IMPACTS OF INDUSTRIAL WASTES ON THE AGRICULTURAL SOIL IN WEST AREA OF ALGERIA: FRACTIONATION AND CONTAMINATION OF HEAVY METALS IN SOILS BY SEQUENTIAL EXTRACTION PROCEDURE

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Abstract

The selected region is west of Algeria Ghazaouet exactly near industrial discharges from the production unit ALZINC which is the main productive zinc, sulfuric acid and copper in Algeria. Releases of the latter are stored in the form of dikes and pose a serious threat to the environment. Agricultural soil around these discharges are characterized by an alkaline pH, resulting mainly high carbonate levels, the average values in the cationic exchange capacity and a texture sandy soil. Geochemical points of view, these soils have high levels of Zn, Cd, Ni, Cr related to industrial discharges. Whereas Fe, Mn, Pb and Cu concentrations recorded in different places does not exceed the maximum tolerated levels in soils**.** Fractionation of these eight metals studied (Zn, Fe, Mn, Pb, Cu, Cr, Ni and Cd) shows that the fractions of the most important metal parts are stored in the remaining phase (Fe, Cr, Pb). The other metals (Zn, Mn, Cu, Cr, Ni and Cd) are mainly concentrated in the labile fraction (or mobilizable) which is represented by fractions: the exchangeable phase, the organic phase, and the carbonate phase phase oxides of iron and manganese which could subsequently contaminate food crops in these regions.

Keywords: Contamination, Sequential Extractions, Tessier, Soil, ALZINC

Introduction

Heavy metals represent a potential hazard to humans and environment, In industrial areas the heavy metal contents from anthropogenic sources are several times higher than those from natural ones

(Nriagu & Pacyna, 1988; Levei, 2010). In addition, areas far from industrial centres also show increasing heavy metal concentrations due to long-range atmospheric transport (Cemek & Kizilkaya, 2006). Mining and ore processing industry is one of the major sources of metals releasing into the environment (Macklin et al., 2003; Levei et al., 2009).

Depending on their origin, natural (rock) and / or anthropogenic (atmospheric inputs, sludge ...), the heavy metals are not in the same form in soils (Podlesakova et al., 1999). Their fate in the environment differ so. It is therefore essential in order to think the environmental impact of heavy metals in soils with different time scales not just their total content but access to their distribution among the various constituent solid phases of the soil, ie speciation in a broad sense.

The term speciation strictly covers the distribution of chemical species of an element in a system, solid or liquid, being the chemical species of the specific shape defined by its molecular structure, complex electronic or nuclear element. Thus, the analysis of speciation is, strictly speaking, to measure the amount of different chemical species of a single or several elements in a sample. This notion, however, has been used in recent years, in a much broader sense covering the location of the element in different solid phases without taking account of the molecular array involved, or the degree of oxidation) and the ability to raise an element of a solid by a particular chemical reagent (bioavailable form, mobilized ...) (Ure et al., 1995). Then it is an operational definition of speciation and non physico-chemical as is the case in the strict definition of the term. It is this common sense that we refer in this literature review. At present, few methods of determining the speciation are the subject of a consensus within the scientific community, despite the need for such an approach to understanding the mobility and monitoring the fate of heavy metals in the environment. We can cite some of sequential extractions those protocols (Chao,1972; Sposito et al., 1982; Tessier et al.,1979; Ure et al., 1993). Diversity of these protocols makes comparison between studies difficult. In general, all studies agree to conclude that the type of extract is not selective for a given mineral phase and the extraction efficiency depends on the element in question (Martin et al., 1987). In addition, some authors have observed the phenomenon of transfer of a cation phase to another during the extraction.

