO₂ 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- μ m 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 M Ω /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) \times 100. Trueness was calculated following the relation: (measured concentration – certified or indicative concentration) / certified or indicative concentration \times 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 μ m 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,

ambient temperature (15–25°C). Pots were regularly watered with distilled water (10 Ω/cm; pH 7) during the experiment. Mass concentration of Cd, Pb and Zn were 1.3, 3.3 and 12.8 µg/L, respectively. The aboveground plant parts were cut after 6 weeks. Fresh mass and dry mass (DM) of plants were determined after harvest. Plant samples were washed three times with reverse-osmosis water, oven-dried at 40°C and digested using a microwave assisted acid digestion (Waterlot et al., 2011, 2013). Quality control was based on the use of CTA-VTL-2 Virginia Tobacco Leaves grown in Bulgaria. The trueness values were 9.2%, 2.2% and 6.2% for As, Fe and Mn, respectively. The transfer coefficients (TC) of As from soil to ryegrass shoots were calculated as the ratio of As concentrations in ryegrass shoots (µg/kg DM) to the As concentrations in soil (µg/kg DM) where the plant grown.

1.4. Analysis of metalloids and metals

An atomic absorption spectrometer (AA-6800, Shimadzu, Tokyo, Japan) with an ASC-6100 auto-sampler was equipped with an HVG-1 hydride vapour generator (Shimadzu, Japan). This continuous reagent flow system was combined with a continuous sample flow to obtain a constant output signal as soon as equilibrium was reached. The quantification of As was achieved by recording the peak height of the As signal obtained at 193.7 nm with a 1.0 nm slit width. The background correction was conducted using a pulsed As hollow cathode lamp (Hamamatsu, Iwata, Japan) with a frequency of 100 Hz and lamp currents ranging from 12 to 500 mA. A pre-chemical reduction of As(V) to As(III) in the digestion and water extracting solutions was conducted to optimize the formation of arsine (AsH₃). Depending on the As concentration, 0.5–1.0 mL of sample was placed into a volumetric flask. Then, 5 mL of a pre-reducing mixture (KI/ascorbic acid 15%/3%; Panreac, Barcelona, Spain) and 6 mL of concentrated HCl (37%; J.T. Baker for metal trace analysis; Deventer, the Netherlands) were added. After 30 min, the solution was made up to 50 mL with ultra-pure water. Arsenic in the +III oxidation state was determined following the procedure described by Macedo et al. (2009). Briefly, an aliquot of variable volume 0.5–2 mL was mixed with 2 mL of citric acid/sodium citrate buffer (Acrös Organics, Noisy-le-Grand, France) at 0.5 mol/L to mask As(V) and diluted to a final volume of 10 mL with ultra-pure water. Finally, the As(V) concentration was determined by the difference between the concentration of As and As(III).

For Fe and Mn, analyses were performed using the traditional FAAS (AA-6800, Shimadzu, Tokyo, Japan) in combination with a deuterium lamp for the background correction. Hollow cathode lamps were used at 248.3 nm for Fe and 279.5 nm for Mn with a 0.2 slit width and lamp currents fixed at 12 and 10 mA, respectively.

1.5. Statistical analysis

Experimental data, including water-extractable As measurements and determination of As concentrations in ryegrass shoots were expressed as mean and standard deviation (SD). Principal component analysis (PCA), based on the correlation matrix, was performed with XLSTAT 2012.6.04 software, used as a Microsoft Excel plug-in.

2. Results and discussion

2.1. Analytical figures of merit and application

As shown in Table 1, very good coefficient of correlation were obtained for As, Fe and Mn. The limits of detection (LOD) and quantification (LOQ) were defined as

$$\text{LOD} = 3\text{SD}/m \quad (1)$$

$$\text{LOQ} = 10\text{SD}/m \quad (2)$$

where, SD is the standard deviation of ten measurements of a reagent blank and m is the slope of the calibration graph. Values of LOD were 0.093 µg/L for As and 0.96 and 0.04 mg/L for Fe and Mn, respectively. The precision of analytical procedures (expressed as relative standard deviation (RSD)) was evaluated during analyses of As at 1 µg/L and Fe and Mn at 1 mg/L sample solutions (ten measurements) and was found to be less than 5.5% for each element.

