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## **First investigations on arsenic content in ultramafic rocks' alterites from Nickel mines, implications for surface waters quality in ultramafic watersheds (New-Caledonia)**

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### **Abstract**

Arsenic is a well-known toxic metalloid and main species in water are arsenate As(V) and arsenite As(III) more toxic. In small tropical islands, tap water is often provided from surface water and the arsenic risk, widely studied in groundwater, is poorly studied in surface water. In New-Caledonia, 61% of the water comes from surface water and opencast nickel mines generate the dispersal of large quantities of ultramafic rocks' alterites rich in iron oxide-hydroxide. Arsenic contents in surface waters exceeding the World Health Organization recommended  $10\mu\text{g}\cdot\text{L}^{-1}$  value, were noted downstream nickel mines. Many studies illustrated the high affinity of arsenite and arsenate for pure or natural iron oxides and hydroxides. Arsenic could therefore be transported by ultramafic rocks' alterites displaced due to mining activities. To evaluate the arsenic risk for surface water in ultramafic catchments, alterites samples were collected in the vicinity of three active mines. They were analyzed for their total and exchangeable arsenic content. Their arsenic adsorption capacity was studied thanks to batch experiments. Results indicate that arsenic is present in all the samples with total contents ranging  $0.20$  to  $5.14\text{mg}\cdot\text{kg}^{-1}$  even though no As minerals occurring in nature were detected. The present work shows that ultramafic rock's alterites contain arsenic even though the primary mineralogical source of As is unknown. No exchangeable arsenite was detected but the median value for exchangeable arsenate is  $0.16\text{mg}\cdot\text{kg}^{-1}$  representing 10.3% of the total As being easily mobile. Adsorption experiments revealed that their maximum adsorption capacity for arsenate and arsenite was  $1.05\text{mg}\cdot\text{kg}^{-1}$ . This study reveals that ultramafic rock's alterites are a source of arsenic to surface water in the form of suspended particulate matter with a significant proportion easily soluble. These results therefore have implications for the survey of surface waters in ultramafic watersheds in New-Caledonia and more broadly in small tropical islands.

**Keywords:** Ultramafic rocks' alterites, Inorganic arsenic, exchangeable arsenate, arsenic and arsenate adsorption capacity, ultramafic watershed, surface water

## 1. Introduction

Arsenic (As) is a well-known toxic metalloid and naturally found in the environment. Exposure to As may occur through contaminated drinking water and it can increase the risk of diseases or lead to death (Sattar 2016; States 2009; Zhang 2018). Inorganic As is found in water as As(V) (arsenate  $H_3AsO_4$ ) in aerobic waters (Prohaska 2005) and As(III) (arsenite  $H_3AsO_3$ ) in anaerobic waters (Pettine 1992). As(III), more mobile, is more toxic than As(V) (Basu 2014).

The occurrence of As in groundwater was studied (Smedley 2002, Bossy 2012, Merola 2015) but in small tropical islands, water resource often comes from surface water collection and the arsenic risk, widely studied in groundwater, is poorly studied in surface water. In New-Caledonia, 61% of the water comes from surface water and a third of the main island is covered by weathered ultramafic rocks, containing high concentrations of Iron (Fe), Manganese, Nickel (Ni), Cobalt and Chromium. The main economic activity is then Ni ore mining with 30 opencast mines. Rains can be intense under the subtropical climate and water runoff can generate ultramafic rock's alterites transport to surface waters and metals enrichment (Gunkel-Grillon 2014). Water quality investigations revealed that in ultramafic catchments, the median total As in rivers may range 4 to  $8\mu g.L^{-1}$  (3<sup>rd</sup> Quartile ranging 9.5 to  $12\mu g.L^{-1}$ ) and in a river affected by a past mining activity, it can be significantly higher with  $21\mu g.L^{-1}$  (Juillot 2019). As content in rivers flowing in ultramafic catchments can then exceed the World Health Organization recommended  $10\mu g.L^{-1}$  value and an exacerbated solid transport seems to increase As content. Alterites are rich in iron oxides and hydroxides and goethite ( $\alpha-FeOOH$ ) is the main mineral phase (Becquer 2001). Iron oxides-hydroxides have been recognized as a solid phase source of As but as pointed out by Seddique et al. (2008), they are secondary phases that form during weathering or diagenetic alteration, and in many cases, the primary mineralogical source of As is unknown. Many studies also illustrated the high affinity of As(III) and As(V) for pure, natural or modified iron oxides and hydroxides in order to determine their efficiency to clean water with very high adsorption capacities ranging 0.6 to  $442.8mg.g^{-1}$  (Siddiqui 2017, Nguyen 2020). Moreover, As in groundwater can be derived from ultramafic rocks dissolution (Ryan 2011). These data suggest that massive ultramafic rocks alterites dispersal due, among others, to mining activities should be a source of As to surface waters in laterized ultramafic watershed and pose problems for the surface water quality in New-Caledonia and more broadly in small tropical islands.