The objective of this study was to investigate the partitioning of Cu, Fe, Mn, Pb, Zn, Cr, Pb, and Ni in soil from industrial wastes collected ALZINC unity, Ghazaouet City. Determinations was the carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Selection of fractions

The procedure of Tessier et al., (1979) is one of the sequential extraction procedures commonly used for the analysis of trace elements in cationic behavior in soils and sediments. From five successive extractions, this procedure allows to distinguish four fractions (labile fraction) plus a residual:

Phase 1: Exchangeable

Elements adsorbed onto mineral surfaces by nonspecific binding type electrostatic attractions are called 'exchangeable fraction. This is for example the case of the exchangeable cations in positions inter leaf in clays. This fraction is commonly extracted by salt solutions to soil pH or pH 7 (Fuentes et al., 2004).

Phase 2: Bound to Carbonates.

The components of this fraction are precipitated or coprecipitated with carbonates (Emmerson et al., 2000). The extraction is carried out at pH = 5 or 5.5 At these pH, elements not included in the carbonate phases, but related to solid surfaces by links pH dependent (adsorbed elements entering into acid-type reactions Basic) are also released into solution (Benitez & Dubois, 1999).

Phase 3: Bound to Iron and Manganese Oxide

This is referred to as sink for heavy metals, scavenging by these secondary oxides, present as coating on mineral surfaces or as fine discrete particles. This can occur as a combination of the precipitation, adsorption, surface complex formation and ion exchange (Gleyzes et al., 2002). Extraction of metals in Fe-Mn oxides phases with 0.1 $mol.L^{-1}$ hydroxylamine when compared with the extraction with 0.5 $mol.L^{-1}$ hydroxylamine.

Phase 4: Bound to Organic Matter

In organic phase, metallic pollutant bound to this phase are assumed to stay in the soil for longer periods but may be immobilized by decomposition process (Gleyzes et al., 2002). Under oxidizing conditions, degradation of organic matter can lead to a release of soluble trace metals bound to this component. The most commonly used reagent for the extraction of metals in organic phases is hydrogen peroxide with ammonium acetate readsorption or precipitation of released metals (Klock et al., 1986). Other reagents such as H_2O_2 / ascorbic acid or HNO_3 + HCl have been used which can dissolve sulphides with enhanced selectivity, but on the other hand, silicates are attacked to some extent (Ure et al., 1995).

Phase 5: Residual

Residual phase serve as a useful tool in the assessment of the long-term potential risk of heavy metal or toxic metals entering the biosphere. Digestion in strong acid such as nitric acid HNO_3, hydrochloric acid HCI or mixture such as aqua regia ($HN0_3$ + HCl) (Klock et al., 1986), that do not dissolve the silicate matrix have been commonly used to leach out the recasistrant metals that are bound to the sediment in the residual phase. Le mélange d'acides concentrés, HF, $HClO_4$, HCl et HNO_3 proposé notamment par (Hall , 1996), est préférable, car il est plus agressif vis-à-vis des silicates. Residual phase give an estimate of the maximum amount of elements that are potentially mobilisable with changes environmental conditions.

1. Experimental section

1-1. Presentation of ALZINC society

Ghazaouet located in the west of Algeria, the Algerian Society of zinc abbreviation ALZINC is a subsidiary of the Company metallurgy and processing of non-ferrous metals (METANOF). The production of zinc and its derivatives such subsidiary began in 1974. Incorporated stock company with 100% owned by METANOF as part of the restructuring of the parent company, the Company is responsible ALZINC accordance with its articles of production and marketing of zinc and its derivatives: Zinc alloys i, e: zamak (Zn, Cu, Al, Mg), Anodes for cathodic protection, Acid 98% concentrated sulfuric Electrolytic copper cathode 99.98% Minimum content.