The accuracy of the methodologies was assessed analysing the 4 reference materials described above (BCR-141R, BCR@-483, NIST 2710a and CTA-VTL-2) for the determination of the *aqua regia*-extractable contents of As, Fe and Mn. All results were summarized in Table 2. The pseudo-total metal/metalloid concentrations were in good agreement with the certified or indicative values. The precision was found to be less than 10% for As, 4.5% for Fe and 5% for Mn. On the other hand, the trueness ranged from 1% to 7.5% for As, 0.15% to 9.1% for Fe and 0.2% to 4.1% for Mn. All of these results

Table 1 – Linear working range, equation of calibration curves, limits of detection (LOD) and quantification for arsenic (As), iron (Fe) and manganese (Mn).

| | Technique | Calibration range (mg/L) | Equation of calibration curve | LOD (mg/L) | LOQ (mg/L) |
|----|----------------------------------|--------------------------|---|--------------------|--------------------|
| As | HGAAS with HSSR-method | 0–10 ^a | $A = 0.42080C_{As} - 0.01205$ $R^2 = 0.9999$ | 0.093 ^a | 0.309 ^a |
| Fe | FAAS with D ₂ -method | 0–1 | $A = 0.04348C_{Fe} - 0.00035$ $R^2 = 0.9998$ | 0.96 | 3.21 |
| Mn | FAAS with D ₂ -method | 0–1 | $A = 0.13193C_{Mn} - 0.00068$ $R^2 = 0.9999$ | 0.04 | 0.15 |

^a The unit is µg/L. A means integrated absorbance; C_{As} (µg/L) is the As concentration; C_{Fe} (mg/L) and C_{Mn} (mg/L) is the Fe and Mn concentrations respectively.

Table 2 – Quality control of the microwave-assisted aqua regia digestion (n = 6).

| Material | As concentration (mg/kg) | | Fe concentration (mg/kg) | | Mn concentration (mg/kg) | |
|----------------|--------------------------|--------------------------|--------------------------|---------------------------|--------------------------|----------------------|
| | Obtained value | Certified value | Obtained value | Certified value | Obtained value | Certified value |
| CRM BCR 141R | 9.50 (0.66) | 8.84 (0.43) ^a | 24,131 (784) | 25,800 (400) ^b | 677 (34) | 653 (20) |
| CRM BCR@-483 | 49.19 (2.74) | 52.4 ^c | 26,642 (1180) | 26,700 (500) ^d | 273 (6) | 270 (8) ^d |
| SRM NIST 2710a | 1540 (52) | 1540 (10) | 39,400 (1075) | 43,200 (800) | 2094 (113) | 2140 (60) |
| CTA-VTL-2 | 0.98 (0.10) | 0.97 (0.07) | 1107 (31) | 1083 (33) | 80.2 (3.1) | 79.7 (2.6) |

^a Indicative value from Bettinelli et al., 2000.

^b Indicative value from Marin et al., 2008.

^c Indicative value from the sum of the 4 steps of the sequential extraction procedure obtained in Ettler et al., 2011.

^d Indicative value from Kubová et al., 2004.

showed good performance and reliable accuracy of the analytical method.

2.2. Soil characteristics and speciation of As

The environmental availability of As depends on the physico-chemical properties of soil such as OM, carbonate, Fe and Mn oxide, As contents and pH. The lowest OM, CaCO₃ and Fe-oxide contents were measured in CS1, CS2 and CS3 (Table 3). High CaCO₃ and Fe-oxide contents were measured in the other three soils. The results showed significant correlation between organic matter and Fe-oxide contents ($r = 0.953$) which may be explained by the potential nature of the organo-iron associations, precipitation, complexation, sorption or inclusion (Bauer and Blodau, 2006; Wagai and Mayer, 2007; Henneberry et al., 2012). The second significant correlation was recorded between pseudo-total As and Fe ($r = 0.908$) as already observed in other studies (García et al., 2009). The non-significant relation between pseudo-total As and Fe-oxide contents ($r = 0.509$) could reveal the adsorption of As by crystallized iron forms (García et al., 2009). Moreover, PCA extracted two components expressing more than 99.3% of the combined variability present in the six contaminated soils (Fig. 1). The first component (73.56%) had higher loadings for the variables OM, pH, Fe-and Mn-oxides, pseudo-total Mn, Fe and As. The second principal component (25.74%) had a higher loading for the variable CaCO₃. The component plot in the rotated space showed three distinct groups of different soil parameters in the four quadrants, indicating that there are relationships between the soil parameters within a group.

