

Clay Mineralogy and Vertical Distribution of Lead, Zinc and Copper in a Soil Profile in the Vicinity of an Abandoned Treatment Plant

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Abstract: The aim of this study was to determine Pb, Zn and Cu content and the clay mineral responsible of their vertical distributions, on spoil heap in the vicinity of an abandoned treatment plant of lead ore located in Mfouati, south east of Congo-Brazzaville. Lead, zinc and copper contents were determined by ICP in a soil profile of a slag heap at different depths (15-45, 45-75, 75-105, 105-135 and 135-150 cm) in the bulk samples and in the clay fractions, respectively. The geochemical study of the soil profile at the different depths has revealed greater amount of Pb, Zn and Cu in the bulk samples and the clay fractions. Pb, Zn and Cu contents decreased in the soil profile as: 11800-2000, 2400-1200 and 270-90 mg/kg in the bulk samples and 6652-2049, 3049-1670 and 495-212 mg/kg in the clays fractions, respectively. Zn and Cu contents in the clay fractions were higher than in the bulk samples in all the profile, except for Pb. Soil samples in the profile were slightly acidic in nature, with pH values ranged from 5.69 to 6.25. CEC was correlated with clay fraction. XRD analysis of the clay fractions at the different depths has revealed the clay minerals such as talc in higher amount, kaolinite, chlorite and smectite in lower amounts. Kaolinite (1:1 type clay minerals) was more present in all the soil profile in high amount than chlorite and smectite and could control the vertical migration of Pb, Zn and Cu.

Key words: Clay, heavy metals, pollution, soil, XRD analysis

INTRODUCTION

Heavy metals are distributed throughout the mineral and organic fraction of soil. Immobilization of heavy metals is mainly due to sorption properties which depend of soil characteristics such as: amount of clay and organic fractions (Stevenson, 1994). In the soil solution, the heavy metals as ions are present in complexed forms. Many studies have shown the effect of clay mineralogy on heavy metals geochemistry (Mc Bride, 1991; Kabata-Pendias, 1993; Sipos and Némeh, 2001; de Matos *et al.*, 2001; Amusan and Adeniyi, 2005; Onweremadu, 2008; Andras *et al.*, 2009). Kaolinite was found to be a very good sorbent of the majority of the heavy metals (Wahba and Zaghloul, 2007; Gupta and Bhattacharyya, 2008). A sorption/desorption study of heavy metals on competing clays shown that Cu, Pb and Zn were preferentially fixed on smectites and that lead was also fixed on illite (Rybicka *et al.*, 1995; Brigatti *et al.*, 1996; Griffin and Au, 1977; Griffin and Shimp, 1978). Clays act as adsorbents and play an important role in ion exchange reactions (Brigatti *et al.*, 1996; Barrow, 1999).

In the south eastern Congo Brazzaville, a treatment plant of non-ferrous metals (Pb, Zn and Cu) the activity of which was to concentrate lead, involved crushing of ore

rich in heavy metals followed by disposal of metal-bearing rock as mine tailings. The treatment plant was abandoned since the Eighties. The present work was undertaken on the soil profile of a spoil heap for:

- Better information about the mechanism of the metal distribution in the soil
- To identify clay mineral responsible of the mobility of heavy metals

MATERIALS AND METHODS

Study area: The site retained for sampling was the spoil heap of an abandoned treatment plant in Mfouati (south east Congo-Brazzaville), which activity was stopped for more than twenty years. The ore treatment plant was built on the side of a hill located at 442 m of altitude between 367178.59-370507.20 UTM south latitude and 9512957.94-9515800.06 UTM east longitude (Fig. 1). The annual rainfall varies from 1050 to 1650 mm. The soils are of ferrallitic type, which have been derived from schisto-limestone.

Sampling: Five composite soil samples were collected in a soil profile of the spoil heap in the vicinity of the abandoned treatment plant, at depth intervals of 15-45,

