

## TRACE ELEMENTS POLLUTION FROM AN ABANDONED MINE AND FACTORS AFFECTING ANTIMONY CONCENTRATIONS IN THE DAHIMINE WADI BANK SOILS (NORTHEAST ALGERIA)

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**Abstract:** The Dahimine wadi starts on a mountain side (Djebel hamimat) where an abandoned antimony mine exists. A previous study indicated great amounts of antimony (Sb) in soils surrounding mine spoils. The objective of this research is, on one hand, to assess the extent of the contamination and/or pollution by Sb and other trace elements to a wadi part situated lower than the mining area. On the other hand, the aim is to determine factors that play a role in determining antimony accumulation in the studied wadi bank soils. For this purpose, several physico-chemical properties (particle size distribution, CaCO<sub>3</sub>, organic matter (OM), total phosphorus (TP), total nitrogen (TN), exchangeable sodium (ENa), exchangeable calcium (ECa), exchangeable magnesium (EMg) and exchangeable potassium (EK) contents, cation exchange capacity (CEC), pH and electrical conductivity (EC) and aqua regia extractable chemical elements Sb, As, Pb, Co, Cu, Cr, Cd, Zn, Fe, Mg, Ca and K were determined. Results show that the majority of soils are severely polluted by Sb and As whose maximal concentrations were respectively 2600 mg.kg<sup>-1</sup> and 450 mg.kg<sup>-1</sup>. They are moderately contaminated by Pb and Zn that respectively reach 145 mg.kg<sup>-1</sup> and 324 mg.kg<sup>-1</sup>. The results of forward stepwise regression analysis show that the most significant variables that explain the soil Sb concentration are, positively, As, ENa, sand, Cd and OM, and, negatively, EK and Zn. These results show that the Sb behaviour differs, partly, from that of the other trace elements, especially in calcareous and semi-arid environments.

**Keywords:** antimony, arsenic, mine, calcareous, semi-arid, stepwise regression

### 1. INTRODUCTION

Antimony (Sb) is one of the most toxic elements that are found among others in soils contaminated by Heavy metals. It is a metalloid belonging to group 15 of the periodic table, which is used in a variety of products worldwide creating and improving dozens of industrial and commercial materials included various alloys, ceramic, glasses, plastics, synthetic fabrics (Shtangeeva et al., 2011), manufacture of semiconductors, diodes, flameproof retardants, lead hardener, batteries, small arms, tracer bullets, automobile brake lining and pigments (Filella et al., 2002).

Antimony and its compounds are considered to be hazardous to human health (Alloway, 1995) and produce injury in organ systems such as the lungs, the heart, the liver and the kidney (Fowler &

Goering, 1991). They are very carcinogenic (Hammel et al., 2000). Antimony is also considered to be pollutant of priority interest by the United States Environmental Protection Agency (Adriano, 2001) and the European Union (Filella et al., 2002). However, even though heavy metals pollution and its environmental impacts has been the subject of numerous researches for decades (Alloway, 1995; Kabata-Pendias & Pendias, 2001; Adriano, 2001; Damian et al., 2008), it is only in the last decade that interest in Sb pollution became increasing (Cal-Prieto et al., 2001; Filella et al., 2009; Wilson et al., 2010; Varga et al., 2012; Marin et al., 2010; Frankova et al., 2012). For this reason, the understanding of its toxicity and environmental behaviour is much more limited (Filella et al., 2002). Additionally, very few studies on the mobility of Sb in calcareous, semi-aridic zones affected by old

mining activities have been undertaken (Pérez-Sirvent et al., 2011).

In the Sb mining area of Djebel Hamimat (Northeast Algeria) which ceased operations in 1952, Rached & Gardou (1988) had identified high rates of Sb in soils surrounding mine spoils. However, the extension of this pollution to the valley of Dahimine Wadi, the Sb dispersion in calcareous soils and its relationships with other edaphic factors has not been examined yet. Moreover, contamination assessment by other trace elements like As, known to accompany often the Sb ore, has not been performed yet in the studied area.

The objective of this work is to assess the pollution or contamination extent in the Dahimine wadi bank soils, not only by Sb but also by other trace elements. Our goal is also to contribute to the knowledge of the environmental Sb behaviour by the

determination of soil physic-chemical variables that affect the Sb dispersion.

## 2. MATERIALS AND METHODS

### 2.1. Site description

The study area has an average altitude of 865 m and is located down a mountain (Djebel Hamimat) whose the summits are at 1039 m and 967 m (Fig. 1). It is characterized by a semiarid Mediterranean climate. The average annual air temperature is 14.3°C and the annual total precipitations are 435 mm in average (mean calculated over the previous thirty years), with the rainfall season extending from November to April. Bank soils are xerofluvent types and sparsely covered with a steppe.

