Distribution and mobility of lead and zinc atmospheric depositions in industrial area soil of Tiaret, Algeria

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Abstract— *Heavy metal contamination is a severe environmental problem. Knowledge of the total heavy metals contents of soils is a necessary step for making an accurate appraisal and quantitative evaluation of the extent of contamination, indeed, wet and dry atmospheric deposits, plays an important role in the cycle of semi-volatile contaminants [1]. Metallurgical industries release heavy metals into the atmosphere, these last, clump together to form fines particles suspended in the air, these metals can be transported by wind via aerosol or aqueous pathway and deposited in the soil. The main aim of this work was to study the mobility and fate of lead and zinc from atmospheric deposits in contaminated soil from the foundry (ALFET) in industrial zone of Tiaret (Western Algeria) and to determine the effect of physicochemical parameters of the soil on their mobility in the topsoil. Physicochemical analysis of 35 soil samples have shown that zinc and lead levels contents in the surface layer soil (0-30 cm) vary depending on the pH, total limestone ($CaCO_3$) and the soil water content. Results clearly show that soil texture and fine fraction (clay and sand) significantly influence mobility of Pb and Zn in soil.*

Keywords— Soil, atmospheric depositions, Pb, Zn, mobility.

I. INTRODUCTION

Heavy metal pollution is a problem associated with the specific nature of the contamination and physicochemical characteristics of the pollutant-soil system. Heavy metals may come from many different sources. Some, endogenous, are inherited from parent rock material and redistributed within the soils [2] and other exogenous, are anthropogenic (industry, spreading) or natural (dust, volcanism) [3]. Atmospheric deposition is one of the most important pathways of soil pollution. Principal industrial sources of atmospheric metal emission are incinerator factory, blast furnaces, burning coal and oil. Their accumulation can have adverse impacts on the environment such as contamination of soil and groundwater. Presently, various polluted chemicals especially heavy metals have been mostly created by human activities of both point and non-point sources e.g. industry, agriculture, transportation, community [4]. The main objective of the present study is to determine the mobility of heavy metals (Pb and Zn) atmospheric depositions from the foundry (ALFET) under semi-arid climatic conditions in the industrial zone of Tiaret (Western Algeria).

II. MATERIAL AND METHODS

1. Study area

Algerian foundry of Tiaret (ALFET) lies southwest of Tiaret city. Its activity is the iron castings and steel fabrication, study and design of tools, manufacture of molded pieces on requests, production and commercialization of foundries Products (molded pieces in cast iron and in steel).

2. Climate Study

The climate of Tiaret region is semi-arid, cold and wet winter, hot and dry summer. Annual average precipitations are of about 350 mm occur primarily in winter and spring. Rainfall is irregular and unreliable, does not exceed 450 mm per year in the north and below 300 mm per year in southern zones of Tiaret. The highest average annual mean temperature (26 °C) is recorded in August and the minimum mean (6 °C) in January. We note the importance of the hot and dry season last six months usually between May and October. The winds in Tiaret region are extremely violent particularly those coming from the Northwest during the winter.

3. Soil sampling

3.1. Study site selection

Sampling sites were chosen such that they are under the influence of atmospheric depositions from the foundry and the dominant winds direction in the region. Given these criteria, two parcels located at similar distance from the foundry and the dominant wind direction. We hypothesized that they had received an amount of pollution. It is therefore difficult to characterize on large surfaces the variability contents on an area contaminated by atmospheric depositions, although studies show that the distribution of soil pollution around the factories depends on the distance and direction of the prevailing winds [5].