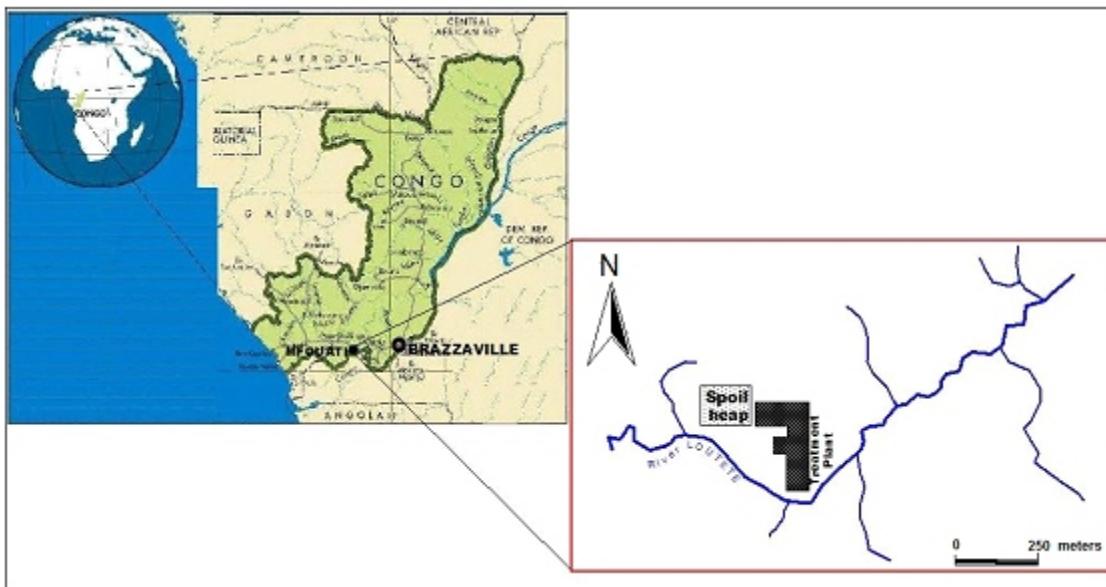


Fig. 1: Location of the spoil heap in the study area

45-75, 75-105, 105-135 and 135-150 cm, using steel stainless. The sampling period was August 2008 (dry season). The first 15 cm was not sampled because of an accumulation of ore. The soil profile did not present distinct horizons. After sampling, the composite soil samples were packed in different polyethylene bags to prevent exposure to air. Sample location is presented in Fig. 1.

Analytical: Heavy metals (Pb, Zn and Cu) were analyzed by ICP at the Service Central du CNRS (Vernaison, France) and the Centre de Géochimie de la Surface (Strasbourg, France) in the bulk samples and the clay fractions, respectively. Briefly, 0.1 g of each homogenized soil sample was digested by triacid attack ($\text{HF-HClO}_4\text{-HNO}_3$) in a Teflon vessel and heated in a microwave oven at 180°C for 10 min. The digested solution was diluted to a known volume with double distilled water, and then it was analyzed for metals by ICP-MS. About the samples of the clay fractions, after crushing of the samples in an agate mortar, 4 g of sample are dried at 110°C, and then burned at 1000°C during 3 h. The residue is crushed, and only 100 mg of this last are mixed with 750 mg of lithium tetraborate. Fusion is carried out at 1000°C during 20 min. After cooling, one obtains an easily soluble pearl in 20 mL of a mixture nitric acid - glycerin - distilled water. This solubilization is carried out at 80°C on a magnetic stirrer. After, the obtained solution is filtered and analyzed by ICP-AES.

The composite soil samples at the depths 15-45, 45-75 and 75-105 cm required an attack of the organic matter by H_2O_2 (35%). To 10 g of powder, was added 50 mL of distilled water. After mechanical agitation, the suspension

was heated in a double boiler at 70°C. H_2O_2 (35%) was added gradually to this suspension, under a constantly agitation. When the emission of the bubbles decreases, the organic matter is completely attacked. Then, the suspension undergoes a washing with distilled water to eliminate the excess of H_2O_2 (35%). The suspension was centrifuged at 2500 laps/min during 10 min. After washing, the base of centrifugation was suspended using mixer. This suspension was poured in a bottle and 100 ml of distilled water was added. After a time of sedimentation of 1 h forty minutes, the upper 2 cm of the suspension was siphoned and correspond to the fraction <2 μm . The clay fraction (<2 μm) was centrifuged at 3500 laps/min during 40 min. The base obtained was recovered with a spatula, deposited in edge of a blade of grooved glass, and then spread out in the groove using a blade of glass. These made blades are dried in the open air. The goal of this method of preparation aims at directing to maximum the clay minerals in order to reinforce their principal reflexion related to the family of plans {001}. The mineral composition of clay fraction was determined by X-Ray diffraction (XRD) on oriented samples. In routine, four diffractograms were obtained for each depth interval in different experimental conditions such as:

- samples non-treated (dried blade in the open air)
- samples treated with ethylene glycol; - samples treated with hydrazine; - samples heated at 490°C, 4 h in air

A relative accumulation ratio of metals in the clay fraction of the soil profile was determined from the ratio:

Table 1: Chemical properties of the soil samples

Depth cm	pH cmol/kg	CEC g/kg	Granulometry			
			Sand	Silt	Clay	OM
15-45	5.69	2.90	306	370	325.0	2.76
45-75	6.010	2.91	268	400	333.2	2.61
75-105	6.04	3.11	258	400	343.0	1.99
105-135	6.25	3.30	239	408	353.0	1.98
135-150	6.15	3.54	145	421	344.0	1.62

$$[M]_{\text{depth}} / [M]_{\text{deepest depth}}$$

where,

- [M]_{depth} = The concentration of a metal M at a given depth
 [M]_{deepest depth} = The concentration of a metal M at the depth 135-150 cm

RESULTS AND DISCUSSION

The analytical results are summarized in Table 1. In terms of texture, the soils in the profile are clay loam and quite uniform, with silt and clay content ranging from 370 to 421 g/kg and 325 to 344 g/kg, respectively. In this soil profile, no significant different texture was observed contrary to the sporadic intervention of layers in reclaimed land. Organic matter content decreased in the soil profile and ranged from 2.76 to 1.62 g/kg.

In the soil profile, an increase in clay content with depth corresponded to a decrease of organic matter and soil pH increased with clay content. Sand content decreased with depth from 306 to 145 g/kg. According to the pH values, which ranged from 5.69 to 6.25, the soil profile was slightly acidic in nature. This can be explained by the presence of sulfide minerals which generate Acid Mine Drainage (AMD) in the spoil heap. The depth 15-45 cm is characteristic of humus accumulation. Cation exchange capacity increased with clay content and was pH-dependent in the soil profile. Indeed, pH-dependent charge sites exist as an aluminol and silanol on clay minerals (smectite and kaolinite) and organic matter in the soil profile. This result is in good agreement with Jaeyoung and Jae-Woo, (2005). Organic matter decreased in the soil profile with a content ranged from 2.76 to 1.62 g/kg.