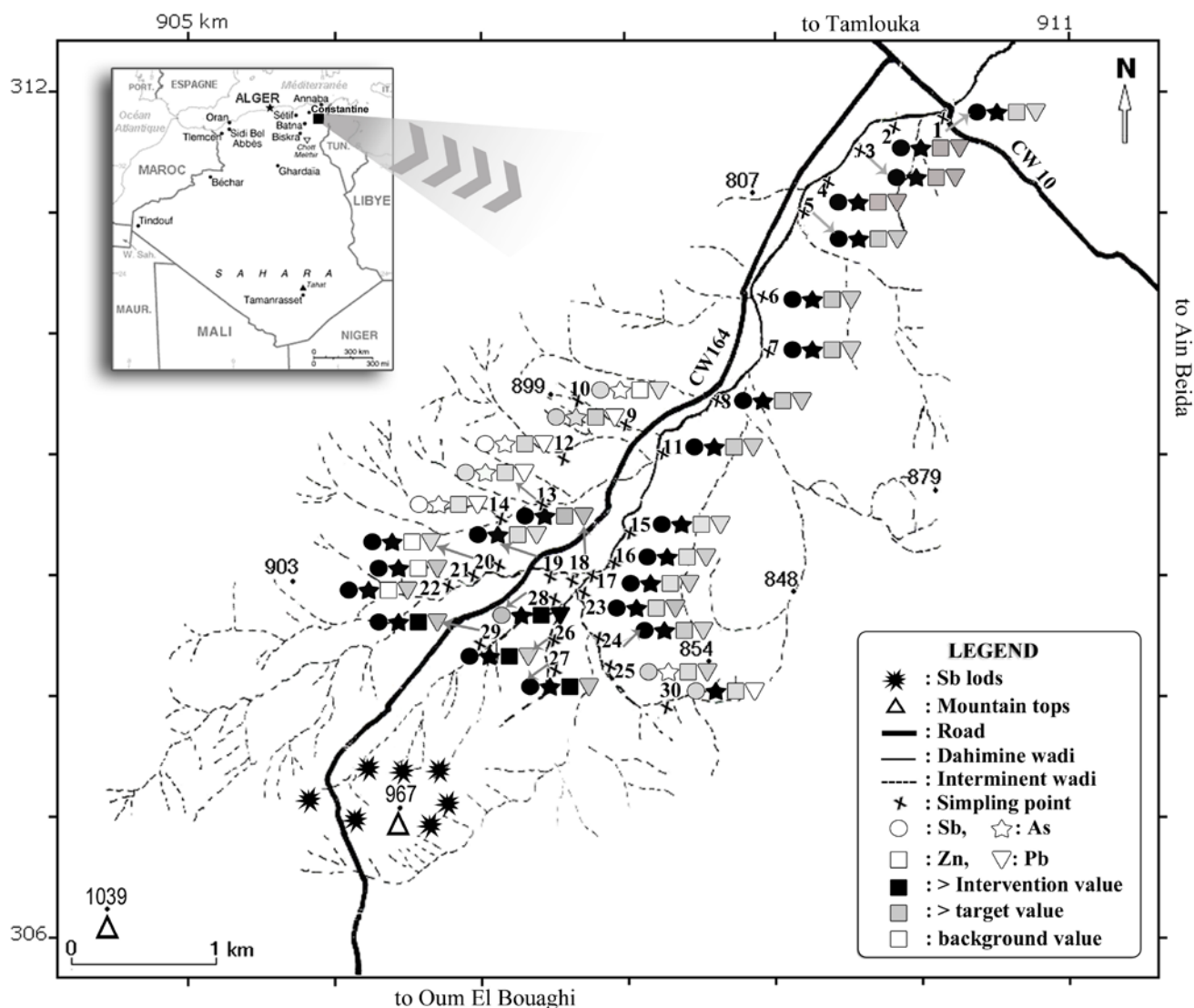


Figure 1. Location of the sampling points and distribution of antimony and other traces elements along the edges of the studied Dahimine wadi part (Algeria)

The sampling area is mainly occupied by sedimentary rocks of the ancient quaternary. It is dominated by the Djebel Hamimat where the Sb ores occur. According to Boisson & Neybergh (1977) This Mountain is an anticline with a SW-NE axis forming an arc with a SE convexity. It comprises on its sides sandstones and marl-sandstone and on its center marly limestone and fine limestone. The series is dated Lower Cretaceous. The antimony metal concentrations appear on the mountain sides in different levels of cracked and fissured limestone.

According to SONATRACH (1977), ore textures range from massive to cellular and from druse to coarsely crystalline. The principal ore minerals are senarmontite ( $\text{Sb}_2\text{O}_3$ ), romeite ( $\text{Ca,Fe}^{2+},\text{Mn,Na}_2(\text{Sb,Ti})_2\text{O}_6(\text{O,OH,F})$ ), stibnite ( $\text{Sb}_2\text{S}_3$ ), boulangerite ( $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ ), kermesite  $\text{Sb}_2\text{S}_{20}$  and berthierite ( $\text{FeSb}_2\text{S}_4$ ), with secondarily sphalerite ( $\text{ZnS}$ , where Mn and Cd can substitute the Zn), bindheimite ( $\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O,OH})$ ), arsenopyrite ( $\text{FeAsS}$ ), cerussite ( $\text{PbCO}_3$ ), orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\text{AsS}$ ), scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ), and cinnabar ( $\text{HgS}$ ). Pyrite ( $\text{FeS}_2$ ), siderite ( $\text{FeCO}_3$ ), hematite ( $\text{Fe}_2\text{O}_3$ ) and malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ) are rare. The main primary gangue mineral is calcite, and the secondary is quartz, barite and gypsum.

The main Sb ore extracted in the studied mining area is senarmontite. It is associated with stibnite in little amounts (Boisson & Neybergh, 1977). According to Hackspill et al., (1964), Sb ore may be associated with many trace elements like Pb, Zn, Cu, As, Co, Cd and Fe.

## 2.2. Soil sampling and analysis

On the map of the studied area, pencil marks were put every 100 m along the main river and all the tributaries of a wadi part situated lower than the mining area. Then, 300 sampling points were obtained whose 30 sampling points were randomly chosen thanks to the random digit table (Fig. 1).