3.2. Field sampling

To study the physicochemical properties of the soils and the mobility and distribution of Pb and Zn, surface soil samples were collected. The points sampling, located in two parcels located at the interior of the foundry with a mesh size 6 meters to limit the horizontal heterogeneity of the medium, 33 soil samples have been collected in (2012) (2013) and (2014). At each sampling point, soil samples were taken to a depth of 0-30 cm. The choice of a constant sampling depth of 0-30 cm soil layer, allows the comparison of stock pollutant. Results of a study conducted on soil profiles near two smelters from the Nord-Pas-de-Calais region [6] show that lead is essentially concentrated in the first 30 cm of the soil profiles. Soil samples were dried in open air for enough time, dried samples were then crushed, homogenized and sieved through a 2 mm mesh and stored in sealed plastic bags in a dry and clean place.

4. Physicochemical analysis of soil

All basic analyzes were performed on these samples; soil moisture is determined by weighing the moist soil sample, drying it at 105 °C for 24 hours to remove water, and reweighing it. Soil pH and electrical conductivity (EC) were analyzed in an aqueous suspension (1/2.5 and 1:5 soil-water ratio, respectively). Matter and organic carbon (OC) were determined using Anne method (modified Walkey-Black method) using wet combustion procedure with potassium dichromate. Total nitrogen was determined using Kjeldahl method. Cation exchange capacity (CEC) was determined using sodium acetate method. The contents of total calcium carbonate ($CaCO_3$) were determined by the method of Bernard calcimeter. For the particle size we used the method of the International pipette Robinson, it is primarily the destruction of soil organic matter using H_2O_2 and dispersion of clays by sodium hexametaphosphate.

5. Determination of Pb and Zn in soil

Metals concentrations were obtained through a triacid attack (HNO_3, HCl and HF). From each sample of dry soil, 150 mg were mineralized at 120 °C for 4 hours in the presence of 4 ml of hydrofluoric acid (HF) and 2ml of a mixture of hydrochloric acid (HCl) and nitric acid (HNO_3). Analysis of heavy metals was performed by atomic absorption spectrophotometer (AAS).

6. Statistical analysis

Statistical analysis was performed using SPSS 23 software. Relationships between metals and other controlling factors were determined by bivariate correlation using Pearson coefficient in a two-tailed test ($p = 0.05$).

III. RESULTS AND DISCUSSION

1. Lead and zinc mobility in soil

Descriptive statistics are shown in Table 1. Soil has a clay content 13,48 ±5,24% and fine sand 22,44 ±10,11%. Indeed, contaminants are often strongly related to the fine soil fraction that promotes dispersion of heavy metal contamination. In several soils contaminated with Cu, Fe, Pb and Zn, the fine fraction often contains highest concentrations of these metals [7].

Soil samples pH of varies from 6.94 to 9.39 with an average of 8.10, observed values reveal that the pH is near-neutral to alkaline, while, total limestone content 9,73 ±8,89% by combination of total and active limestone, which means that the soil is slightly calcareous. Indeed, carbonates with their adsorption sites can retain heavy metals [8].

Results obtained show that the average Pb content in the soil was 3,42 ±2,47 ppm, and Zn 7,45 ±25,21 ppm. soil moisture varies from 3,73% to 26,58% with an average of 11,98%. This variation depends on the soil size distribution.

Table 1. Descriptive analysis of physicochemical parameters

	N	Min	Max	Mean	SD
Pb (ppm)	99	0,00	13,70	3,42	2,47
Zn (ppm)	99	0,00	21,96	7,45	5,02
Moisture (%)	98	3,73	26,58	11,98	4,90
pH	99	6,94	9,39	8,10	0,52
$CaCO_3$ (%)	99	0,00	40,00	9,73	8,89
Clay (%)	99	7,02	33,65	13,48	5,24
Fine sand (%)	99	2,10	39,39	22,44	10,11

The correlations that summarize the relationship between physicochemical parameters influencing the mobility of Pb and Sb in soil are shown in Table 2.