Pb, Zn and Cu contents in the soil profile decreased with depth which is the effect of an anthropogenic pollution (Fig. 2). In the composite soil samples of the profile, the contents of Pb, Zn and Cu decreased from 11800 to 2000 mg/Kg, 2400 to 1200 mg/kg and 270 to 90 mg/kg, respectively. At the depth 75-105 cm, Pb content gives a rise. This could suggest an illuviation. Figure 3, 4 and 5 present changes of Pb, Zn and Cu content in the bulk samples and the clay fraction of the soil profile. Zn and Cu contents in the clay fraction are higher than in the bulk samples of the soil profile which denotes the high adsorption capacity of the clay fraction for Zn and Cu.

The highest Pb contents were described in the bulk samples of the profile, between 15-105 cm of depth. The

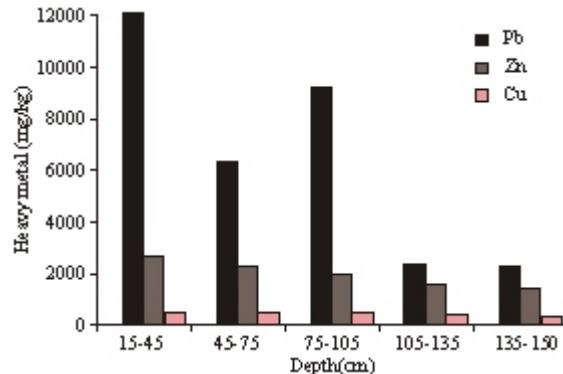


Fig. 2: Distribution of Pb, Zn and Cu content in the soil profile

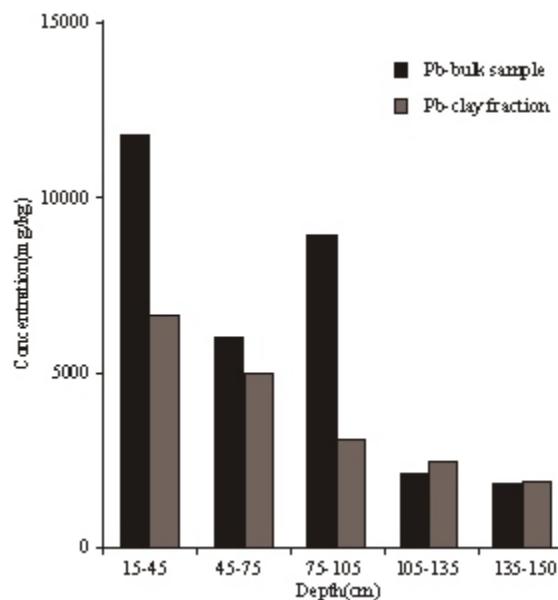


Fig. 3: Vertical distribution of Pb in the bulk samples and clay fraction

Pb contents in the clay fraction are lower than in the bulk samples to 105 cm of depth. From the depth 105-135 cm, the Pb content in the clay fraction was approximately the same as in the bulk samples.

The distribution pattern of Pb, Zn and Cu in the bulk samples of the soil profile suggested an accumulation of these metals in the first 15 cm of the soil and are gradually leached down in-depth, which is the conventional view for the mechanism of heavy metal distribution in soil profiles. Zn and Cu contents in the clay fraction were higher than in the bulk samples. The clay fraction proved a good ability to fix the mentioned heavy metals (Zn and Cu) on their surface.

A relative accumulation ratio of metals in the clay fraction was determined from the ratio $[M]_{\text{depth}} / [M]_{\text{deepest depth}}$ (Fig. 6). The following orders of the metal