In the chosen sampling points, on a quadrat of  $4\text{m}^2$ , an average soil sample was taken. It was composed of 10 subsamples taken to a depth of 20 cm and thoroughly mixed.

Prior to analysis in the laboratory, soil samples were air dried at ambient temperature ( $22\text{--}25^\circ\text{C}$ ), crushed manually in a porcelain mortar and sieved through a 2 mm plastic screen.

The soils were characterized by conducting standard soil property tests: Particle size analyses were conducted following oxidation of organic matter with hydrogen peroxide, dispersion with sodium hexametaphosphate and stirring for 16 hours, determination of silt and clay fractions by using the

Robinson pipette method and separation of Sand by sieving (Pansu & Gautheyrou, 2006). Soil pH ( $\text{H}_2\text{O}$ ) was determined with glass-electrode in a 1: 2.5 soil water suspension (W/V), thanks to a pH-meter calibrated with three buffer solution (pH=4.0; 7. 0; and 11).  $\text{CaCO}_3$  contents were determined by volumetric method using a Bernard calcimeter. Organic matter (OM) was analyzed by dichromate oxidation and titration with ferrous ammonium sulphate (Walkley & Black, 1974). Cation exchange capacity (CEC) was measured by displacement method, using sodium acetate ( $\text{NaOAc}$ ) buffered at pH 8.2 (Pansu & Gautheyrou, 2006). The exchangeable cations ( $\text{Na}^+$ ,  $\text{Ca}^+$ ,  $\text{Mg}^+$  and  $\text{K}^+$ ) were determined, by flame photometer, in the liquid phase obtained after  $\text{NaOAc}$  saturation. Total nitrogen was analyzed by Kjeldhal method and titrimetry according to the procedure described by Pansu & Gautheyrou (2006). Total phosphorus was determined, after an acid digestion, by spectrophotometry and the electrical conductivity was measured in the extract of saturated paste (Pansu & Gautheyrou, 2006).

Soil pseudo-total chemical elements contents (Sb, As, Cd, Cr, Co, Cu, Pb, Zn, Mg, Fe, Ca, Na and K) were extracted by using an aqua regia digestion. Therefore, 7.5 ml HCl and 2.5 ml  $\text{HNO}_3$  were added to 0.5 g of soil inside teflon vessels and digested by high pressure in a microwave oven (Berghof-speedwave MWS-2). Na, Ca and K were measured by flame photometer (Jenway PFP7). Co, Cu, Pb, Zn, Mg and Fe were determined by flame atomic absorption spectrometry (F.A.A.S., Perkin Elmer A.Analyst 300). The analysis of Cd, Cr, As and Sb was performed with an electrothermal-AAS (EAAS Perkin Elmer HGA 800 - A.Analyst 300).

The accuracy of the methods was checked by analyzing standard reference materials (with six replicates): CRM052-050 (Trace Metals – Loamy Clay 1).

In order to assess the quality of the studied soils, from trace element concentrations point of view, we used the Dutch methodology of risk assessment (VROM, 2000). For this purpose, the values for a standard soil were converted to values applying to the actual soil concerned on the basis of the measured organic matter and clay content. Then, the converted values were represented in terms of soil quality standards (target values and intervention value), on the map of the sampling points (Fig. 1).

## 2.3. Statistics

Univariate distribution of all variables included in the analysis was carefully examined and Shapiro-Wilk Tests of normality were performed. If a

strong departure from normality was identified, transformation to normality was considered.

The goal of the statistical analysis is to explain the concentration of antimony in the soil by concentration of other metals and environmental variables.

Univariate associations were measured through marginal Pearson-correlation between antimony and each of the other variables included in the analysis.

Due to the small number of statistical units, thirty (30), and a forward stepwise regression analysis with antimony as dependent response variable and all the remaining variables as independents, was performed.

The first variable entered in the model is the most strongly associated with the antimony, while a variable that is not in the model is not associated with the antimony. The estimation of parameters in the final model and their significance (p-value) has been also presented.

SAS software (SAS® 9.3, SAS Institute Inc., North Carolina) was used for the statistical analyses.

### **3. RESULTS AND DISCUSSION**

#### **3.1. Principal soil properties**

The studied soils have (Tab. 1) largely a loamy texture, a moderately alkaline pH, low to medium contents of organic matter, high contents in total  $\text{CaCO}_3$ , total nitrogen, total phosphorus, total calcium, total sodium and total iron. In general, the soil contents in potassium and magnesium are low. The electrical conductivity corresponds to a salinity that varies between low to very high. The cation exchange capacity values vary between low to average and seem to fit illite clay. In the studied soils, the exchange complex is dominated by the cations Na and Ca which both present very high values. Except electrical conductivity and organic matter, which vary a lot, all the other soil properties are not very variable. This indicates a relative homogeneity of the studied soils.

#### **3.2. Trace elements contents**

The study of table 1 shows that the Sb and As soil concentrations are very high. They exceed, in all the soils, the average values for world soils (respectively:  $0.62 \text{ mg.kg}^{-1}$  and  $4.7 \text{ mg.kg}^{-1}$ ) reported by Alloway (2013) and in 80% of the samples, the soil maximum allowable concentration reported by Kabata-Pendias & Pendias (2001) for Poland and Germany. The Sb maximum concentration reached

( $2600 \text{ mg.kg}^{-1}$ ) is higher than the maximum Sb concentration ( $1565 \text{ mg.kg}^{-1}$ ) found in a mining area of China (He & Yang 1999). The As maximum concentration reached ( $450 \text{ mg.kg}^{-1}$ ) is greater than the highest concentrations (100 to  $115 \text{ mg.kg}^{-1}$ ) reported for polluted soils of some parts of Europe by Göd & Heiss (1996).