Arsenic in contaminated soils was mainly in the form of arsenate. The ratio of As(V)/As varied from 56.8% to 72.7%

(Fig. S1). This result confirms that the studied soils were under oxidizing conditions. In a thermodynamic point of view, As(V) species are stable under oxidizing conditions while the As(III) species are favoured under mildly reducing conditions and lower pH (Masscheleyn et al., 1991; Ascar et al., 2008). Very good positive correlation was obtained between As(V) and As:

$$C_{As(V)} = 0.758C_{As} - 2.548 \quad r = 0.994, p < 0.0001 \quad (3)$$

where, $C_{As(V)}$ is the As(V) concentration, and C_{As} is the As concentration. Percentages of As(III) were the lowest in CS3 and CS6 while the As concentrations were the highest (Fig. S1) and the ratios (Mn + Fe)/As were the lowest. This result indicates that Fe and Mn could play an important role in the partitioning of As onto solid fractions of soils (García et al., 2009; Zhu et al., 2009; Komárek et al., 2013). Arsenate binds strongly to most mineral constituents of soils, whereas As(III) retention is dependent on soil chemical conditions (pH, redox potential (E_h), ionic strengths) and so, more convoluted.

2.3. Water extractable As and speciation

The determination of As speciation in water extracting solution is an important step in determining potential phytoavailability and toxicity (Komorowicz and Baralkiewicz, 2011). The water-soluble As concentrations ranged from 61 to 803 $\mu\text{g}/\text{kg}$ (Fig. 2a) and represented 0.6% to 1.7% of the pseudo-total As concentrations. Very good relations were obtained between extractable As(III) (Fig. 2b) and As(V) (Fig. 2c) vs. extractable As. An exception occurred with CS2 for which the ratio extractable-As(III)/extractable-As(V) was the lowest. Taking into account the low As(III) and As(V) concentrations in each extract and the pKa values (Eqs. (S1)–(S6); Smith et al.,

Table 3 – Physical and chemical parameters of studied soils.

| Sample | OM (%) | pH | CaCO ₃ (mg/kg) | Available P (mg/kg) | Oxides | | Metal/metalloid | | |
|--------|--------|------|---------------------------|---------------------|------------|------------|-----------------|------------|------------|
| | | | | | Fe (mg/kg) | Mn (mg/kg) | As (mg/kg) | Fe (mg/kg) | Mn (mg/kg) |
| CS1 | 4.67 | 6.78 | 2203 | 100 | 5870 | 4.6 | 14.7 | 21,809 | 313 |
| CS2 | 2.85 | 6.09 | 1397 | 23 | 789 | 17.8 | 18.7 | 17,851 | 347 |
| CS3 | 7.25 | 7.06 | 7690 | 282 | 8374 | 13.6 | 47.2 | 26,439 | 429 |
| CS4 | 9.78 | 7.78 | 32,700 | 452 | 8230 | 8.7 | 10.1 | 16,116 | 291 |
| CS5 | 9.66 | 6.89 | 52,259 | 321 | 10,758 | 24.5 | 21.7 | 20,906 | 488 |
| CS6 | 13.23 | 7.05 | 40,821 | 187 | 15,165 | 22.7 | 42.4 | 27,004 | 502 |

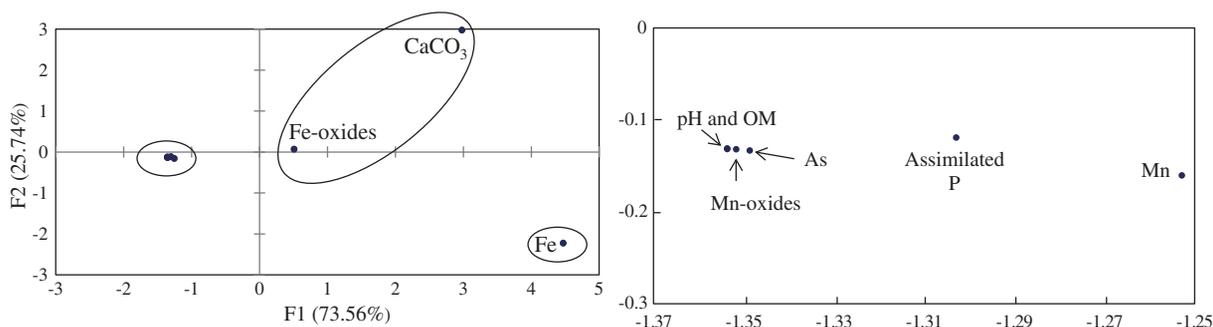


Fig. 1 – Factor loading pattern of the physicochemical parameters of the six contaminated soils obtained by Principal Component Analysis followed by Varimax rotation.