Figure 1. Overview METANOF-ALZINC Zinc Electrolysis Unit

1-2. Collection and pretreatment of samples before analysis

The three selected regions: ***Location1***, latitude 35° 05'41"N, longitude 01° 53'34" W; ***Location2,*** 35° 05'39 "N, 01 ° 53'28" W and ***Location3,*** 35° 05 '35 "N, 01 ° 53'27" W. The soil samples were taken in zigzag (six points on average) with a helical auger surface (plowed horizons) 0-20cm of agricultural land soils even mixed region, placed in plastic bags and transported to the laboratory. They were dried at 40°C for three days (AFNOR, 1996) and reduced the porcelain mortar into a fine powder to promote complete dissolution of the analytes (goal: increase the surface area of the materials). Further more a 2mm sieve to remove large solid fragments that are not considered part of the ground (AFNOR, 1992). At the end of these operations quartering is necessary to end homogenizes and obtains a representative sample in which the concentration of pollution is as close as that present in the original soil, end is bagged for later analysis. The collection also collected analyzes current agropedological characterization performed on the same samples: three size fractions, pH, cation exchange capacity (CEC) rate carbonates (AFNOR, 1997-1994).

1-3. Sequential extraction procedure

In our work, the target method is that of Tessier et al., (1979) because it is most commonly used to assess possible chemical associations of metals in sediments and soils. The extractions were carried out in five successive steps (batch 25 ml to 1 g of less than 2 mm of a sample of dried and finely ground soil particle size fraction). The extraction of the various fractions was made as follows:

1-1-1. Exchangeable (F1)

The soil was extracted at room temperature for 1h with 8 mL of either magnesium chloride solution (1 $mol.L^{-1}$ $MgCl_2$, pH 7.0*)* with continuous agitation.

1-1-2. Bound to carbonates (F2)

The residue from (**3-3-1.**) was leached at room temperature with 8 mL of 1$mol.L^{-1}$ NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained and the time necessary for complete extraction was evaluated (5h).

1-1-3. Bound to iron and manganese oxides (F3)

The residue from (**3-3-2**) was extracted with 20 mL 0.04 $mol.L^{-1}$ $NH_2OH.HCl$ in 25% (v/v) HOAc. The extraction was performed at 96 ± 3^oC for with occasional agitation for 5h.

1-1-4. Bound to organic matter (F4)

The residue from (**3-3-3**) was added 3 mL of 0.02M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HN03, and the mixture was heated to 85±2°C for 2h with occasional agitation. A second 3 mL aliquot of 30% H_2O_2 (pH 2 with HNO_3) was then added and the sample was heated again to 85±2 °C for 3 h with intermittent agitation. After cooling, 5 mL of 3.2M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted to 20 mL and agitated continuously for 30 min.

1-1-5. Bound to the soil matrix (residual fraction) (F5)

The residue from (**3-3-4**) was quantitatively transferred into a digestion vessel and metals were dissolved in aqua regia using 7,5 mL of 10 M HCl and 2.5 mL of 15.8M HNO_3. The temperature of the reaction mixture was slowly risen until reflux conditions and maintained for 2h. Three parallel extractions were carried out, in each case using 2.5g soil. All solid/liquid separations were performed by centrifuging, at 5000 rpm for 15 min. The supernatant was removed and analyzed for metals. The residue was washed with 20 mL of de-ionized water. After centrifugation for 15 min the supernatant was discarded. All dilutions were made to 25 mL with 2 % (v/v) HNO_3. For each fraction, a blank was subjected to the same procedure.

1-4. Chemical analysis

An instrument: inductively coupled plasma- atomic emission spectrometry (ICP-AES) standard reference (Vista Pro Varian), France equipped with parallel flow nebulizer and cyclonic spray chamber was used for the monitoring of the heavy metals. The concentrations of heavy metals have been expressed as mg/kg dry weight. The absorption wavelengths were 205.560 nm for Cr**;** 324.754 nm for Cu; 259.940nm for Fe; 257.610 nm for Mn; 216.555nm for Ni; 220.353nm for Pb; 213.857 nm for Zn and 214.439 nm for Cd, respectively.