The Co, Cr, Cu, Pb and Zn concentrations, in all the studied soils (Table 1), are higher than the average values for world soils (respectively:  $6.9 \text{ mg.kg}^{-1}$ ,  $42 \text{ mg.kg}^{-1}$ ,  $25 \text{ mg.kg}^{-1}$ ,  $14 \text{ mg.kg}^{-1}$  and  $62 \text{ mg.kg}^{-1}$ ) reported by Alloway (2013). However, only the Cr, Pb and Zn concentrations exceed the maximum allowable concentration reported by Kabata-Pendias & Pendias (2001) for Germany and solely for 10 to 13% of the studied soils. The maximum of Co, Cr, and Zn concentrations of the studied soils are higher than those found in mining areas by Pratas et al., (2005). All the studied soil Pb concentrations are included in the soil concentrations range ( $35.7\text{--}416 \text{ mg.kg}^{-1}$ ) found by the same author and the Cu maximum value is close to that found by this latter ( $40.7 \text{ mg.kg}^{-1}$ ).

The Cd concentrations of the studied soils are very low. They are included in the Cd concentration interval ( $0.06\text{--}1.1 \text{ mg.kg}^{-1}$ ) agreed by Kabata-Pendias & Mukherjee (2007) for uncontaminated soils and do not exceed the Cd average concentration ( $1.1 \text{ mg.kg}^{-1}$ ) reported for world soils by Alloway (2013).

Likewise, the study of table 1 shows that the Sb, As and Cd are very variable from a sampling station to another. Besides, the Sb variation exceeds by far that of all the other soil factors. Pb, Cr and Cu are also variable, but much less than the elements previously referred to. Such important variability of the trace elements reflects an important pollution by the trace elements quoted and especially by the Sb.

#### **3.3. Trace elements distribution along the wadi banks in relation to the Dutch reference values.**

The representation (Fig. 1), in terms of soil quality standards of the concentrations of the most contaminant trace elements, shows that Sb and As concentrations are above the Dutch Intervention Value in almost all the sampled plots. They are found in the plots located on the bank gullies starting near the ore deposits and in the main river branch which receives flows of those gullies. The soil plots (number 9, 10, 12, 13, 14 and 25) containing the lowest levels of Sb and As (lower or equal to the target value) are located in the gullies starting from the mountain sides that do not comprise ore deposits.

Table 1. Descriptive basic statistics of pseudo total trace elements contents and principal properties of soils and environments factors (30 samples) and results of forward stepwise regression analysis

Variable	Mean	Standard deviation	Min	Max	Marginal correlation with (p-value)	Step (1)	$\beta$ (2)	P-value (3)
Sb <sup>T</sup> ( $\mu\text{g. g}^{-1}$ )	383.07	596.87	1.10	2600.00				
As <sup>T</sup> ( $\mu\text{g. g}^{-1}$ )	131.83	121.50	8.00	450.00	0.97 ***	1	4.95	$3.10^{-4}$ ***
Pb <sup>T</sup> ( $\mu\text{g. g}^{-1}$ )	61.78	29.5	34.00	145.00	0.87***	14	1.41	0.18
Zn ( $\mu\text{g. g}^{-1}$ )	182.46	63.37	92.00	324.00	0.86 ***	10	-2.39	0.03*
Cd <sup>T</sup> ( $\mu\text{g. g}^{-1}$ )	0.22	0.29	0.05	1.1	0.73 ***	8	2.55	0.02*
Co( $\mu\text{g. g}^{-1}$ )	28.73	6.12	16.00	40.00	0.64 ***	15	1.16	0.27
Cu( $\mu\text{g. g}^{-1}$ )	32.49	4.55	23.20	42.00	0.54 **			
Cr( $\mu\text{g. g}^{-1}$ )	92.00	12.97	70.00	130.00	0.10	6	-1.44	0.17
Fe (%)	5.76	0.94	3.60	7.30	0.69 ***			
K( $\mu\text{g. g}^{-1}$ )	2698	530.73	1494	3736	0.58 ***			
Ca <sup>T</sup> (%)	6.41	2.46	3.10	13.10	0.57 ***			
TP( $\mu\text{g. g}^{-1}$ )	1955	310.66	1462	2837	0.55 **	13	-1.81	0.09
Mg ( $\mu\text{g. g}^{-1}$ )	1011	173.07	663.00	1447	0.46 *			
TN <sup>T</sup> (‰)	1.35	0.49	0.90	3.12	-0.34	3	-1.19	0.25
Na ( $\mu\text{g. g}^{-1}$ )	4697	710.26	3300	6100	0.03			
ENa <sup>T</sup> ( $\text{cmol}^+. \text{kg}^{-1}$ )	12.62	3.03	8.40	21.00	-0.72 ***	9	3.02	0.01*
ECa <sup>T</sup> ( $\text{cmol}^+. \text{kg}^{-1}$ )	11.14	3.20	6.80	22.00	-0.54 **			
EMg ( $\text{cmol}^+. \text{kg}^{-1}$ )	3.42	1.05	1.40	6.00	0.21	5	-0.29	0.78
EK <sup>T</sup> ( $\text{cmol}^+. \text{kg}^{-1}$ )	0.64	0.26	0.27	1.46	-0.06	4	-2.86	0.01*
Sand (%)	44.86	9.39	25.60	62.00	0.81 ***	2	2.60	0.02*
Silt (%)	34.47	6.86	18.18	49.54	-0.70 ***			
Clay <sup>T</sup> (%)	18.14	3.99	11.79	27.56	-0.57 **			
CaCO <sub>3</sub> (%)	16.15	5.24	6.75	29.70	0.63 ***			
OM <sup>T</sup> (%)	0.82	0.55	0.29	2.96	-0.07	7	2.47	0.03*
CEC ( $\text{cmol}^+. \text{kg}^{-1}$ )	32.01	3.99	25.20	44.00	-0.59 ***	11	-1.36	0.19
EC <sup>T</sup> ( $\text{mS. cm}^{-1}$ )	7.53	6.69	0.84	27.00	0.50 **			
pH	7.86	0.17	7.40	8.30	0.23			
Road distance (km)	0.56	0.49	0.09	2.09	-0.58 ***	16	-0.71	0.49
Mine distance (km)	2.73	2.09	0.63	7.72	0.23	12	-0.22	0.83
1) Entry step in the final regression model (forward method). 2) Regression parameter in the final model. 3) Significance of parameters in the final model. T : variable transformed (Log); TP : total phosphorus; TN : total nitrogen; E Na: exchangeable sodium; E Ca: exchangeable calcium; E Mg: exchangeable magnesium; E K: exchangeable potassium; OM: organic matter; CEC: cation exchange capacity; EC: electrical conductivity. * $p < 0.05$ , ** $p < 10^{-2}$ , *** $p < 10^{-3}$								