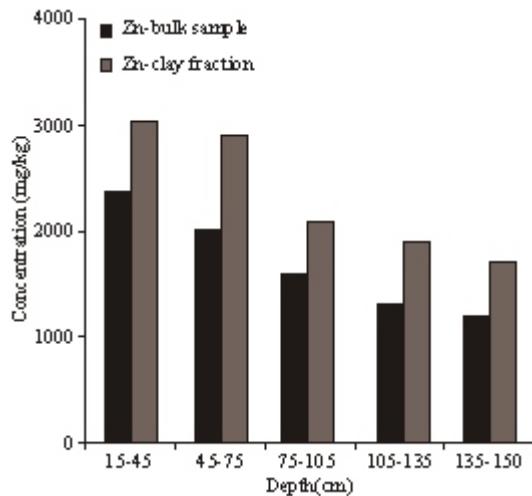


Fig. 4: Vertical distribution of Zn in the bulk samples and clay fraction

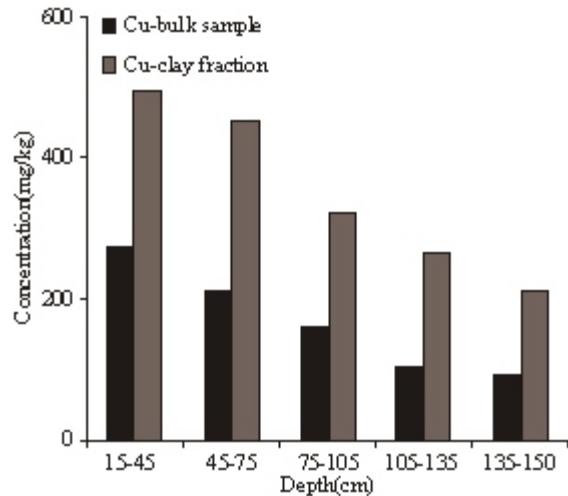


Fig. 5: Vertical distribution of Cu in the bulk samples and clay fraction

accumulation in the clay fraction characterized the soil profile: Pb>Cu>Zn and Cu ≈ Pb>Zn between 15-105 cm and 105-135 cm in depth, respectively. It would seem that in the soil profile, a strong adsorption of lead in the clay fraction was supported by a very high concentration of metal as it is showed by the relative accumulation ratio at the depths 15-45 cm and 45-75 cm. Therefore, for higher initial concentration, more efficient utilization of sorption sites is expected due to a greater driving force by a higher concentration gradient (Amer *et al.*, 2010).

Metal sorption is a competitive process between metals in solution and those sorbed onto the solid surface (Echeverria *et al.*, 1998; Harter, 1992). Therefore,

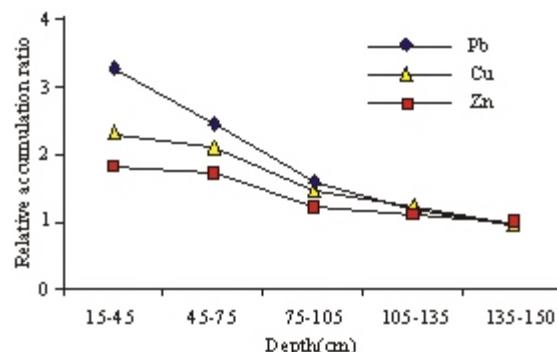


Fig. 6: Relative accumulation ratio of Pb, Zn and Cu in the clay fraction at different depths

Table 2: Mineralogy of the clay fraction (<2 µm) of the soil profile

Depth cm	Talc	Kaolinite	Chlorite	Smectite
15-45	+++	++	+	-
45-75	+++	++	+	-
75-105	+++	++	+	+
105-135	+++	++	+	+
135-150	+++	++	+	+

solution metal composition strongly affects metal retention onto solid surfaces (Elrashidi and O'Connor, 1982).

In the environment, the mobility of the heavy metals depend mostly of their solubility and sorption ability on natural colloids, among which the most important are the clay minerals (Missana *et al.*, 2008). The dominant process in the sorption of heavy metals, in the case of clay minerals, is represented by ionic replacement between solution and solid phase, and physical process of adsorption (Sposito, 1989; Kabata-Pendias, 1993; Alloway, 1995).

The abundance of clay minerals present in the soil profile is shown in Table 2. The presence of talc as major clay mineral in all the clay fractions do not affect the exchange capacity because talc has not a significant CEC. Thus, kaolinite which is 1:1 type clay minerals and present in all the soil profile in high amount than chlorite and smectite, could control the increase in CEC in the soil profile. The range of affinities of heavy metals ions to kaolinite is in the order: Pb²⁺ > Cu²⁺ > Zn²⁺ (Benedetti *et al.*, 1995). This order is the same than the one obtained from the relative accumulation ratio (Fig. 6). Excess sorption is influenced by the type of clay minerals and solution phase composition (Benedetti *et al.*, 1995; Evans, 1989). A review related to adsorption and migration of heavy metals in soils, pointed out that competitive sorption phenomena of heavy metals in soils are dependant on strict mineralogical composition of soils (Dube *et al.* 2001).

