

Application of Phosphates in Mine Affected Soils Increases Arsenic Availability for Plant Uptake: Preliminary Results

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Background and objectives

Arsenic is an element that can cause toxicity even at low concentrations jeopardizing human and animal health (Shankar *et al.*, 2014). Assessment of pedo-environmental factors that affect the geochemical behaviour of As, especially mobility and bioavailability of the element, provides substantial information that may be applied for the restoration of contaminated soil using phytoremediation techniques. Among factors regulating As uptake by plants is the concentration of phosphates in soil since P and As oxyanions show similar geochemical behaviour (Strawn, 2018). According to relevant literature, the As hyperaccumulator plant *Pteris vittata*, can accumulate from some hundred up to some thousand mg of As per kg of dry weight, depending on soil properties and experimental conditions (Danh *et al.*, 2014). No study, however, systematically questioned the optimum As:P molar ratio in soil in relation to the ability of *P. vittata* to accumulate As under field conditions.

In the present work, batch experiments were conducted aiming to: (a) comparatively evaluate As mobilisation in two highly contaminated mine soil samples following the application of phosphates either in the form of a commercial triple superphosphate fertiliser (TSP) or in the form of $\text{NH}_4\text{H}_2\text{PO}_4$, (b) study As desorption behaviour in the two soil samples and (c) estimate a TSP agronomic dose that can safely enhance As removal from soil in case of phyto-remediation scenario.

Materials and Methods

Two topsoil samples were collected from the wider area of Lavrion (Attica, Greece) and analysed for their physicochemical properties (Page, 1982) (Table 1). To study the desorption of As in the presence of P in these soil samples, a two factor experiment in three replicates was applied (P source X P rate). Stock solutions of varying phosphate concentrations (2.36-88.88 mg/l) were prepared by dilution of appropriate amounts of TSP (0-46-0) in deionised water, of TSP in 0.01 M NaNO_3 electrolyte solution and of $\text{NH}_4\text{H}_2\text{PO}_4$ in 0.01 M NaNO_3 electrolyte solution. One gram of air dried soil was weighed into a series of 50 ml falcon tubes and 20 ml of solution containing the appropriate phosphorous concentrations (P rates) from each P source were added. The tubes were gently shaken at 125 rpm for 24 hours in a reciprocal shaker placed in an incubator with standard temperature of $22\pm 1^\circ\text{C}$ and centrifuged for 5 min at 2200 rpm afterwards. The supernatants were filtered through a Whatman paper No 42 and As and P concentrations determined by hydride generator Varian model VGA 77 and Shimadzu UV-1700 spectrophotometer, respectively.

Table 1. Physicochemical soil properties and As fractions obtained according to Wenzel *et al.* (2001) sequential extraction protocol (SEP). W1: non-specifically sorbed; W2: specifically sorbed; W3: sorbed on amorphous and poorly crystalline hydrous oxides of Fe and Al; W4: sorbed on well-crystallised hydrous oxides of Fe and Al; W5: residual.

| Soil properties | | | Soil properties (mg/kg) | | | Fraction | S.E.P. (mg/kg) | |
|-----------------------------|--------|--------|-------------------------|--------|--------|----------|----------------|--------|
| Parameter | Soil 1 | Soil 2 | Parameter | Soil 1 | Soil 2 | | Soil 1 | Soil 2 |
| Clay (g/kg) | 328 | 230 | Fe_d | 41.5 | 45.3 | W1 | 5.0 | 4.1 |
| Silt (g/kg) | 220 | 210 | Fe_o | 4.8 | 7.0 | W2 | 104 | 64.3 |
| Sand (g/kg) | 458 | 560 | Al_d | 728 | 575 | W3 | 313 | 645 |
| pH (1:1) | 8.0 | 7.7 | Al_o | 2390 | 1098 | W4 | 241 | 394 |
| CaCO_3 (g/kg) | 115 | 64 | As total | 852 | 1745 | W5 | 106.0 | 303 |
| Act. CaCO_3 (g/kg) | 27 | 3 | P total | 733 | 1061 | | | |
| O.M. (g/kg) | 22 | 52 | P inorganic | 391 | 796 | | | |
| CEC (cmol./kg) | 30 | 27 | P organic | 342 | 265 | | | |
| | | | P available | 10.7 | 11.0 | | | |

Results and Discussion

The soil samples are alkaline and medium textured with similar pH values and available P content. However, in soil 1 carbonates, active carbonates and amorphous Al contents are much higher than in soil 2, while soil 2 exhibits higher organic matter and amorphous Fe oxides contents (Table 1). Total As concentration is very high in both soil samples but over two-times in soil 2 (852 vs 1745 mg/kg). Most As was found in W3 and W4 fractions, showing that As in the studied soil is preferentially bound to Fe oxides and especially to amorphous and poorly crystalline hydrous oxides of Fe.