The Zn concentrations exceed the contamination threshold (target value) in all soils studied and the pollution threshold (intervention value) in plots 26, 27, 28 and 29. These plots are those which are near several lodes.

The soil Pb concentrations do not reach the Intervention value in all the studied soils. They are higher than the target value, except in plots 9, 12, 13, 14 and 30 (mentioned above) where they are below this one.

On the basis of the study of the trace elements distribution in terms of soil quality standards, it

appears that important pollution and contamination, by Sb, As, Pb and Zn were generated along the wadi banks by the mining proximity and that the hydrologic network is the principal responsible of the contamination and pollution extension towards the valley bottom.

### 3.4. Relationships between Sb concentrations and physic-chemicals characteristics

Pearson's correlations between Sb and all the soil parameters studied are presented in table 1 which

shows particularly high and very significant ( $P < 0.0001$ ) positive correlations of antimony with (in the order of correlation coefficient importance) As, Pb, Zn, Cd, Fe, Co and sand. It also shows moderately high and significant ( $0.0006 < p < 0.0273$ ) positive correlation of Sb with (in the order of correlation coefficient importance) total limestone ( $\text{CaCO}_3$ ), total potassium, total calcium, total phosphorus, Cu, electrical conductivity and total magnesium.

The very strong correlations between Sb and As, Pb, Zn, Cd, Co and to a less extent with Cu, indicate that these elements are associated with Sb and that they originate from the same source, namely mining. This is also confirmed by the existence of very strong inter-correlations ( $P < 0.0001$ ) between As and Zn, Pb, Cd, Co and Cu (respectively  $r = 0.970$ ,  $r = 0.968$ ,  $r = 0.878$ ,  $r = 0.727$ , and  $r = 0.643$ ), between Zn and Pb, Co, Cd and Cu (respectively  $r = 0.931$ ,  $r = 0.772$ ,  $r = 0.809$  and  $r = 0.702$ ), between Pb and Cd, Co and Cu (respectively  $r = 0.932$ ,  $r = 0.687$  and  $r = 0.644$ ) and between Co and Cd and Cu ( $r = 0.647$  and  $r = 0.851$ ). Such result was predictable due to the chemical composition of the mineral ores that accompany the Sb or and also because according to Hackspill et al., (1964) Sb ore may be found to be combined with several trace elements. Moreover, Rafiei et al., (2010) also determine significant correlations between Sb and As, Pb and Cd.

The strong correlation of Sb with sand, which indicates therefore the presence of this element in soils with the highest percentage of sand, can be accounted for the fact that in the study area Sb veins are associated with undifferentiated Cretaceous (Voute, 1957) which corresponds to sandy clays, marl and limestone lenses. Ore extraction is thus accompanied by the sand which is transported along at the same time as Sb during floods. Moreover, according to Ritchie et al., (2013), the Sb ore is often surrounded by a matrix of sand and limestone. However, this can also be explained by the fact that the sands may have a significant sorption of Sb, as has been highlighted by Hasany & Chaudhary (1996).

The high correlation between Sb and Fe may be due to the fact that Sb is closely linked to Fe (Gal et al., 2006; Denys et al., 2008; Ritchie et al., 2013.). Indeed, this element is considered as one of the most important factors that control the contents and behaviour of trace metals in soil (Kabata-Pendias & Krakowiak, 1995). Moreover, Mitsunobu et al., (2010) found that a significant amount of Sb bound to quartz particles coated by Fe (hydr)oxides was present as Sb(III) in Sb mining area. According to Hockmann & Schulin (2013), Fe (hydr)oxides in particular can effectively limit the Sb displacement in soils due to their ubiquitous occurrence and their high

sorption capacity for Sb. Iron may also limit Sb solubility by the formation of low-soluble Fe-bearing Sb minerals.