To test the hypothesis that ultramafic rocks alterites can be a significant As source in surface waters, their total arsenic content around Ni mining sites was analyzed and their ability to release or adsorb As was also investigated. To the best of our knowledge, this is the first investigation on arsenic risk associated to potential ultramafic rock's alterites dispersal in ultramafic catchments.

## 2. Experimental

### 2.1. Sites description

The climate of New-Caledonia is subtropical with 1700mm annual rainfall and the mean annual temperature is 25°C. 33 samples were collected from the top layer 0-10cm in three different mining areas, the Mont-Koniambo, Poro and Maï Kouaoua Mines (Figure 1). K1 to K10 and P1 to P10 are mining technosoils. K-C3-A, K-C3-B, K-T, M-3B, M-3C, P-E, P-G and P-H are mining sediments sampled in decanters or on banks of impacted rivers. K-C1, K-C2, K-FA1, M-2 and M-3A are river sands and P-F is beach sand, collected downstream mining sites.

### 2.2. Physicochemical parameters of alterites

Samples were dried at 45°C. The pH and redox potential were measured in ultrapure water (1/5 mass/volume). pH values are approximately neutral and redox potential ranges 126mV to 274mV (Table 1). According to potential/pH diagram, As is expected to be As(V).

The particle-size distribution was determined with a Mastersizer S2000 laser Particle Size Analyzer (Malvern, UK), particle and water refractive indices of 2.9 and 1.33. The median diameter ( $D_{0.5}$  in  $\mu\text{m}$ ) is the central tendency of the size distribution.

Mineralogical characterization was determined by X-ray diffraction (INEL CPS 120° Curved Position Sensitive Detector,  $K\alpha\text{Co}$ ). All samples contain iron oxides/hydroxydes and mainly goethite but also others expected mineral phases in ultramafic rocks alterites (Table 1). No As minerals occurring in nature were detected and As is probably associated with iron oxides/hydroxides secondary phases (Seddique 2008).

### 2.3. As content in alterites

For total As, 0.5g was digested with aqua regia (HCl 5mL;  $\text{HNO}_3$  1mL) in a microwave digester (Perkin Elmer - Multiwave 3000). The volume was then adjusted to 25mL. For exchangeable As, 1g was extracted with  $\text{KH}_2\text{PO}_4$  (25mL, 0.2M) for 2h before 10min centrifugation at 4200rpm. All reagents are of analytical grade and Milli-Q water from Millipore was used.