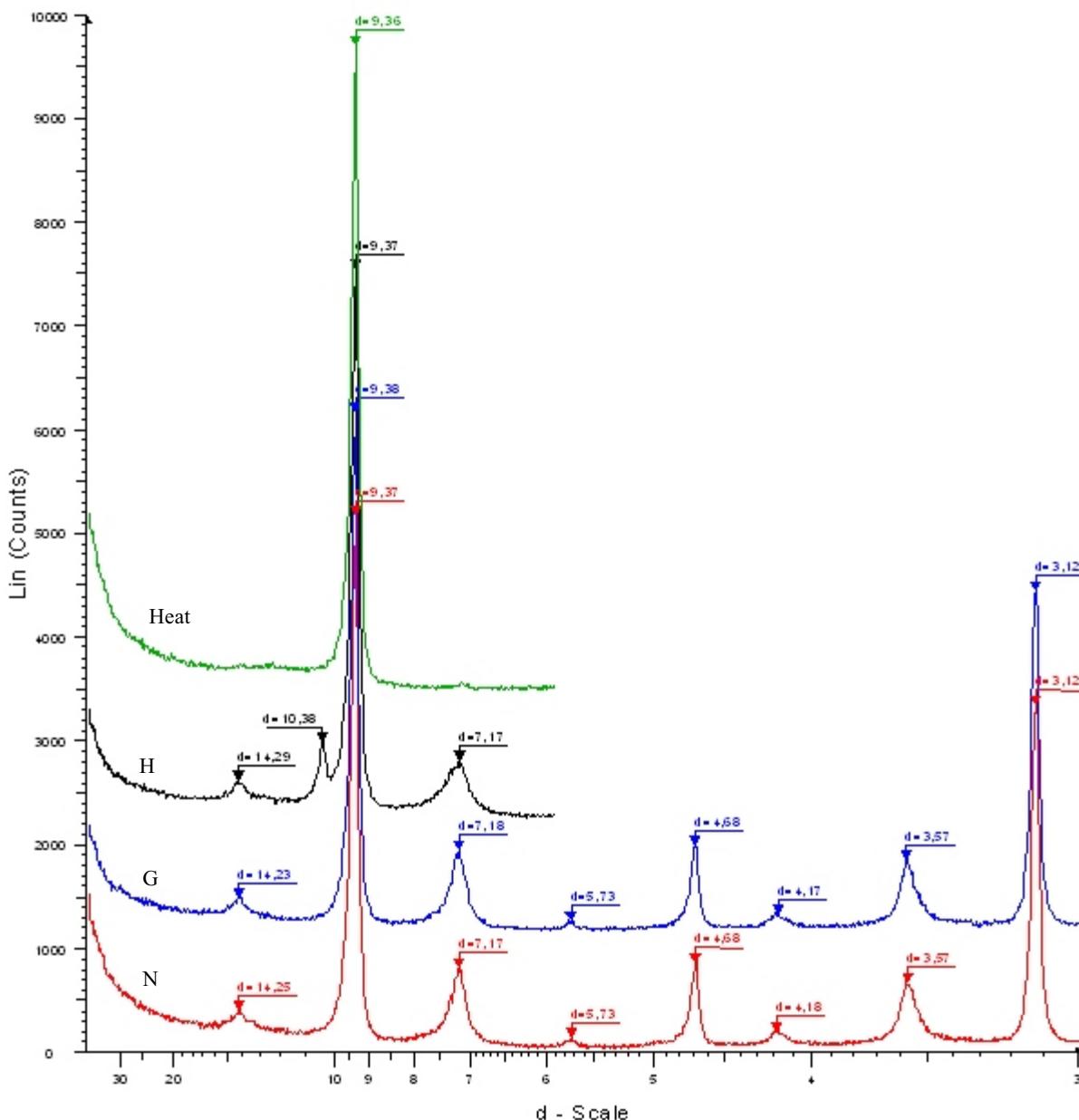


Fig. 7: Diffractograms of the clay fraction at the depth 15-45 cm

Figure 7-11 show the compiled X-RAY diffractograms of the clay fraction ($<2\text{ }\mu\text{m}$) at different interval depths in the soil profile, from top to bottom in the following order: samples heated, treated with hydrazine, treated with ethyleneglycol, non-treated, respectively. The 15 \AA (001 diffraction) peak of smectite in untreated clay samples mostly shifted to 17 \AA after

treatment with ethyleneglycol. The ethyleneglycol-treated samples showed 001 diffractions at 16.69 , 16.68 and 16.91 \AA at the depths 75 - 105 , 105 - 135 and 135 - 150 cm, respectively. These features indicate the presence of smectite. The intensity of peaks 9.37 , 4.68 and 3.12 \AA which correspond, respectively to diffractions 001, 002 and 003, indicate the presence of the talc of which the