Both P source and P rate significantly affected As extraction from the tested soil samples. The significant differences between the P sources can be mainly attributed to the presence of NaNO_3 in equilibrating solutions that probably assisted the ability of phosphates to extract As from both soil samples (Smith *et al.*, 2002), and not to differences between TSP and $\text{NH}_4\text{H}_2\text{PO}_4$ extracting efficiency. Increased phosphates rate application resulted to higher As concentrations in the equilibrium solutions, but different As desorption patterns for the two soil samples were observed (Fig. 1). In soil 1, by increasing the P rate, As desorption constantly and significantly increased in relation to the preceding P rate. For soil 2, increasing P rates did not always produce significant differences in As desorption. Though in soil 2 maximum As desorption was obtained by the highest P rate, and an almost steady extracting ability of added phosphates concentrations was observed from the 3rd P rate and onwards. Arsenic amounts extracted from the tested soil samples ranged between 8 and 64.4 mg/kg for soil 1 and between 16.5 and 35.3 mg/kg for soil 2. Considering that the initial As concentration that could be extracted by phosphates was 108.6 and 68.4 mg/kg for soil 1 and 2, respectively (sum of W1 and W2 fractions, Table 1), it is very clear that within 24 hours of equilibration more than 50% of non-specifically and specifically sorbed As (highest P rate) was replaced by phosphates. Interestingly, the lowest P rate showed much lower As desorption from soil 1, in spite that the potentially available As concentration was higher compared to soil 2 (Table 1). The observed As desorption hysteresis in soil 1 compared to soil 2, can be attributed to the higher Al amorphous oxides content in soil 1 that show high P adsorption capacity reducing the extracting ability of phosphates at low concentrations or/and to easily exchangeable by phosphates As forms in soil 2.

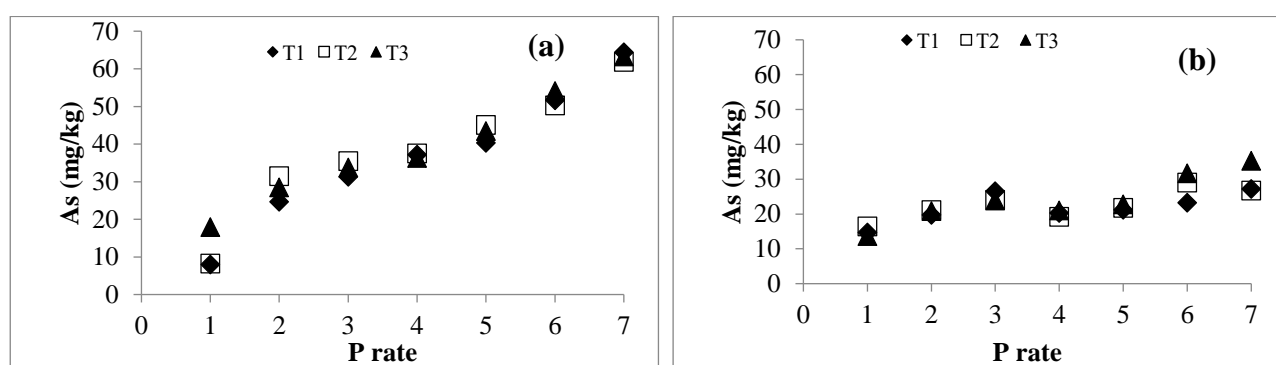


Figure 1. As desorption from (a) Soil 1, and (b) Soil 2. T1: TSP in water; T2: TSP in 0.01 M NaNO_3 ; T3: $\text{NH}_4\text{H}_2\text{PO}_4$ in 0.01 M NaNO_3 . P rates (mg/l); 1: 2.36, 2: 6.77, 3: 11.08, 4: 15.9, 5: 22.0, 6: 40.6, 7: 88.9.

Recently, by growing *P. vittata* in pots containing a soil from the same area with very high As concentration, Kalyvas *et al.* (2018) found that the maximum extraction ability of the plant ranged from 42 to 73% of available As in the tested soil (W1+W2 fractions). Compared to the results of the present study and independently from the P source, the highest P rate liberated up to 59% and 52% of available As from soil 1 and 2, respectively, suggesting that released As can be up taken by *P. vittata*. However, the maximum adsorbing capacity of both soil samples for P, do not exceed 550 mg/kg in the case of TSP in water (data not shown). For phytoremediation purposes, and to avoid possible leaching of excess As and P, an application rate of 500 mg P/kg as TSP in the studied soil samples appears as a safe recommendation. This application rate leads to the liberation of approximately 40 and 30% of available As in the solution of soil 1 and 2, respectively, that could safely be up taken by *P. vittata* if no antagonism between As and P in the rizosphere of the plant occurs.

Conclusions

The findings of this preliminary work propose that the application of a relatively high TSP dose in the As polluted soil can increase the availability of As for plant uptake without raising great environmental concerns. Nevertheless, pot experiments are needed to thoroughly study the effect of different phosphate fertiliser rates on the ability of *P. vittata* to extract As from the studied soil samples by avoiding As and P leaching due to excess concentrations in soil solution.

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