1998), the distribution of As species in water extracting solution was established for each soil (Fig. 2d). This diagram suggests the presence of 3 main species. Arsenites were present as the uncharged species (H_3AsO_3) except for CS4 in which $H_2AsO_3^-$ was found at ultra-trace level. Arsenates were present as the charged species, $H_2AsO_4^-$ and $HAsO_4^{2-}$, in the water extracts of each soil. These results were in accordance with the fact that under pH range 4–8, the most thermodynamically stable As species present in soils are H_3AsO_3 for As(III) and $H_2AsO_4^-$ and $HAsO_4^{2-}$ for As(V) (Masscheleyn et al., 1991). $HAsO_4^{2-}$ was the major As(V) species (86.6%) in CS4 while for CS2, $H_2AsO_4^-$ represents 88.4% of the As(V) species. These results were related to the alkaline and acid pH of CS2 and CS4 (7.78 and 6.09, respectively). On the other hand,

H_3AsO_4 was the major of the As species (69.5%) present in the water extracting solution of CS4, indicating reducing conditions. The first (F1) and second (F2) principal components of the PCA revealed 29.02% and 52.23% variance of data, respectively, describing 81.25% of the total variance of the data (Fig. 3a). F1 was positively determined by $CaCO_3$, OM, Fe- and Mn-oxide, and Mn contents while F2 was positively determined by the assimilated-phosphorus (P) content and pH (Fig. 3b). Note that Fe and As concentrations were positively correlated to F1 and F2 (Fig. 3b). Regarding these parameters, the distribution of the 6 urban soils was in two groups (Fig. 3a). The alkaline CS4 with the lowest As concentration was found in Group A while the other 5 contaminated soils were in Group B. This one was divided