2. Resultats and Discussion

2-1. Agro-pedological characterization of soils sampled

On the Table 1 are represented the characteristics of soils sampled. The pH is considered the main chemical parameter controlling the bioavailability of heavy metals in the soil (Brallier et al., 1996). The average pH indicates that decreases closer to the release, this subsequently will increase the passage of heavy metals from solid to soil solution and to plants (Thornton et al., 1996) phase. The alkaline nature reflects as well as clays and silts, the calcareous nature of the bedrock. The texture of our soils studied is a kind of sandy soil sandy precisely (Calvet, 2003). The cation exchange capacity (CEC) is also an important characteristic of a solid matrix, it is average by Manceau et al (1996), it corresponds to the amount of saturating cations determined by the soil in a buffered medium, it includes all the exchangeable ions in the soil according to the following formula:

$CEC= \sum EM^{x+} = Ca^{++} + Mg^{++} + K^{+} + Na^{+} + Mn^{++} + Fe^{++} + H^{+}$

According Ekalund et al, (2003) mineral soils have a CEC 0.6meq.g^{-1} and organic soils have a CEC of 2 meq.g^{-1} (200meq/100g). The CEC estimated in our soils are medium range from 29.52 ± 2.96 to 31.26 ± 3.14 Cmoles $^{+}$ / kg. Carbonates are found in large quantities, which explains the basicity of the soils studied, they exceed the no 4g/kg, according to studies by Giller et al., (1998) these are called calcareous soils.

Soils *location*1 and *location3* have low organic matter content unlike ground location 2 or level the class as humus soil (MO:4-10%) (Manceau et al., 1996).

Table 1. Physico-chemical characteristics of soils sampled; has average value b, standard deviation (n = 3).

Location N°	CEC	Carbonates $g.kg^{-1}$	Organic Matter %	pH $_{eau}$	Silts %	Coarse sand %	Fine Sand%
Plots sampled							
location 1	29.52^a $\pm 2.96^b$	4.73 ± 0.15	3.07 ± 0.10	8.34 ± 0.26	2.50	5.13	89.07
location 2	31.26 ± 3.14	6.83 ± 0.21	6.52 ± 0.20	8.89 ± 0.28	2.82	15.88	73.21
location 3	31.14 ± 3.12	5.17 ± 0.16	3.29 ± 0.10	8.52 ± 0.26	2.42	3.50	89.96

2-2. Mineralogical characteristics of soils sampled

The results of analysis of heavy metals (Pb, Zn, Cd, Cr, Cu and Ni) in 5 profiles locations 1, 2 and 3 are shown in Table 2. All the results of each fraction is expressed in $mg.kg^{-1}$dry weight and shown in percentage (%) by weight based on the sum of fractions (F1, F2, F3, F4 and F5) in Figure 2 by the following relationship:

% = weight Fi / Σ weight fractions (F1 + F2 + F3 + F4 + F5), i = 1, 2, 3, 4, 5.

Table 2. **Distribution of Pb, Cd, Cu, Zn, Ni, Mn, Cr and Fe in the different fractions of the three locations sampled in mg . kg^{-1} dry weight.**

	Pb	Cd	Cu	Zn	Ni	Mn	Cr	Fe
Location 1								
F1	0.020 ±0.006	0.060 ±0.018	0.120 ±0.008	8.371 ±2.018	0.010 ±0.003	0.098 ±0.007	0.520 ±0.029	3.0 ± 1.0
F2	0.160 ±0.049	0.090 ±0.028	0.660 ±0.047	1802.492 ±43.419	0.660 ±0.129	60.337 ±4.210	0.771 ±0.042	11.0 ± 1.0
F3	2.300 ±0,692	0.087 ±0.026	0.320 ±0.023	272.247 ±25.476	0.170 ±0.033	5.861 ±0.409	3.700 ±0.202	110.0 ± 6.0
F4	0.170 ±0.052	< DL	0.090 ±0.006	1738.73 ±48.086	0.020 ±0.004	0.398 ±0.028	0.700 ±0.038	0.10 ± 0.03
F5	8.850 ±1.665	0.010 ±0.004	1.090 ±0.078	164,225 ±19.465	0.130 ±0.025	3.070 ±0.214	11.682 ±0.654	410.0 ±22.0
Total	11.50	0.25	2.280	3986.05	0.99	69.76	17.68	534.1
Location 2								
F1	0.091 ± 0.023	0.388 ± 0.116	0.011 ± 0.001	2 .538 ± 0.234	0.263 ± 0.048	0.632 ± 0.044	1.387 ± 0.076	2.0 ± 1.0
F2	2.746 ± 0.824	0.613 ± 0.185	0.490 ± 0.035	314.192 ± 15.929	14.341 ± 2.813	83.680 ± 5.838	1.136 ± 0.061	5.0 ±2.0
F3	94.375 ± 8.408	1.131 ± 0.340	3.081 ± 0.219	1112.615 ± 62.399	92.430 ± 8.121	220.013 ± 15.350	16.071 ± 0.877	1810.0 ± 42.0
F4	12.642 ± 3.803	58.519 ± 7.671	3.461 ± 0.246	479.156 ± 23.140	93.349 ± 9.304	0.372 ± 0.025	12.129 ± 0.662	10.0 ± 1,0
F5	191.888	1.850	20.320	629.653	62.303	66.922	136.338	8080.0