The Sb being significantly and positively related to  $\text{CaCO}_3$  and total Ca may mean that in soils heavily contaminate by Sb and containing high amounts of  $\text{CaCO}_3$  and of  $\text{Ca}^{2+}$ , like our soils, precipitation of  $\text{Ca}[\text{Sb}(\text{OH})_6]_2$  may control Sb concentrations in soil water (Johnson et al., 2005). The formation of  $\text{Ca}[\text{Sb}(\text{OH})_6]_2$  has also been suggested by other authors to explain unexpectedly low Sb concentrations in extracts of alkaline soils (Conesa et al., 2010; Okkenhaug et al., 2011; Oorts et al., 2008). It is the same case for K and Mg that are the most prominent candidates to form precipitates with Sb according to Hockmann & Schulin (2013). They associate with Sb to form the compounds  $\text{K}[\text{Sb}(\text{OH})_6]$  and  $[\text{Mg}(\text{H}_2\text{O})_6][\text{Sb}(\text{OH})_6]_2$ .

The significant positive correlation of Sb with P seems to be the consequence of the very strong correlations between P and the other metals that are strongly related to Sb. Indeed, P is highly and positively ( $p < 0.0001$ ) correlated to As, Cd, Pb and Zn (respectively  $r = 0.760$ ,  $r = 0.739$ ,  $r = 0.810$  and  $r = 0.714$ ) and moderately and positively ( $p < 0.05$ ) correlated to Cu and Co (respectively  $r = 0.444$  and  $r = 0.433$ ). In fact, precipitation as metal phosphates is considered as one of the mechanisms for the phosphate-induced immobilization of heavy metals, especially in substrates containing high concentration of metals (Adriano et al., 2004).

The significant positive relationship with the electrical conductivity may be due to the presence of Sb salts (Bothorel, 1958) which results in an increase in the salinity of the soils studied.

Table 1 shows highly significant negative correlations ( $P < 0.0001$ ) of Sb with silt and exchangeable sodium and significant negative correlations ( $0.0006 < P < 0.0273$ ) with clay, CEC, exchangeable calcium and the distance to the road. Nitrogen has a very small and insignificant negative correlation ( $p = 0.0671$ ) with Sb.

The negative relationship of Sb with CEC means that the more soil CEC increases, the less Sb is retained in the soil. This is contrary to what is usually reported by most authors for most heavy metals (Du Laing et al., 2009; Kabata-Pendias & Pendias, 2001). According to Wilson & Webster-Brown (2009), little is known about the effects of competitive adsorption of Sb and even less in an alkaline environment. However, this can be explained by the fact that as Sb is strongly and positively correlated to sand, it is all the more present as the soil is sandy and therefore with a low CEC. Indeed, it is well-known that the CEC increases as

the fine soil fraction increases (McDonald et al., 2005). Moreover, in the case of our soils, the CEC presents a significant negative correlation with sand ( $r = -0,481$ ,  $p = 0,007$ ) and a significant positive correlation with clay ( $r = 0,491$ ,  $p = 0,006$ ). In the same vein, the negative strong correlation between Sb and exchangeable Na might result from the combination of the significant negative correlation between the Sb and the CEC on the one hand, and the significant positive correlation ( $r = 0,901$ ,  $p < 0,0001$ ) between the exchangeable Na and the CEC on the other hand.

Contrary to what has often been reported by many authors for most heavy metals (Du Laing et al., 2009; Kabata-Pendias & Pendias, 2001; Young, 2013) clay and silt show significant negative relationships with Sb concentrations in the study area. This can be explained by the fact that as Sb is strongly related to sand it cannot be related to clay, because if the soil is rich in sand it cannot be rich in clay or silt at the same time.

The negative significant correlation between Sb concentrations and road distance means that the closer you get to the road the greater the Sb concentrations are. The traffic seems to contribute to the Sb pollution of the studied area. Some authors have highlighted the impact of road traffic on soil contamination by Sb (Dietl et al., 1997; Cal-Prieto et al., 2001). However, in our case, this result may also be due to the fact that the locations containing the highest concentrations (Fig. 1) are located mainly along the main river which is along the road and very close to it. Therefore, this river starting closely to the mine spoils is the principal responsible for the spread of this toxic pollution.

### 3.5. Factors affecting Sb concentrations in the Dahimine wadi bank soils

The results, of the stepwise linear regression (Table 1), show that among the variables correlated with Sb, mentioned above, only Pb, Zn, As, Co, Cd, cationic exchange capacity, sand, exchangeable sodium, total phosphorus, nitrogen and the distance to the road are involved in the explanation of the soil Sb concentrations (Fig. 2). Variables, like Cr, organic matter, exchangeable potassium, exchangeable magnesium, and the distance to the mine, that were not correlated with Sb, are also involved in the Sb explanation.

Arsenic appears to be the most important variable (step 1) having the largest  $\beta$  (4.95) and the most significant  $p$  (0.0003). It is the most important trace element that gives the better explanation of the soil Sb concentrations. This variable has, therefore, the

maximum weight in the prediction of soil Sb contents. In fact these two metaloids often exist simultaneously in mining areas (Arik & Yaldiz, 2010; Oprea et al., 2010; Marin et al., 2010; Bech et al., 2012; Frankova et al., 2012). Both have a similar structure and both belong to the same group of the periodic table. Adriano (2001), has suggested that the As and Sb may exhibit similar behaviour in the environment.

Exchangeable Na is the second most important variable, after the As that has the best weight in the Sb contents prediction. It is significantly and positively associated with the Sb. According to Hockman & Schulin (2013), this can be due to the fact that since Na occurs often in high concentrations in soil solutions (the case of our soils) it is the most prominent candidates to form precipitates with Sb.