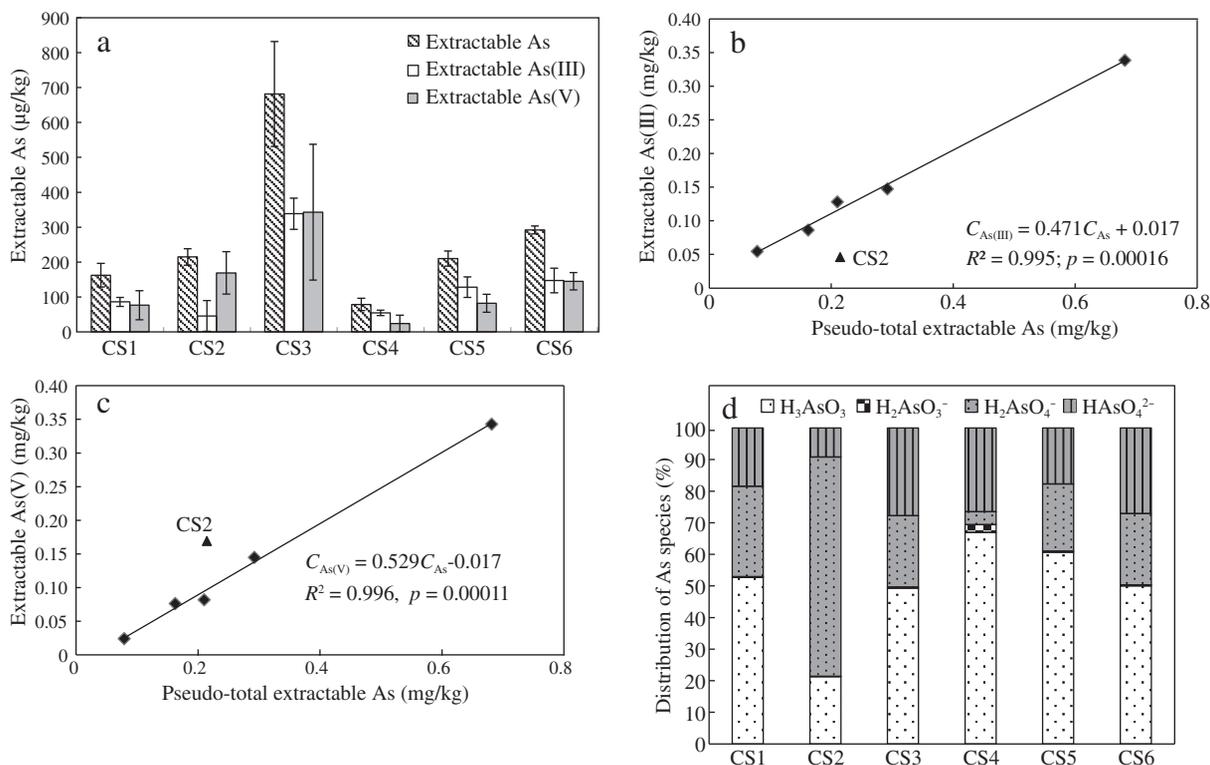


Fig. 2 – Water extractable arsenic (As): a) concentrations of As, As(III) and As(V) ; b) linear correlations between extractable As(III) ; c) extractable As(V) versus pseudo-total extractable As ; d) distribution of As species.

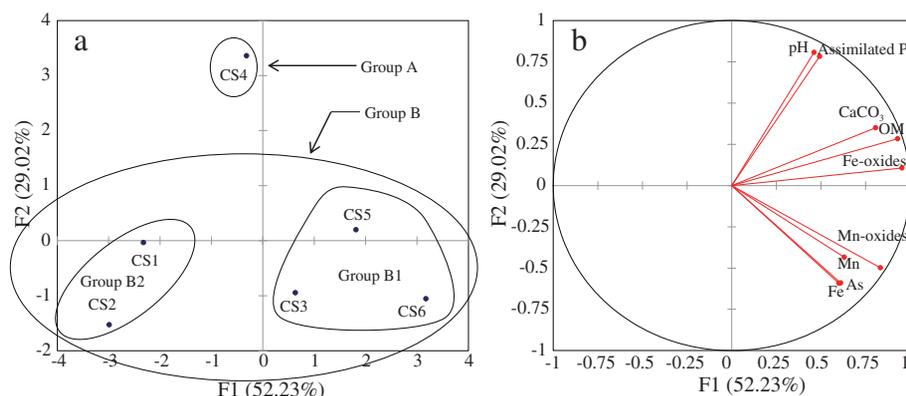
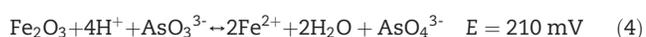


Fig. 3 – Situation of urban soils along axes 1 and 2 issued from Principal Component Analysis (a) and plot of the two principal components from Principal Component Analysis of selected soil parameters and arsenic (As), iron (Fe) and manganese (Mn) concentrations (b).

into two sub-groups, B1 which gathered CS3, CS5 and CS6 and Group B2, in which CS1 and CS2 were found. These two soils were characterized by the lowest assimilated-P, Fe-oxide/hydroxide, carbonate contents and the most acidic soils whereas soils of Group B1 presented the highest Fe- and Mn-oxide/hydroxide, assimilated-P and OM contents.

The data collected from the water extracts are summarized in Table 4. Regarding the potential values (E_h), the redox conditions (moderate reducing or oxidizing) cannot be easily defined. In the same way, there is no evident explanation for the ratio As(III)/As values (21.30% to 69.40%). These values appeared somewhat at odds with the findings of Xie and Huang (1998), who found that when a soil redox potential was $E_h = 50$ mV, the ratio As(III)/As was about 65%, and the fact that As(III) concentrations increased under reducing conditions (Marin et al., 1993). The free electron activities ($pE + pH$) were in the range of 8.16–9.30. Taking into account the range of pH, these values did not indicate real oxidizing conditions (Sadiq et al., 1983) but could explain why the As(V) extractable concentration was higher than the As(III) in CS2 and CS3. The results in Tables 3 and 4 suggest different mechanisms able to explain the water-extractable As(III) and As(V) in soils. In comparison with Mn, the high water-extractable Fe contents could explain that the effect of redox potential on As solubility was mainly governed by the dissolution of Fe-oxides/hydroxides and then the release of As(V). Under the experimental redox conditions, the As(V) concentrations could be also explained by the oxidation of As(III) (Masscheleyn et al., 1991) following Eq. (4) and by the slow

kinetic for the conversion of As(V) to As(III) (Ascar et al., 2008) despite the thermodynamical stability of As(III) to As(V).