	± 57.776	**± 0.557**	**± 1.447**	**± 31.604**	**±9.215**	**± 4.668**	**± 7.437**	**±745.0**
Total	**301.74**	**62.50**	**27.36**	**2538.15**	**262.67**	**371.62**	**167.06**	**9907.0**
	Location 3							
F1	**0.092 ± 0.027**	**0.970 ± 0.294**	**0.099 ± 0.007**	**108.008 ± 5.992**	**0.311 ± 0.060**	**0.542 ± 0.038**	**2.086 ± 0.114**	**6.0 ± 1.0**
F2	**0.879 ± 0.266**	**0.020 ± 0.007**	**0.740 ± 0.053**	**922.083 ± 21.734**	**4.814 ± 0.943**	**37.569 ± 2.620**	**0.211 ± 0.011**	**9.0 ± 2.0**
F3	**7.088 ± 2.136**	**0.030 ± 0.010**	**1.519 ± 0.108**	**1382.678 ± 33.480**	**13.473 ± 2.641**	**74.518 ± 5.201**	**8.345 ± 0.455**	**780.0 ± 98.0**
F4	**1.540 ± 0.463**	**0.740 ± 0.223**	**0.279 ± 0,020**	**29.457 ± 7.109**	**0.162 ± 0.032**	**0.852 ± 0.059**	**3.483 ± 0.190**	**10.0 ± 1.0**
F5	**44.631 ± 3.438**	**9.971 ± 3.012**	**29.409 ± 2.095**	**2020.659 ±45.861**	**105.653 ± 9.716**	**661.138 ± 46.125**	**177.275 ± 9.669**	**13821.0 ± 436.0**
Total	**54.23**	**11.73**	**32.05**	**4462.68**	**124.41**	**774.62**	**191.40**	**14626**

DL: detection limit

Table 3. Different standards and references - total content of ETM in soil (mg .kg $^{-1}$ dry weight) (Baize, 1997 ; Baba, A. A, & Bouhadjera, K. 2014; Kebir & Bouhadjera, 2011-2012); Manceau et al., 1996)

Norme	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Mn
D. Baise, 1997 et 2002 *Sol typique* *Sédiments* *Sol agricole* *Valeurs d'intervention*	**2.9 2.4 2 12**	**55 85 150 380**	**200 230 100 190**	**50 - 1-100 250**	**258 480 100 530**	**320 2550 300 720**	**500-1000 - 1000 2050**	**- - 270 3000**
Article 11 de l'arrêté du 8/01/1998	**2**	**150**	**100**	**50**	**100**	**300**	**40000**	**300**
France (1985) *Norme AFNOR NF U44-041*	**2**	**150**	**100**	**50**	**100**	**300**	**40000**	**300**
T. Kebir, 2011 et 2012	**1-3**	**150**	**50-100**	**1-100**	**100-400**	**20-300**	**1000**	**270**

-: Not determined values.