### 2.4. As(III) or As(V) adsorption tests on alterites

Adsorption experiments were performed on few samples previously washed (4h in  $\text{KH}_2\text{PO}_4$  0.4M) in order to remove naturally adsorbed As. Then 1g of washed sample was introduced into 25mL of As(III) or As(V) solutions prepared with  $\text{As}_2\text{O}_3$  and  $\text{H}_3\text{AsO}_4$  (6 to  $50\mu\text{g}\cdot\text{L}^{-1}$ ). The solution was agitated for 48h at pH ranging 6.5 to 7.3 before As(III) or As(V) analysis remaining in the supernatant. As adsorbed (%) was calculated with As concentration in the solution at initial time ( $C_0$ ,  $\mu\text{g}\cdot\text{L}^{-1}$ ) and at time t ( $C_t$ ,  $\mu\text{g}\cdot\text{L}^{-1}$ ) (Eq. (1)):

$$\text{As adsorbed (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

The distribution coefficient,  $K_d$ , ( $\text{L}\cdot\text{kg}^{-1}$ ) was calculated using Eq. (2):

$$K_d = \frac{\text{As adsorbed at equilibrium}(\text{mg}\cdot\text{kg}^{-1})}{\text{Initial As concentration in solution}(\text{mg}\cdot\text{L}^{-1})} \quad (2)$$

### 2.5. As analysis

All solutions were filtrated through  $0.45\mu\text{m}$  acetate filters before analysis. Three references materials (soils Wepal ISE 884, 885 and 961) were used for aqua regia digestion (n=1 for ISE 884, n=12 for ISE 885 and n=3 for ISE 96) and analytical measurements (3 analytical replicates) validation (supplementary material SM1).

Aqua regia digested samples were analyzed by ICP-OES (Varian -730-ES at wavelengths 198.980nm and 197.198nm). In alterites, total As contents were below the ICP-OES quantification limit ( $\text{QL}=100\mu\text{g}\cdot\text{L}^{-1}$  or  $5\text{mg}\cdot\text{kg}^{-1}$ ) and were then analyzed by Voltammetry (Metrohm - 884 Professional VA) with a gold microwire working electrode, scTRACE gold (Metrohm Application Bulletin 416). 2mL of electrolyte (Sulfamic acid 1M, Citric acid 0.5M, KCl 0.45M) was added to 10mL of diluted sample solution. For As(III+V) measurement, the deposition potential is -1V for 90s, the sweep potential is -0.3 to 0.2V with 0.01V step and a sweep rate of  $0.4\text{V}\cdot\text{s}^{-1}$ . As peak is detected around 81mV (supplementary material

SM2). In order to reduce interferences (interfering peak at -52mV), samples were diluted 10 times and a cationic exchange resin was added (1g DOWEX 50WX8 Hydrogen form) for excess of metallic ions removal. Due to ICP-OES detection limits, exchangeable As was analyzed by voltammetry, for As(III+V) and As(III). As(III) is measured with a deposition potential at -0.5V (other parameters being unchanged). As(V) content is the difference between the two voltammetric measurements. No purification step with chelex resin was required. As remaining in the supernatant after As(III) and As(V) adsorption experiments were also analyzed by voltammetry and As(III) possible oxidation or As(V) possible reduction through contact of alterites particles during the adsorption experiments was controlled.

### **3. Results and discussion**

In order to see if ultramafic rocks alterites can be a significant source of As in surface waters by their total content and ability to absorb and release As. We studied the total and the exchangeable As content in all samples using aqua regia digestion and monopotassium phosphate leaching. Then we also studied the adsorption capacity of some samples using batch experiments.

#### **3.1. Total As**

Total As content ranges 0.20 to 5.14mg.kg<sup>-1</sup> (Table 1) (1<sup>st</sup> quartile, median and 3<sup>rd</sup> quartile values are respectively 0.9; 1.48 and 2.42mg.kg<sup>-1</sup>). No significant difference is noted between the three mining sites for mean total As (Figure 1) or between mining technosols and mining sediments collected in the decanters or downstream mining sites. As contents are in agreement with those measured in ultramafic rocks like peridotite, dunite, kimberlite (0.03 to 15.8mg.kg<sup>-1</sup>) (Smedley 2002) but in Serpentine, contents can range 19 to 449mg.kg<sup>-1</sup> and it can reach 1104mg.kg<sup>-1</sup> in mining contaminated lake sediments or 8000mg.kg<sup>-1</sup> in soils near sulphide deposits (Ryan 2011). As contents in New Caledonian alterites are then rather low in view of literature data and measurements could be made due to the high sensitivity of voltammetric analysis. No high over-concentration in alterites collected in or around mines are fortunately observed and they do not seem to be highly enriched due to Ni-mining activities but As is detected in all alterites and seems then to be systematically present. The systematic presence of arsenic was not expected and ultramafic rock's alterites, if massively dispersed as suspended particulate matter, are therefore a significant source of particulate As in surface waters.