Differences between the ratio As(III)/As(V) values of CS2 and the others could be explained by the great differences in assimilated-P and OM contents (Table 3). Soils with high P and OM contents can enhance the As release into the soil solution by the replacement of arsenate through competitive anion exchange (Peryea, 1998). Then, the microbial activity, favoured by the high OM content coupled with neutral pH, may induce a decrease of the soil redox potential, inducing a reduction of As(V) to As(III) (Turpeinen et al., 1999; Fitz and Wenzel, 2002). Regarding the low assimilated-P and OM contents in CS2, this mechanism could be limited, explaining the lowest value of the ratio As(III)/As(V).

The PCA in Fig. 4 was performed with the As(III) and As(V) concentrations measured in water extracting solution and selected soil parameters (pH, assimilated-P, Fe-oxide/hydroxide, and OM contents). The first principal component (Fig. 4a), with a relative inertia of 53.04% was positively determined by the selected physicochemical parameters of the soils. The secondary one, with a relative inertia of 31.42%, was positively determined by As(III) and As(V) concentrations. As shown in Fig. 4b, the third component of the PCA explained only 12.68% of the total variance. This figure showed clearly the influence of pH and assimilated-P on the As(III) concentration in water but also the contribution of Fe and OM on the water extractable As(V). These observations helped us to

Table 4 – Concentrations of water-extractable manganese (Mn), iron (Fe), arsenic (As(III) and As(V)) as a function of soil solution redox-pH conditions.

| Soil | pH | E_h (mV) | Mn (mg/kg) | Fe (mg/kg) | As(III) ($\mu\text{g}/\text{kg}$) | As(V) ($\mu\text{g}/\text{kg}$) | As(III)/As(V) | As(III)/As |
|------|------|---------------|---------------|---------------|--|--------------------------------------|---------------|------------|
| CS1 | 7.05 | 76 | 1.01 | 20.34 | 86.01 | 76.38 | 1.13 | 53 |
| CS2 | 6.7 | 103 | 1.24 | 21.95 | 45.81 | 168.95 | 0.27 | 21.3 |
| CS3 | 6.94 | 94 | 0.49 | 7.83 | 338.51 | 343.1 | 0.99 | 49.7 |
| CS4 | 7.13 | 93 | 0.87 | 22.96 | 54.62 | 24.07 | 2.27 | 69.4 |
| CS5 | 6.97 | 93 | 0.97 | 22.08 | 128.1 | 81.99 | 1.56 | 61 |
| CS6 | 6.85 | 104 | 0.69 | 14.09 | 147.24 | 145.04 | 1.02 | 50.4 |

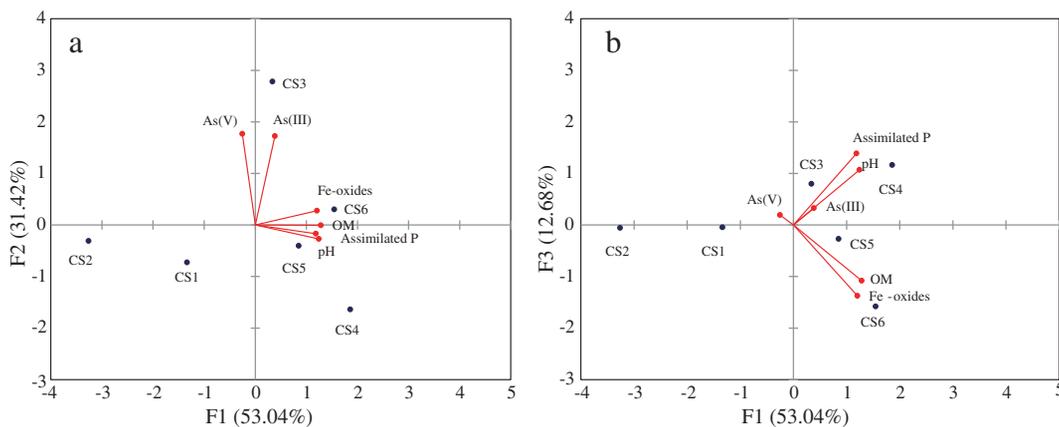


Fig. 4 – Loading plots of extractable metals and selected physicochemical parameters of soils. (a) F1 versus F2; (b) F3 versus F1.

understand the spatial distribution of CS2 in the middle extreme left quadrant, related to the high As(III)/As(V) ratio.