From these results shown in table 2, it appears that:

Lead (Pb):

The analysis of the results of Table 2 shows that in the 0-20cm depth of three *locations*: 1-3, Pb is strongly present in the residual phase F5 and F3 respectively reducible stage a mass percentage of 82.30% and 13.07%; 63.60% and 31.28%; 76.96% and 20% (Figure 2). The affinity of the Pb to the residual phase and reducible phase was demonstrated by Oste et al, (2001) and by McKenzie et al, (1980) in soils and sediments. Are then successively the fraction bound to the organic material (F4), the carbonate fraction (F2) and, finally, the exchangeable fraction (F1). Pb is more stable and low mobility in the three soils. Only the values of Pb in Rent 2 exceed the standards defined in the Table 3, so soil was contaminating with Pb.

Cadmium (Cd):

Cadmium in soils is very low levels and yet it is the element most feared because it is toxic. It is mobile, and could be readily bioavailable to pass into the food chain through plants, either migrate towards go contaminate groundwater. The results of the sequential extraction show that surface location 3 Cd is predominantly present in the residual phase F5 by a relative weight ratio of 85% (Figure 2). This means that the majority of the disks is included in the alumina silicates , the result was described by Andersen et al, (2002) report that they Cd has a high affinity for the clay due to its atomic radius that is similar than that usually associated with potassium clays . By cons in location 2, we note that the Cd is mainly associated with organic matter, oxidisable F4 stage with a weight percentage of 93.63% (Figure 2). The dominant presence of Cd in this fraction can make mobile. As for location1, Cd was equally dividing between the carbonate stage F2 and F3 stage reducible with a weight percentage of 36% and 36% (Figure 2).

Cd is potentially mobilized with a significant proportion re-deployable for soils location 1 and 2, because it is mostly not associated with residual phase F5 (F1 + F2 + F3 + F4 > F5). Total average levels contained in the different fractions of Cd in these soils greatly exceed reported in Table 3. Cd has contaminated these soils, and this presents a risk and a danger to the environment.

Copper (Cu):

Copper is a very mobile element in soils, except under extreme conditions of acidity or gelling. Chemical fractionation (Table 3) shows that in both locations 3 and 2, Cu is in the majority residual phase F5, with a weight percentage of 91.76% and 74.27% (Figure 2). While in the surface soil of location 1 it is preferably linked to the residual phase F5 and acid-soluble phase (carbonate) F2 by a weight percentage of 47.81% and 28.95% (Figure;2).

It seems obvious that the maximum tolerated soil set at 100 ppm (Table 3) content was placing too high to report anomalies, whether natural or anthropogenic. Therefore, Cu is safe.

Zinc (Zn):

Zinc was considering freely soluble, compared to other metals in the soil (Baize, 1997). The synthesis results of the sequential extraction shows that the ground surface *location 3*, Zn is distributed in the remaining phases F5, F3 and reducible carbonate F2 respectively with a weight percentage of 45.27%, 30.98 % and 20.66 % (Figure 2). As for *location 2*, the Zn is present in essentially reducible phases F3, F5 and residual oxidizable F4 with a mass fraction of 43.84%, 24.81% and 18.86% (Figure 2). For soil location1, Zn is returned mainly carbonate phases between F2 and F4 oxidizable with a weight percentage of 45.22% and 43.62% (Figure 2). Following this, we note that the Zn is stable in soil for *location 3* while mobile in soils locations (1,2) Ghoraby (1983), the zinc can be according absorbed or co- precipitated with the iron oxides and manganese . By cons, Morillo et al, (2003) attribute the exchangeable zinc in line with levels exceeding 50 %, which is not the case the results obtained in this study. Laterally, the total contents recorded (Table 2) far beyond the standards set out in Table 3, it makes contaminated. These concentrations are the result of accidental pollution from waterborne dikes storage of sewage drains, which depart crossing some soil and enrich lead and zinc, in addition to wind contamination wind especially for fine particles without forgetting the agricultural spraying, urban activities and traffic.