Table 2. Pearson's correlation analysis between Bb content, soil pH, CEC, $CaCO_3$, moisture, and Zn content

		Pb (ppm)	pH	CEC (meq/100g)	$CaCO_3$ (%)	Moisture (%)
Pb (ppm)	Corr.	1	0,365**	-0,218*	0,352**	0,275**
	Sig.		0,000	0,030	0,000	0,006
	N	99	99	99	99	99
Zn	Corr.	0,275**	-0,082	0,055	0,097	0,239*

(pp	Sig.	0,006	0,421	0,613	0,341	0,018
m)	N	99	99	99	99	99

**: Significant at the 0.01 level (bilateral)

*: Significant at the 0.05 level (bilateral)

According to results shown in Table 2, soil Pb content is influenced by several factors such as pH, CEC, total limestone ($CaCO_3$) and Zn. These results are justified by the correlations between soil pH and soil Pb content (r = 0,365**, p = 0,000), total limestone ($CaCO_3$) (r = 0,352**, p = 0,000) and Zn (r = 0,275**, p = 0,006). Pb was negatively correlated with CEC (r = –0,218*, p = 0,030). A significantly positive correlation was found between Zn and soil moisture content (r = 0,239*, p = 0,018). These results showed that the solubility of heavy metal ions in soil was mainly influence by many factors such as pH, Conductivity, Moisture content and soil texture.

1.1. Effect of pH

Obtained results indicate that potential hydrogen is near-neutral to alkaline ranging from 6,94 to 9,39 (Table 1). Soil pH influences the solubility of heavy metals by altering distribution balance between liquid and solid phases, it Influences the number of negative charges brought into solution. It is one of the main parameters controlling the solubility and mobility of heavy metals in soils [9].

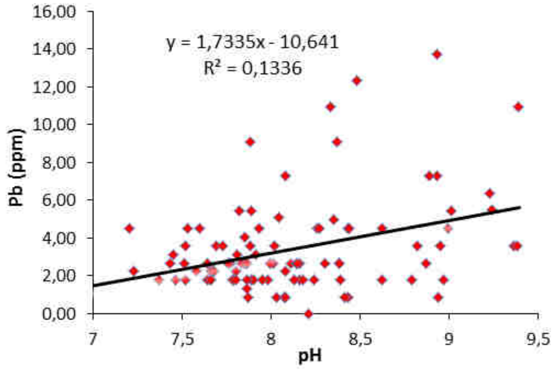

Fig. 1: Correlation between soil pH and Pb content

Figure 1 shows highly significant linear correlation between pH soil and Pb (r = 0,365**). [10] show that high pH favors the dissolution of humic acids and increased concentrations of dissolved trace metals because of the formation of metal-organic complexes in soil solution. Adsorption of Pb^{2+} ion was strongly affected by pH. Adsorption rate of lead decreases with an increase of pH. This can be explained by the formation of lead hydroxide. The pH increase also contributes to the decrease in surface potential, by decreasing competition of metal ions and protons. Precipitation reactions occur at high pH. When elements are stable in cationic form (Zn^{2+}, Pb^{2+}). Increasing soil pH favors deprotonation of soil particles and increase fixation of cations.

According to [11], pH has a role in mobility of Pb in soil decreasing pH is accompanied by lead dissolution. It has been proven that Pb adsorption in soils increases with increasing pH and metal hydroxides may also be formed such as $Pb(OH)_2$. Acidic pH cause dissolution of metal salts, dissolution of retention phases, desorption and adsorption of cations and anions [12].

1.2. Effect of limestone ($CaCO_3$)

According to [13], heavy metal accumulation is affected by organic matter, $CaCO_3$, pH, and soil texture. Soil total limestone content is 9,73 ±8,89% (Table 1) they are moderately calcareous soils. Carbonates play an important role in the mobility of some metallic elements.