2.4. Phytoavailability of As

2.4.1. Arsenic concentration in the shoots of ryegrass

Arsenic concentrations measured in the ryegrass shoots ranged from (124 ± 9) to (1460 ± 166) µg/kg DM. No evident relation between As accumulation in ryegrass shoots and the water-extractable As concentrations was underscoring, except for the three soils of Group B1 ($C_{AsRG} = 1.56 C_{As} - 125.60$; $R^2 = 0.9982$). In the same way, very good relations were obtained between As in the ryegrass shoots grown in CS3, CS5 and CS6 and the water-extractable As(III) and As(V) (Fig. 5). The water extraction appears as a good alternative tool to evaluate the As availability in ryegrass shoots. However, no evident relation was obtained after adding the three soils from groups A and B2, suggesting that As phytoavailability depended on the physicochemical parameters of the soils, the speciation of As and the arsenic mechanism uptake by plants (competition adsorption/desorption, phosphorous, dissolved organic matter, clay mineral, translocation of arsenate from root to shoot, silicium pathway) (Zhao et al., 2009). Many studies reported that arsenate uptake mechanism was inhibited by phosphate, suggesting that phosphate and As(V) are transported across the plasma membrane by the same uptake system (Cox et al.,

1996; Meharg and Jardine, 2003). By contrast, it was demonstrated that As(III) uptake into plants occurred via aquaporins (Wysocki et al., 2001; Meharg and Jardine, 2003) and so, that the As(III) uptake was unaffected by phosphate in non-accumulators (Asher and Reay, 1979).

2.4.2. Key factors affecting As phytoavailability

A very good linear relation was obtained between the transfer coefficients (TC) and the ratio P/Fe ($R_{P/Fe}$, m/m) for the three soils within group B1 ($TC = 0.769R_{P/Fe} + 0.0041$; $R^2 = 0.985$). The lowest TC value (0.0066) was obtained from ryegrass grown in CS6 for which the lowest assimilated-P and the highest Fe-oxide contents were measured. In contrast, the highest calculated TC value (0.037) was from the ryegrass grown in CS3 for which low Fe-oxide content was measured in comparison with CS5 and CS6. It has been reported that competition between P and As occurred in soils with low P content due to the exudation of carboxylic acids from roots of plants (Kirk et al., 1999; Cao et al., 2003). The low difference in the P level of these three soils (134 mg/kg), Fe-oxides/hydroxides could play a role in the As accumulation in ryegrass shoots with respect to its affinity for this minerals (Dixit and Hering, 2003). In this regard, many studies have reported the effect of iron amendment on the reduction in As accumulation into the ryegrass shoots (Hartley and Lepp, 2008a, 2008b).

Percentages of As(III) in shoots of ryegrass grown in CS1, CS2, CS3, CS4, CS5 and CS6 were 64.4%, 92.5%, 58.7%, 76.4%, 72.0%, and 86.4%, respectively. Many factors can explain these results. For the contaminated soils with the highest OM contents, the development of microbial activities could be favoured and so, the reduction of As(V) to As(III). Moreover, Cummings et al. (1999) showed that the microbial activities could accelerate the release of As bound to iron-oxides/hydroxides. In our study, very good linear relations were obtained between the percentage of As(III) in ryegrass shoots grown in CS3, CS5 and CS6 (Group B1; Fig. 3a) and the percentage of OM or Fe-oxides in these soils (Fig. 6). The role of organic matter in modifying mobility of As in contaminated soil remains still unclear. Soluble organic compounds, especially those occurring in anionic form, may compete with arsenates for soil sorption sites. Thus, organic matter rich in soluble fraction may increase the potential phytoavailability

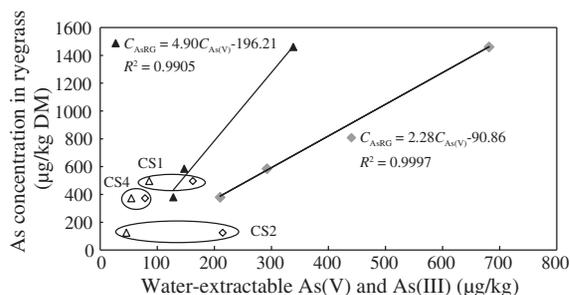


Fig. 5 – Linear correlations between arsenic (As) concentrations in ryegrass shoots (C_{AsRG}) and water-extractable concentration As(III) or As(V) called $C_{As(III)}$ and $C_{As(V)}$, respectively.