The third significant variable with a good weight in Sb concentrations explanation is the exchangeable potassium. The  $\beta$  negative sign of this explicative variable shows that the more exchangeable potassium concentration in the middle there is the less antimony there is. This can result from the fact that the highest antimony concentrations are found in sandier soils, thus containing less clay. So, as exchangeable potassium is a major component of clays (Schulze, 2005), and as soils with a lot of sand contain less clay, they will therefore contain less exchangeable potassium. However, according to Okkenhaug et al., (2011), salts like  $\text{KSb(OH)}_6$  are completely dissolved in oxalate-ascorbic acid extractions which indicate a higher mobile fraction of Sb in the soil than estimated previously. Therefore, it is possible to deduce that the Sb will bind to the exchangeable K to form  $\text{KSb(OH)}_6$ , then, being more mobile it will be eliminated from the soil.

The sand is the fourth independent variable that best explains significantly ( $p=0.0221$ ) the soil Sb concentrations. This result confirms the strong association of this variable with Sb, explained above. The fifth variable that intervenes significantly and positively in the Sb concentrations prediction is the Cd. It is the second most important trace element, after As, that is associated with the Sb. According to Brookins (1986), Sb, As and Cd have been proposed as pathfinder elements, among others, for telethermal-xenothermal-epithermal ore deposits of gold. So, the three elements seem to occur often together and to originate from the same source in the studied area. It seems to be also the case of the Pb and the Co. Indeed, despite being not related significantly to the Sb, these two trace elements appear as the best predictor trace elements of the Sb, after the As and Cd among those studied.



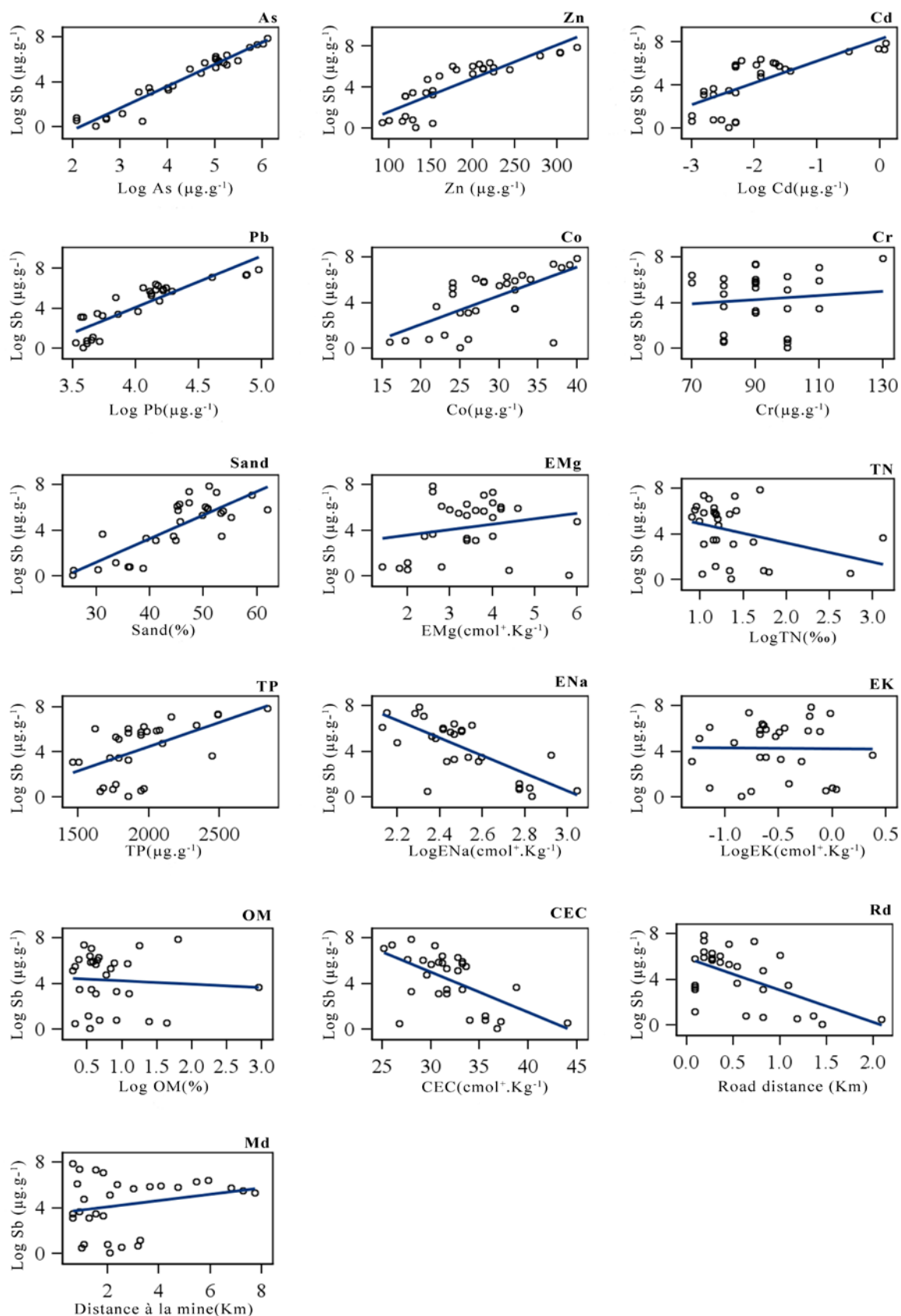


Figure 2. Correlations between Sb concentrations and variables involved in its explanation by stepwise linear regression. Rd: road distance, Md: mine distance, TP: total phosphorus; TN: total nitrogen; E Na: exchangeable sodium; E Mg: exchangeable magnesium; E K: exchangeable potassium; OM: organic matter; CEC: cation exchange capacity.