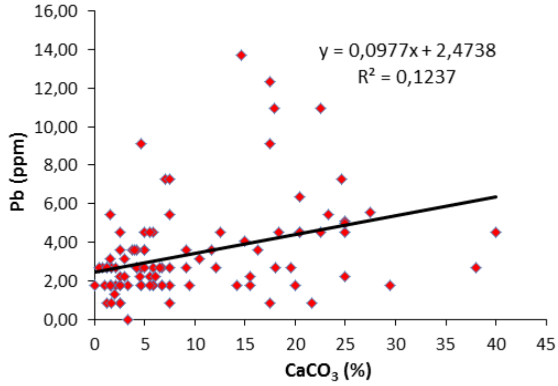

Fig. 2: Correlation between Pb and $CaCO_3$ content

Linear regression analysis between $CaCO_3$ content and Pb Figure 2 shows that levels of lead is primarily due to carbonate content in soil samples, these results are justified by a highly significant correlation (r = 0,352**). Several studies have shown that Pb adsorbs onto calcite and that Pb ions go into Ca sites, despite the large ionic radius of Pb relative to Ca. [14]. Equilibrium dissolution of carbonates and carbon dioxide control the soil pH. Indeed, high carbonate content makes the soil alkaline and thus favors all types of adsorption. Incorporation of metal cations into the lattice of the carbonate crystal [15]. In most cases co-precipitated species are hydrozincite [$Zn_5(CO_3)_2(OH)_6$], malachite [$Cu_2(OH)_2CO_3$], azurite [$Cu_3(OH)_2(CO_3)_2$].

In soils rich in carbonates, substantial quantities of heavy metal ions co-precipitate with the calcium carbonate precipitate, precipitation of heavy metal carbonates is an important retention mechanism and heavy metal are dissolved at higher pH values than the pH at which heavy metals are desorbed in non-calcareous soils. In calcareous soils, lead and zinc fixed by calcium carbonates either by adsorption, hydroxides and carbonates precipitation, or by insertion in $CaCO_3$ system.

1.3. Relationship Pb-Zn

Correlation between lead and zinc content is shown in Figure 3. Main forms of Zn in the soil solution are active Zn^{2+} ions more easily adsorbed onto mineral components (clays, iron and aluminum hydroxides) and organic, which leads to an accumulation in the upper layers [16].

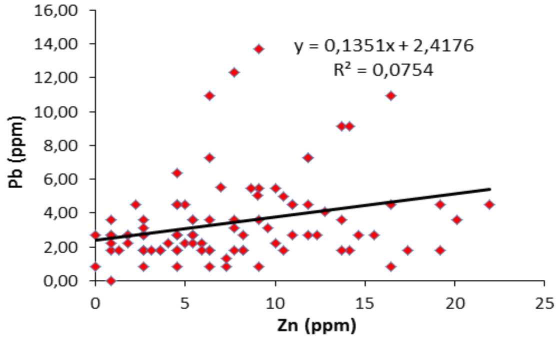

Fig. 3: Correlation between Pb and Zn content

According to obtained results (Figure 3), we find that lead in soil correlates positively with Zn (r = 0,275**). Several studies showed that Zn^{2+} is the predominant form of Zn in soil solution in wide range of soil pH [17].

The existence of a correlation between Pb and Zn show that there is a high chemical affinity between these two metals. Zinc adsorption in soil can be done by two mechanisms in acidic medium by cation exchange, in an alkaline medium by chemisorption.

1.4. Effect of soil moisture content

Numerous extrinsic parameters such as climate affect the mobility of heavy metals in the soil such as climate affect the metal mobility in soil. Study of rainfall effect on adsorption of heavy metal has been the subject of many studies, this parameter affects mobility and distribution of lead in soil in a direct manner by dissolution and horizontal transport and dispersion in the surface layer. Rain can also affect lead mobility in soil in an indirect manner by effect of intrinsic parameters such as pH, $CaCO_3$ and organic matter.