#### **3.2. Exchangeable As**

Exchangeable As represents the fraction that is adsorbed onto the particle surface and that can be mobile *i.e* easily soluble. No exchangeable As(III) was detected and mean exchangeable As(V) is 0.25mg.kg<sup>-1</sup> (1<sup>st</sup> quartile, median and 3<sup>rd</sup> quartile values are respectively 0.09; 0.157 and 0.268mg.kg<sup>-1</sup>). High values, above the 3<sup>rd</sup> quartile are noted for samples K-C1, K-C3, K-T, P-F, M-3A, M3-B and M3-C (0.33 to 1.19mg.kg<sup>-1</sup>), all collected downstream the mines (Figure 2). For these displaced materials, a light over-concentration onto alterites' surface is then not excluded, they could have possibly behave as As sink during their course. No relationship could be established between exchangeable As content and the size particle distribution and no significant difference is noticed between the three mining sites (Figure 1). Anyway, the proportion of exchangeable As(V) with 1<sup>st</sup> quartile, median and 3<sup>rd</sup> quartile values being respectively 4.2; 10.3 and 33.5% of the total As indicates that if carried as suspended particulate matter, alterites can be a significant source of soluble As(V) to surface waters.

#### **3.3. As adsorption tests**

Adsorption reach saturation with 70 to 95% of initial As(III) or As(V) adsorbed, excepted for sample K-C1 adsorbing 100% of initial As(III) (Table 2). As(III) as well as As(V) are highly adsorbed and no significant conversion occurred in solution (which does not exclude conversion at the surface of alterites). As(III) and As(V) adsorption onto alterites, ranging 0.0003 to 0.0044mg.m<sup>-2</sup>, is in agreement with 0.00061, 0.0041 and 0.055mgAs(V).m<sup>-2</sup> obtained with Laterite, Goethite and Hematite respectively (Aredes 2013). As(III) and As(V) partition coefficient for alterites ranges 17.5 to 51.4L.kg<sup>-1</sup> in accordance with 25 to 200L.kg<sup>-1</sup> for respectively natural Hematite and Goethite (Bowell 1994). These adsorption tests revealed that their maximum adsorption capacity for arsenate and arsenite are 1.05 mg.kg<sup>-1</sup>. Ultramafic rock's alterites rich in Goethite are effective in adsorbing arsenite and arsenate confirming that they may be source or sink of As for surface waters.

#### **4. Conclusion**

Arsenic is present in all the samples with total contents ranging 0.20 to 5.14mg.kg<sup>-1</sup>. The present work demonstrate that ultramafic rock's alterites contain arsenic even though the primary mineralogical source of As is unknown. They can be a source of particulate As if transported as suspended particulate matter. No exchangeable arsenite was detected but the median value for exchangeable arsenate is 0.16mg.kg<sup>-1</sup> representing 10.3% of the total As content. Ultramafic materials contain then a significant proportion of arsenate that can be dissolved to surface waters. Adsorption experiments revealed that their maximum adsorption capacity for arsenate and arsenite was 1.05 mg.kg<sup>-1</sup>. Displaced materials can then be a source or sink of As. Mining companies are encouraged to prevent For tropical islands with ultramafic catchments providing water resource for the population, these results underline that As should be systematically measured for water quality survey and that As behavior and distribution in ultramafic catchments affected or not by mining activities should be studied in more details.

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