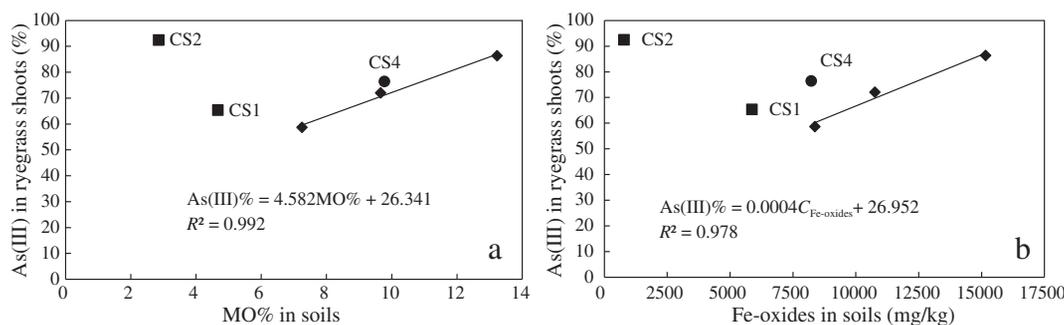


Fig. 6 – Linear correlations between (a) As in ryegrass shoots and organic matter (MO); (b) arsenic (As) in ryegrass shoots and iron-oxides (Fe-oxides).

of As (Wang and Mulligan, 2006). On the other hand, organic matter can enhance the dissolution Fe and Mn oxides under reductive conditions, leading to the release of As compounds that were bound to them (Mukwaturi and Lin, 2015).

The role of pH in adsorption and desorption processes of As on Fe-oxides/hydroxides surface is also very important. In addition to the mechanism described above, the alkaline pH of CS4 (pH 7.78) could favour the desorption of arsenate from iron-oxides. In contrast, for CS1 and CS2, the percentage of As(III) in ryegrass shoots cannot be only due to the desorption or desorption/reduction mechanisms. Competition between P and As could be favoured in CS1 due to their apparent chemical similarities to form oxyanions in the +V oxidation state and the fact that As(V) and phosphate have comparable dissociation constants and solubility product values for their acids and salts, respectively (Smith et al., 1998). In CS2, low Fe-oxide, assimilated-P, OM contents and pH were measured (Table 4) whilst the highest percentage of As(III) was obtained for ryegrass shoots grown in this soil (92.5%). The high percentage of As(III) in the ryegrass shoots could be explained by the presence of As(V) in CS2 in spite of many studies have shown that a decline in soil pH decreases the As(V) availability for plant uptake (Smith et al., 1998; Xu et al., 2010). Indeed, acid pH value is favourable to the desorption process of As(V)–Fe(III) minerals (Takamatsu et al., 1982). Many studies reported the formation of inner sphere complexes of As(V) with soil components (Grossl et al., 1997, Manning et al., 2002). Bidentate complexes were observed between As(V) and Fe and were favoured at higher surface coverages (Fendorf et al., 1997). With respect to the experimental work of Huang et al. (2012), the high percentage of As(III) in shoots of ryegrass grown on CS2 could be explained by the reduction of As(V) on the roots of ryegrass and then sequestered in vacuoles as As(III)-Phytochelatin Complexes or other thiols-contained compounds, for which As has a strong affinity, in enzymes and tissue proteins. There is so a need to study the dynamic of the As transfer from each of the soil studied to the ryegrass shoots.

3. Conclusions

Urban topsoils (kitchen gardens and lawns) in the vicinity of two former lead and zinc plants were studied using a combination of analysis of As, As(III) and As(V) concentrations, single extraction

procedure and pot experiments using ryegrass (*L. perenne* L.) as plant model. It was highlighted that As in the shoots of ryegrass was mainly in the arsenite forms. Depending on the studied soils, it was shown that assimilated-P, organic matter, Fe, Mn and pH were the main parameters controlling the As oxidation states in soils or/and in water extracting solutions. Relevant information about the determination of the physicochemical parameters capable of controlling As uptake by ryegrass grown on contaminated topsoils was highlighted using chemometric methods. For soils in the same group, the phytoavailability of As in the shoots of ryegrass depended on the ratio assimilated-P/Fe-oxides in the soils. Moreover, As(III) uptake by the shoots of ryegrass was controlled by the organic matter and Fe-oxide contents. For soils statistically located in different groups, the chemometric approach did not permit to explain the transfer of As from the soil to the shoot of ryegrass. This process should be explained from chemometric angle in combination with biological processes.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2015.12.028>.

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