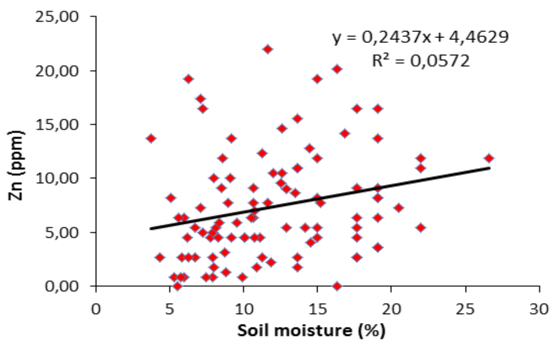

Fig. 4: Correlation between soil moisture and Zn content

According to the results shown in Figure 4, Zn mobility in soil is affected by soil moisture. This is justified by the correlation between Zn content and soil moisture (r = 0,239*, p = 0,018). This means that soil moisture influences precipitation processes and metals solubilization. Rainfall increased contact time between water and lead in soil. It thus increases the risk of contamination during the transport of mineral and organic particles by runoff. Soil moisture regime is one of the most important factors for the control of physical, chemical, and biological properties of soil. It can affect pH, Eh, organic matter and $CaCO_3$ contents of soil [18].

1.5. Effect of soil texture

Statistical results of the correlations analysis between total Pb and Zn soil contents and different soil grain size fractions are shown in Table 3.

Table 3. Pearson's correlation analysis between Pb, Zn and soil granulometric fractions

		Clay (%)	Fine sand (%)
Pb (ppm)	Pearson's correlation	–0,328**	–0,406**
	Sig. (bilateral)	0,001	0,000
	N	99	99
Zn (ppm)	Pearson's correlation	0,055	-0,314**
	Sig. (bilateral)	0,589	0,002
	N	99	99

According to the results shown in Table 3, we note that there is a highly significant negative correlation between Pb and clay content (r = –0,328**, p = 0,001) and fine sand (r = –0,406**, p = 0,000). Highly significant negative correlation between Zn content and fine sand fraction (r = –0,314**, p = 0,002).

- **Effect of clay**

Clay minerals are hydrous aluminum phyllosilicates, by their physicochemical properties, play a very important role in heavy metal availability. Clay soils sorb relatively great amount of metallic trace-elements, in the soils containing calcite sorption and precipitation take place. The content of heavy metals in soils, chiefly in the clay fraction, is a very good indicator of environmental pollution.

Solid matrix, generally negatively charged, attracts cations from the solution. Sorption of heavy metals on clay minerals happened due to the ion exchange and surface complexation. These are the clay minerals and organic matter, often form complexes, participates in the solid negative charge [19].

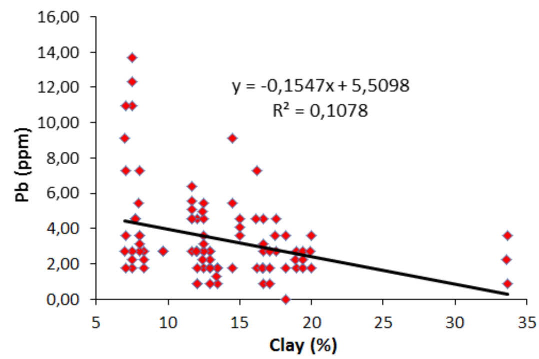

Fig.5: Correlation between Pb content and clay

According to Figure 5, there is a statistically significant negative relationship between clay and Pb soil content (r = –0,328**). Clay minerals have large specific surface and negative charges onto their leaves, which allows them to retain cations by adsorption. Clays, of course, differ in their surface activity and ability to absorb or orient water and organic molecules and this is reflected in soil properties.

The adsorbent capacity of clay varies from one family to another. Phyllosilicates having a high cation exchange capacity and large specific surfaces, they contribute to adsorb large amounts of heavy metals [20], this justifies results obtained in (Table 2) significant negative correlations between CEC and Pb soil content (r = –0,218*, p = 0,030). Clays can therefore retain a large amount of heavy metals by adsorption. [21] show the important role of clay fractions on the adsorption of lead.