Nickel (Ni):

The chemical fractionation (Table 2) shows that the sol *location 3,* the Ni has a high affinity to the residual phase F5 and medium affinity to the stage F3 reducible with a weight percentage respectively of 84.93% and 10.83% (Figure 2). As ground location 2, Ni is predominantly associated with the oxidizable phase F4, reducible phase F3 and the residual phase F5 respectively by a maximum of 35.54%, 35.19% and 23.72% (Figure 02). However, in the ground *location1,* Ni has a different behavior, it is bound to the carbonate phase F2 with a mass ratio of 66.67% (Figure 2) and it is associated with the reducible phase F3 and F5 with maximum residual phase weight ratio of 17.17% and 13.13% respectively. These results show that soil *location3,* Ni is still the fact that it is almost associated with the residual phase, this association was severed authors (Added, 1981; Lopez- sanchez et al., 1996) highlighted this association. By cons in both *locations* 1 and 2, Ni reveals a potential for mobilization and widespread availability to plants. Ni contamination was reporting in nearby soils *locations* 2 and 3 industrial discharges or releases (Table 3).

Manganese (Mn):

The result of the sequential extraction (Table 3) shows that, in the Mn *location3* is predominantly associated with the residual fraction F5 with 85.35%. While for *location2* is found to leave the oxide phase of Fe-Mn (F3) and the carbonate phase (F2) with respective percentage 59.21% and 22.52%. Mn in *location1* is essentially present in the carbonate phase of F2 with a percentage of 86.48% of order (Figure 2).

The total average concentrations of Mn contained in the different fractions of the soil exceeds the standards reported in Table 3. Thereafter, we note that Mn causes pollution and contamination in these soils.

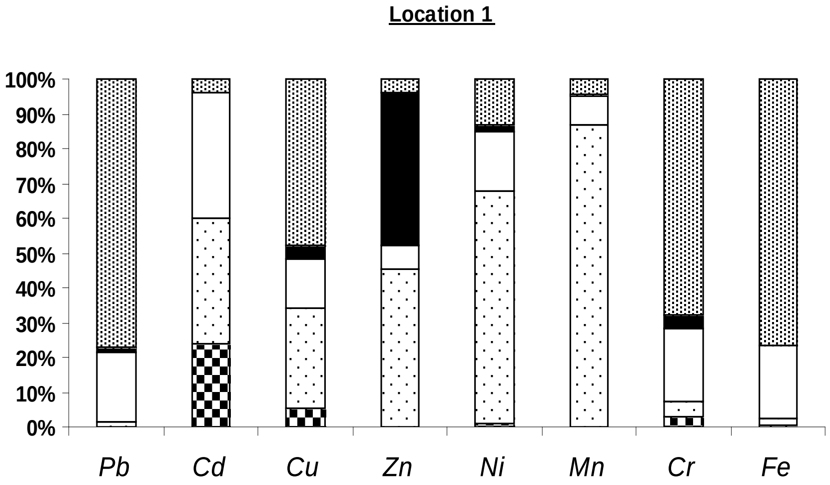
Chromium (Cr):

The chemical fractionation shows that the Cr is mainly relating to the residual phase (F5) in *locations* 2-3 with the respective percentages 92.62% and 81.61%. However, in location1, this trend appears to be different, where it is associated with two phases: residual (F5) and reducible (F3) each with a weight percentage of 67.82% and 20.93%, his association with other phases is low (Figure 2).

The total average levels of Cr found in the various constituents of the soil exceeds the standards given in Table 03. Therefore, Cr manifests a threat to the environment.