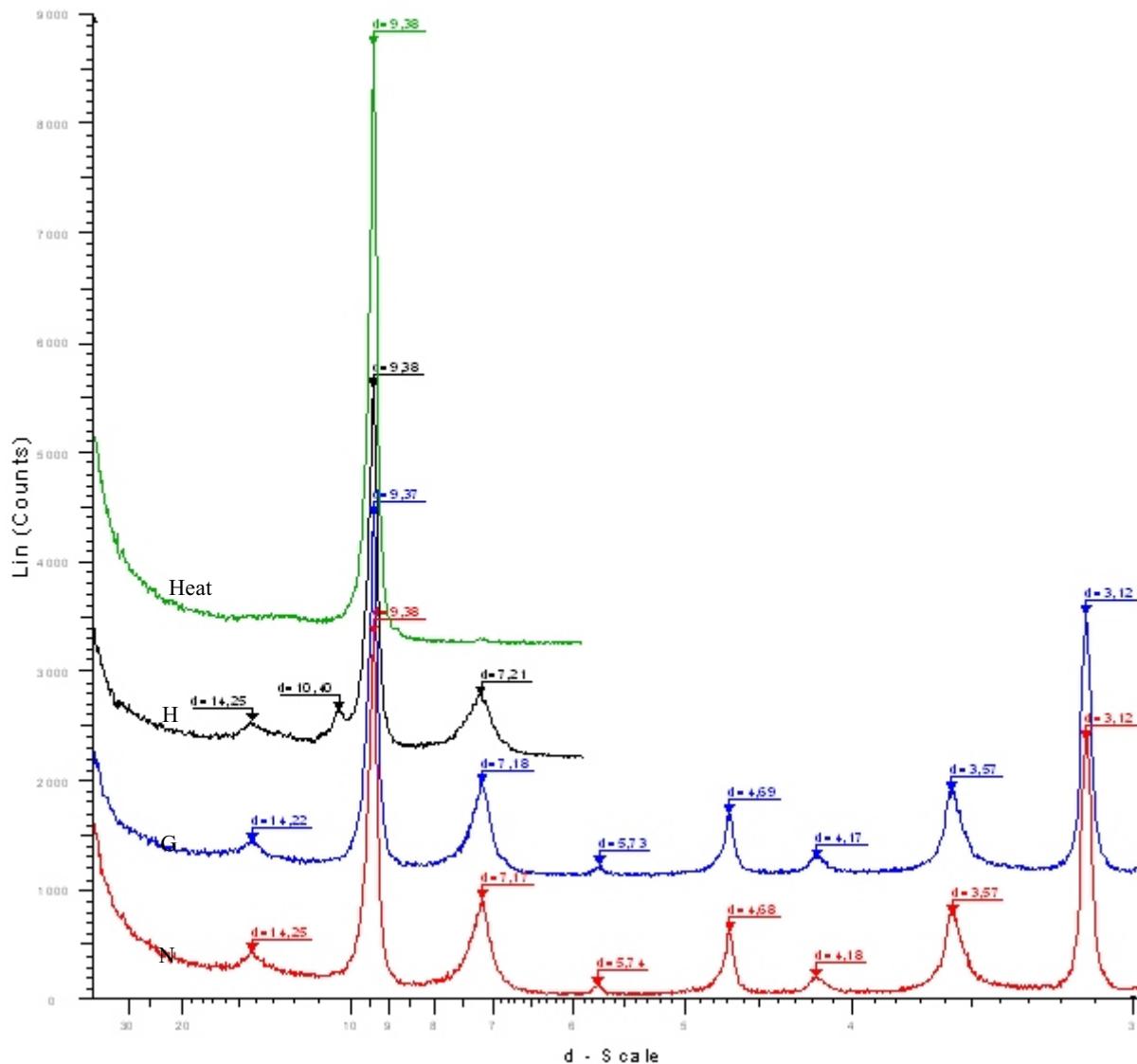


Fig. 8: Diffractograms of the clay fraction at the depth 45-75 cm

amount increased with the depth in the soil profile. The peaks at 7.15 \AA (001 diffraction) and 3.57 \AA (002 diffraction) in the untreated clay samples, which persist after ethyleneglycol treatment and disappear after heat at 490°C for 4 h, are attributed to Kaolinite. The peaks 14.25 \AA , 7.17 \AA , 4.68 \AA and 3.57\AA are attributed to chlorite.

The diffraction patterns from clays samples that were subjected to a same chemical treatment are strikingly similar, indicating that the clay mineral composition is

almost identical in the soil profile, except for smectite which appears in small amount from the depth 75-105 cm. The great capacity of cation exchange of smectites could explain the accumulation of lead at the depth 75-105 cm. The soil samples at the different depths of the profile are mineralogically uniform with clay minerals as talc, kaolinite, chlorite.

Lead, zinc and copper are strongly retained by soil minerals such as clay sized layer silicate minerals