Organic matter has also a good weight in the Sb concentrations prediction. It is the sixth variable that significantly explains the presence of Sb concentrations in the studied soils. The  $\beta$  positive sign means that when soil organic matter contents increase soil Sb concentrations increase too. Thus, Sb is all the more retained in the soil as the organic matter contents are high. Indeed, according to Gluskoter et al., (1977), Sb is among the elements that have the highest organic affinity. Therefore, Rafiei et al., (2010) highlights a very strong correlation between Sb and organic matter in soils of a gold mining area and, according to Wilson et al., (2010), Sb association with soil organic matter in environmental samples has been confirmed in recent years.

The seventh and latter variable that affects the soil Sb concentrations significantly is the Zn. Its  $\beta$  negative sign can be explained by the fact that substantial reduction in the sorption of Sb on sand was noticed in the presence of the Zn(II), the Cr(III) and the Mg(II) (Hasany & Chaudhary, 1996). These cations, according to the same authors, appear to have strong affinity towards the sand surface and may occupy the sorption sites more strongly than Sb ions or may displace the sorbed Sb ions from the sorbent surface and get themselves sorbed on the surface of the sand. This may explain why the Cr and the exchangeable Mg are among the variables that affect negatively the soil Sb concentrations, although not significantly.

Soil Sb concentrations are affected, almost significantly but negatively, by the total phosphor concentrations. Thus, the more total P is present in the soil, the less Sb there is. This may be linked to the fact that the soil P presence leads to the Sb mobilization and then to its reduction in the soil. Indeed, Kilgour et al., (2008) reported significant release of Sb from contaminated firing range soils where P was added as superphosphate. Moreover, soil-solution distribution coefficients for Sb on Japanese agricultural soils decreased with increasing phosphate concentrations (Nakamaru et al., 2006).

Despite the fact that it is not significantly correlated with the Sb, nitrogen has been selected by the stepwise regression among a lot of other variables, as Sb concentrations predictor. So, it affects the soil Sb presence, although not significantly. The  $\beta$  negative sign means that the soil N presence would lead to a reduction of the soil Sb contents. According to Wilson et al., (2013) the addition of fertilizers to soil (including nitrogen), supplemented with limestone, increases Sb solubility and plant uptake. Therefore it is likely that the richest soil in nutrients, thus in nitrogen, will contain relatively less Sb which would have been dissolved and then less retained by

the soil.

The CEC appears as an independent variable which explains the soil Sb concentrations negatively, but not significantly. This result confirms the one obtained by the Pearson's correlation for the same reasons mentioned above.

The distance to the mine accounts for the soil Sb concentrations negatively, although not significantly. Thus, the closer one gets to the mine, the higher Sb concentrations one gets. Such a result confirms the mine responsibility in the Dahimine river borders pollution by Sb. The low value of this relationship is probably due to the fact that some sampling locations present high Sb contents despite being far from the mine exploitation. Such irregularity in the Sb distribution, along the bank river, finds its explanation in the river border irregularities which are sometimes relatively elevated, from the riverbed, and sometimes at the same level as the water, thus being more or less contaminated by the floods.

The soil Sb concentrations are in negative correlation with the distance to the road. Such result confirms the relationship, although not significantly, of this variable with Sb obtained with the Pearson correlation and explained above.

It appears that, as opposed to what has been reported for the majority of the other trace elements, neither the pH nor the clay affected the soil Sb concentrations. However, these results are consistent with those of other authors. Indeed, according to Hockmann & Schulin (2013), it was found that sorption of Sb(III) and Sb(V) to clay minerals such as montmorillonite and kaolinite at pH values around 7.5 was one to two orders of magnitude weaker than sorption to Fe and Mn (hydr)oxides in the same pH range. Moreover, Kabata-Pendias & Mukherjee (2007) have reported that Sb mobility is not based on the pH value of soils. However, the lack of association between the soil pH and the soil Sb concentrations could be explained by the fact that the pH of the studied soils is not at all variable.

#### 4. CONCLUSION

The bank soils of the studied Dahimine wadi part, although located well below the mining and the ore deposits, are seriously polluted by Sb and As that exceed the remediation threshold in almost all the sampled plots. They are contaminated by Zn and Pb in the majority of the plots and moderately contaminated by Co, Cr and Cu in some plots. It appears that the pollution and the contamination by the studied trace elements are the consequence of the ancient mining remnants. The spread of the pollution

is favoured by the Dahimine wadi and its numerous branches whose waters, thanks to the heavy rains that occur often in the semi-arid climate, carry the toxic elements towards the valley's bottom and deposit them on the wadi edges where they concentrate, during the floods. The Sb concentration in the studied soils, with very great amounts of CaCO<sub>3</sub> and a semi-arid climate is favoured significantly and principally by the high concentration of exchangeable Na, the great amounts of sand and OM. On the contrary, it is disadvantaged by the CEC increase and the high concentrations of the exchangeable K, the total Zn and the total P. As opposed to what has been often reported for the majority of trace elements in the case of acid soils and wet climate, neither the fine particles (clay and silt) nor the pH favour the Sb accumulation. It appears, in the case of semi-arid and calcareous environments, that the Sb behaviour differs from that of the other trace elements.

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