Fer (Fe):

The fractional allocation of this ion in three locations studied (1,2,3) indicates that it is completely concentrated in the residual phase F5 with respective percentage 76.78%, 81.56% and 94.50% (Figure 2). Contrary to what one might think a priori, the major fraction is the residual fraction and not the fraction representing the elements to oxides of iron and manganese (reducible). This result indicates that a small percentage of Fe is in the form of oxide or hydroxide of iron as Goethite, ferrihydrite or hematite. As to the presence of Fe in the oxidizable phase, it may be due to the complexation of a part of oxides and hydroxides of Fe with the humic substance (Andersen et al, 2002). It may also be due to the presence of Fe in the form of sulfide such as FeS_2 (pyrite) or FeS. These results show that Fe is not available (F1 + F2 + F3 + F4 F5 <<<) and therefore not mobile. The total contents of Fe contained in the various fractions (Table 2) are below the limits defined in Table 3. These values cause no risk to plants and the environment.



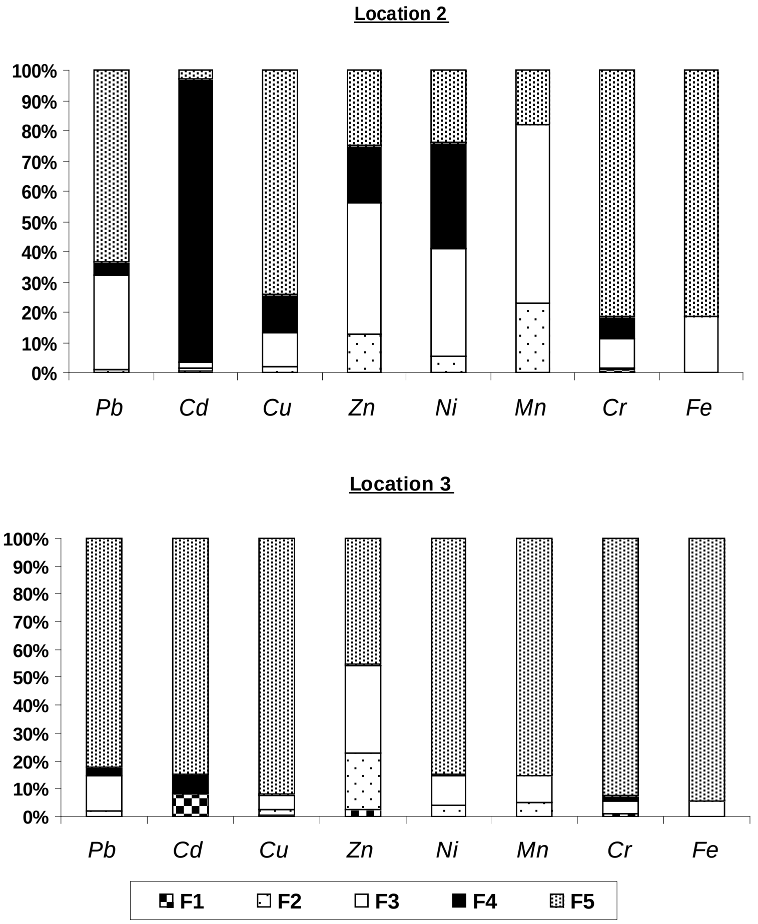


Figure 2. Histograms showing the distribution of trace metals in percentage of the total contents contained in the various phases of the soils studied surface.

Conclusion

Elements that disturb the environment are many, among which we find the heavy metal pollutants that are considered high risk . These two sources , endogenous and exogenous . The latter is due in our case mainly to industrial activities. Based on some work we report soil contamination in the region mainly by Zn, Cd, Ni and Cr. Soil contamination is particularly noticeable approximately discharges. This accumulation is the result of several factors that include exposure to atmospheric fallout, the physico-chemical characteristics of the soil and climate conditions.

Indeed, the soils were surveyed carbonate and have a pH greater than 7. At these pH values, the mobility of heavy metals decreases resulting in their accumulation in the superficial levels. In addition, this region belongs to a bioclimatic characterized by erratic rains that reduce the continuous renewal of the soil, and prevailing winds that are causing a wind pollution by metal elements in soils surrounding the source of pollution. Faced with this degradation, rehabilitation of the mine action site may require a valuation of tailings dams and / or implantation of plants capable of cleaning up the soils of the region

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