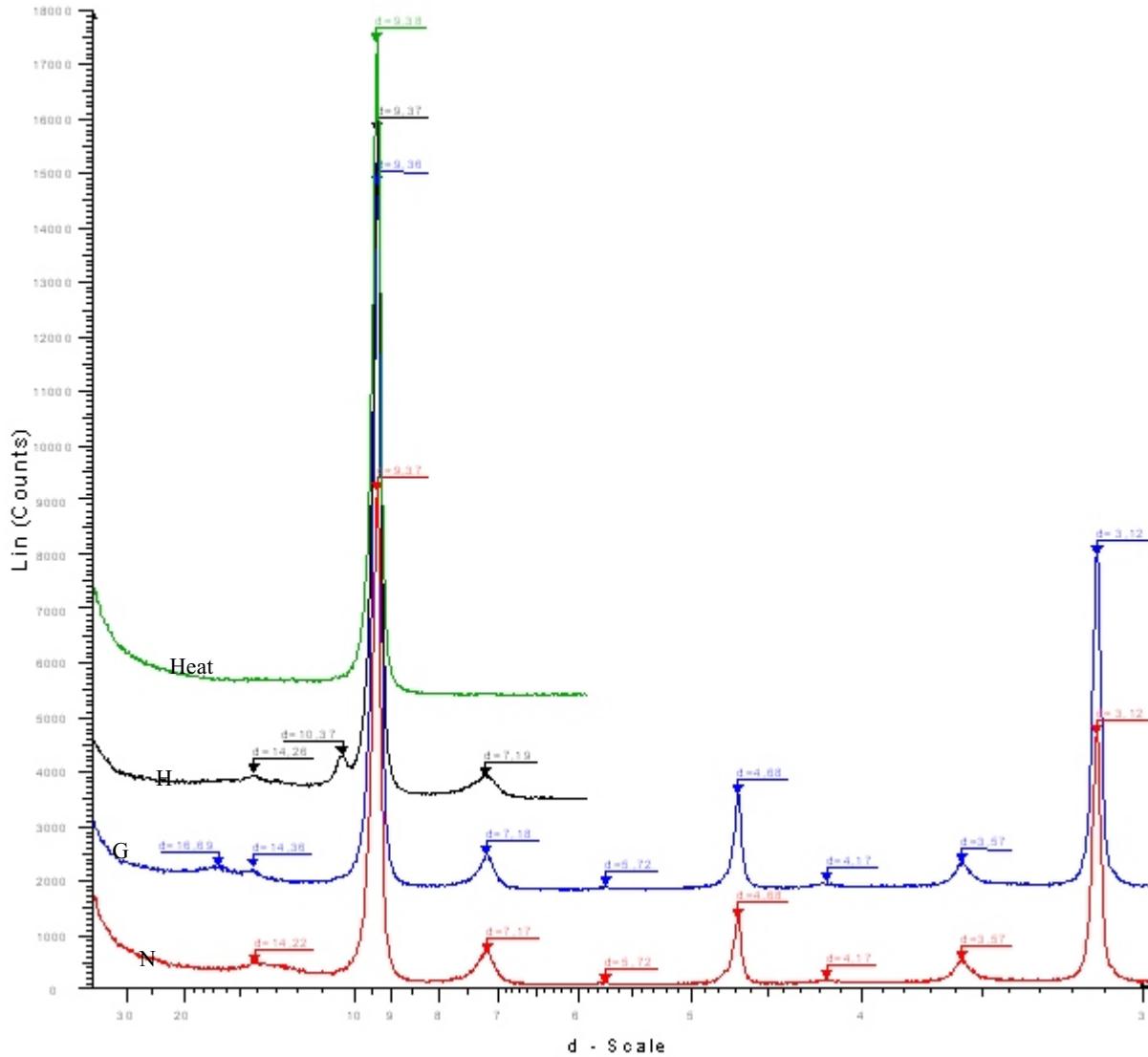


Fig. 9: Diffractograms of the clay fraction at the depth 75-105 cm

(Darmawan and Wada, 2002; Mori and Wada, 2002). Heavy metals content per kg of adsorbent rather per kg of bulk sample would give a better information about the mechanism of the metal distribution (Huy *et al.*, 2003). Ganjala and Deo (2005) have showed the sorption of zinc in soils of different clay mineralogical composition. They found that in kaolinite dominant soils, zinc was sorbed in

excess of their exchange capacity. The great amount of zinc and copper in the clay fraction of the composite soil samples (bulk samples) as illustrated in Fig. 4 and 5 could be the result of an excess sorption (DeMumbrum and Jackson, 1956). In the case of zinc, other forms than Zn^{2+} such as the hydrolyzed form $ZnOH^+$ may be adsorbed on the surface (Ganjala and Deo, 2005).