- **Effect of fine sand**

Soil texture reflects the particle size distribution of soil. Particle size distribution can influence the level of metal contamination in a soil. Fine particles (<100 μm) are more reactive and have a higher surface area than coarser material. These compounds are important adsorption media for heavy metals in soils.

Correlation between fine sand, lead and zinc content is shown in Figure 6.

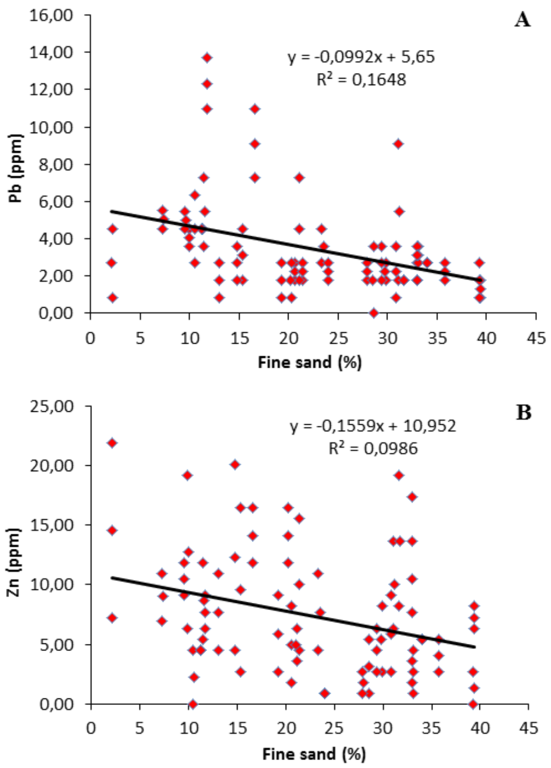

Fig. 6: Correlation between Pb and fine sand (A) and Zn and fine sand (B)

Results from correlation test showed that the mobility of lead and zinc in soil. According [22], the behavior of heavy metals in sand depends on the nature and proportion of various components of the soil, clays can retain significant amounts of heavy metals by adsorption. According to Figure 6(A), lead content of soils will vary depending on fine sand content, which confirms the existence of a highly significant negative correlation (r = –0,406**; p = 0,000).

These results could be explained by influence of sand fraction on zinc mobility in soil. In sandy texture soils, or through preferential flow paths, migration of heavy metals across depth profile is favored because reactions with constituents don't have time to establish themselves due to release and micropollutants transport in soil solution in a colloidal form. Statistical analysis Figure 6(B) shows the strong negative correlation between sandy texture soils and Zn content (r = –0,314**; p = 0,002), the presence of sand reduces the contact time micro pollutants and solid phase by increased water infiltration capacity into the soil. [23], observed a very high levels of metals in particular lead and zinc at 80 cm depth into soil underlying an infiltration basin.

IV. CONCLUSION

Heavy metals can exist in soils in a number of different forms depending on the source of metals, soil composition and environmental conditions. In conclusion, according to results obtained in our study, the mean total content of lead (3,42 ppm) in the soil samples, this content is mainly controlled by aqueous phase speciation and some physicochemical parameters such as pH and total limestone that show significant correlations (r = 0,365**, r = 0,352**) respectively. The most common and mobile Zn form in soil is Zn^{+2} which is easily adsorbed by mineral and organic components in most soil types, which leads to an accumulation in the surface layers, these results are justified by the correlations between soil moisture content and fine sand (r = 0.239 *). Significant effect of clay and fine sand on lead content (r = –0,328**, r = –0,406**) respectively indicate that metal mobility depends mainly on soil texture, it is the fine particle fraction (clay and fine sand) which affect the mobility of heavy metals in soil. After this study we can conclude that, Mobility and distribution of lead and zinc from atmospheric depositions essentially depends on the physicochemical properties and soil granulometric composition.

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