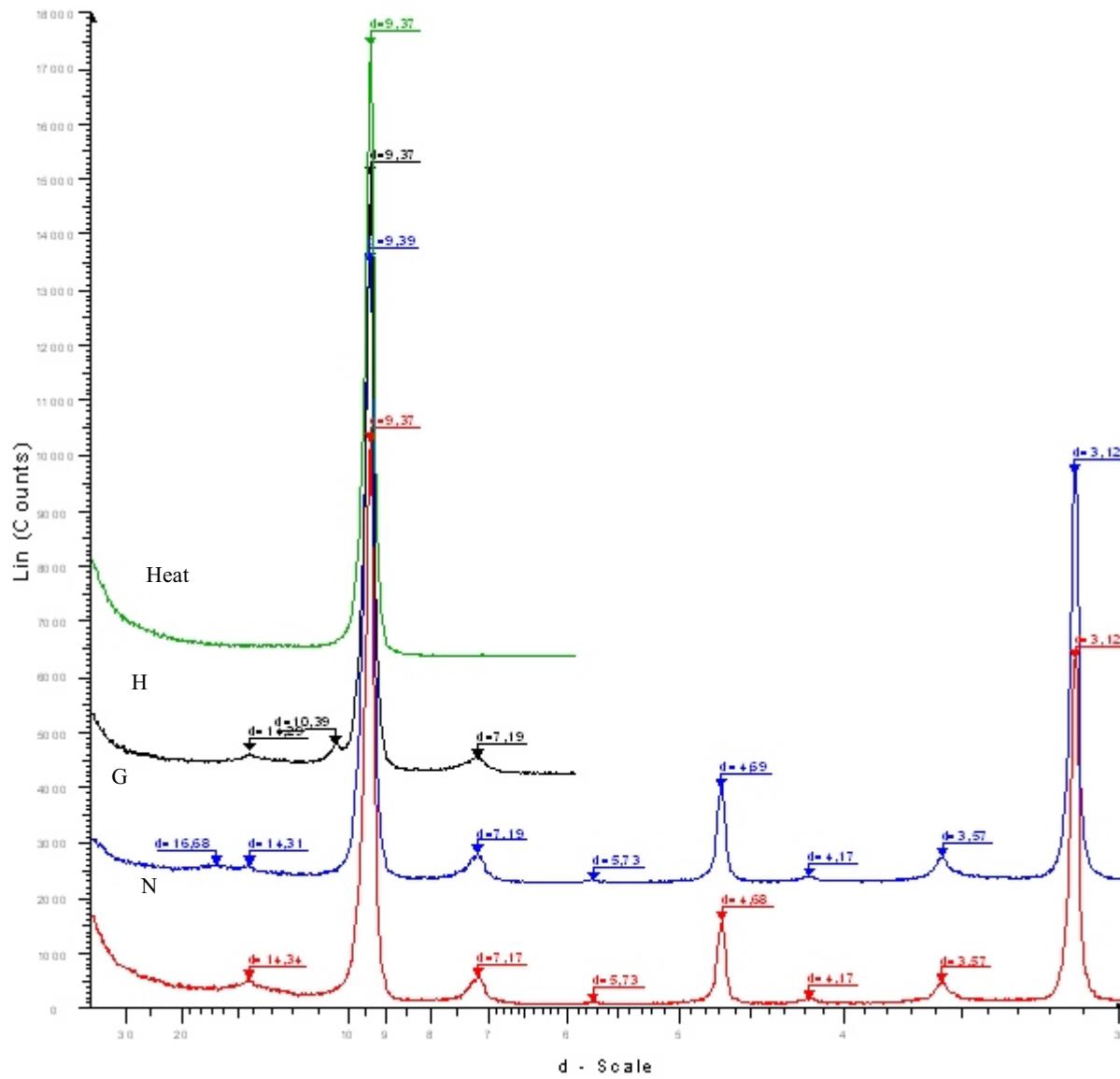


Fig. 10: Diffractograms of the clay fraction at the depth 105-135 cm

CONCLUSION

The distribution of lead, zinc and copper in the soil profile highlighted an anthropogenic pollution. Clay fraction of the soil samples of the spoil heap contained large amounts of these metals. The presence of ore rich in heavy metals at the soil surface explains the great amounts of Pb, Zn and Cu adsorbed in the clay fraction.

Strong relationship between the heavy metals and OM revealed that OM contributed to the vertical migration of Pb, Zn and Cu in the soil profile. Mineralogical analysis (XRD) of the clay fractions has revealed the presence of talc in greater amount, followed by kaolinite and chlorite, smectite in lower amounts. Kaolinite was the dominant clay mineral responsible of the vertical migration of Pb, Zn and Cu in the soil profile.

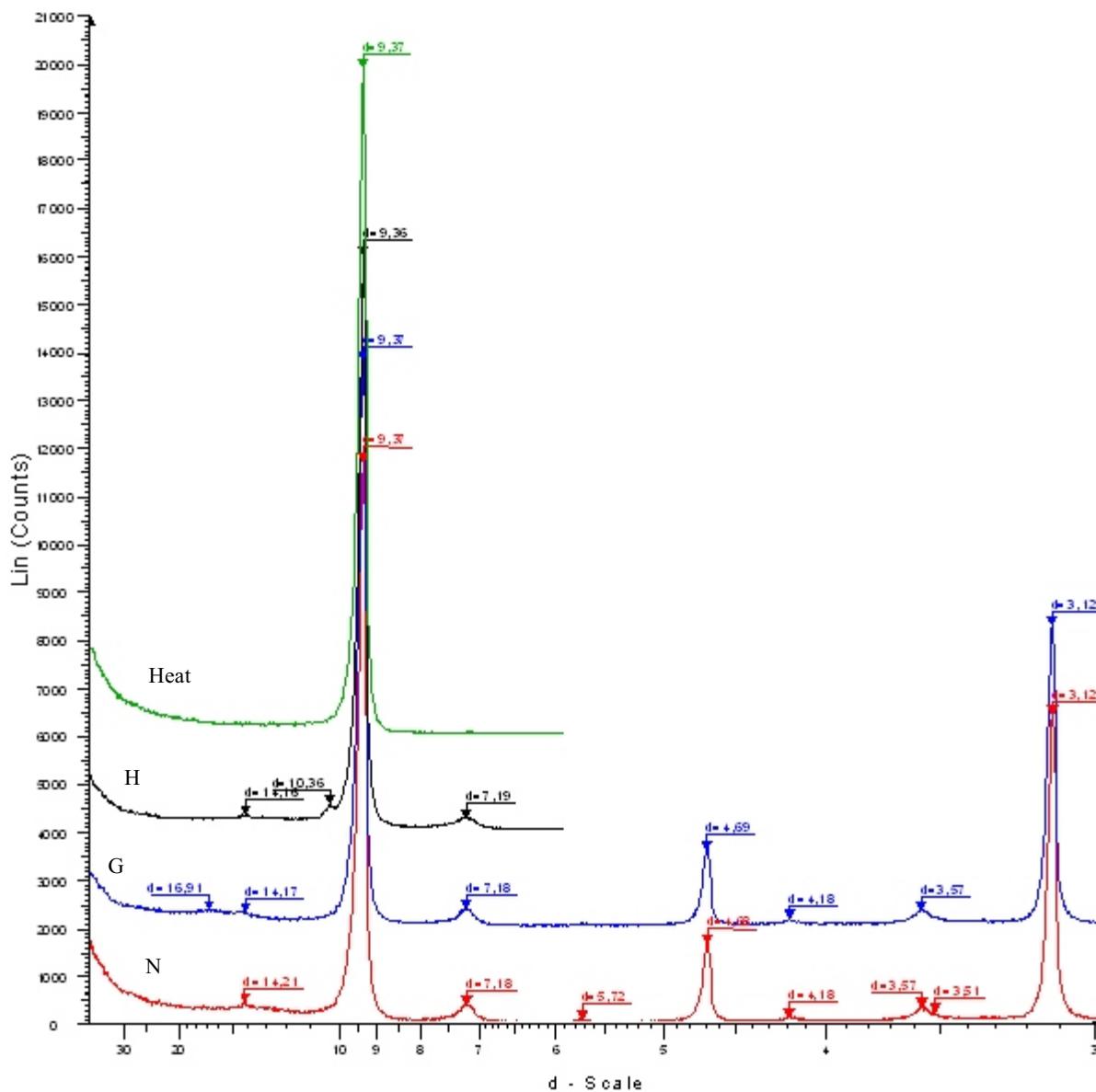


Fig. 11: Diffractograms of the clay fraction at the depth 135-150 cm

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