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Speciation and Pollution Assessment of Chromium and Zinc in Landfill Soils of Brazzaville: Physico-Chemical Analyses and Heavy Metal Contamination

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Abstract: ***The aim of this work is to study the speciation of chromium and zinc, and their pollution in the soil of landfills in Brazzaville. In each site studied (Glacière, Moukondo and Tsiémé), soil samples were taken from different points and then mixed to obtain a composite sample which underwent some physical treatments before proceeding to the various analyses. Physico-chemical parameters: pH, electrical conductivity and organic matter were determined, and concentrations of Chomium and zinc The results of physicochemical analyses showed that soils have neutral pH between 6.92 and 7.02 and that the organic matter content varies between 1.72 and 7.24%. The results of the determination of heavy metals by inductively coupled plasma-optical emission spectrometry showed that chromium is present in large quantities compared to zinc and that the Tsiémé landfill contains large quantities of these two heavy metals. Studies of sequential extractions showed that chromium is more bound to the exchangeable and acid-soluble fractions while more than half of zinc is bound to the exchangeable fraction. The pollution intensities expressed by the contamination factor (CF) and the geo-accumulation index (Igeo), indicated that the soils of all landfills are largely polluted by zinc and pose a risk to the environment.***

Keywords: Landfill, pollution index, sequential extraction, contamination factor, geo-accumulation index

1. Introduction

Soil is a non-renewable natural resource and it's pollution is a process that has consequences for human health and the environment. Its depollution sometimes requires very high costs. The problem of soil pollution by heavy metals has been going on for decades. Landfills are among the sources of soil contamination by heavy metals. For many years, landfilling has been the simplest route to waste disposal. This solid waste, a potential source of pollution, can undergo various physical and chemical alterations and gradually release metals into the liquid phase of the soil. Heavy metals are present in most waste constituents (Rousseau et al. 1990). Soils can be affected by burial or deposition of solid materials containing high metal contents. In soil pollution phenomena by heavy metals, soil-metal cation interactions play a key role that regulates their behavior, their distribution in the solid phase. The pollutants released can be transported by seepage to the underlying natural soil and groundwater (Gérald D. 2008).

In order to assess the soil pollution of public landfills by heavy metals, our research work is based on the study of zinc and chromium speciation in soils collected from three landfills in Brazzaville. Indeed, the chemical speciation of heavy metals in soils and their distribution in the different fractions therefore appear essential to better understand the factors controlling their transfer in ecosystems and their bioavailability (Waris et al, 2018), and to assess the extent of metal pollution and the risks involved (Thomas et al. 2021).

2. Materials and Methods

Location and description of the study area

Brazzaville, which is the capital of the Republic of Congo, is between latitudes 4°6' and 4°23' South and longitudes 15°5' and 15°25' East. It is located in the south of the Republic of Congo, on the banks of the Congo River, on the north bank of the Pool Malebo opposite Kinshasa (Democratic Republic of the Congo). It has a very extensive peri-urban area in both its northern and southwestern parts. Brazzaville has about 1,838,348 inhabitants, an area of more than 309 km^2 and eleven districts (Makélékélé, Bacongo, Poto-Poto, Moungali, Ouenzé, Talangaï, Mfilou, Madibou and Djiri).

Figure 1 shows the map of the city of Brazzaville, as well as the location of the landfills studied.

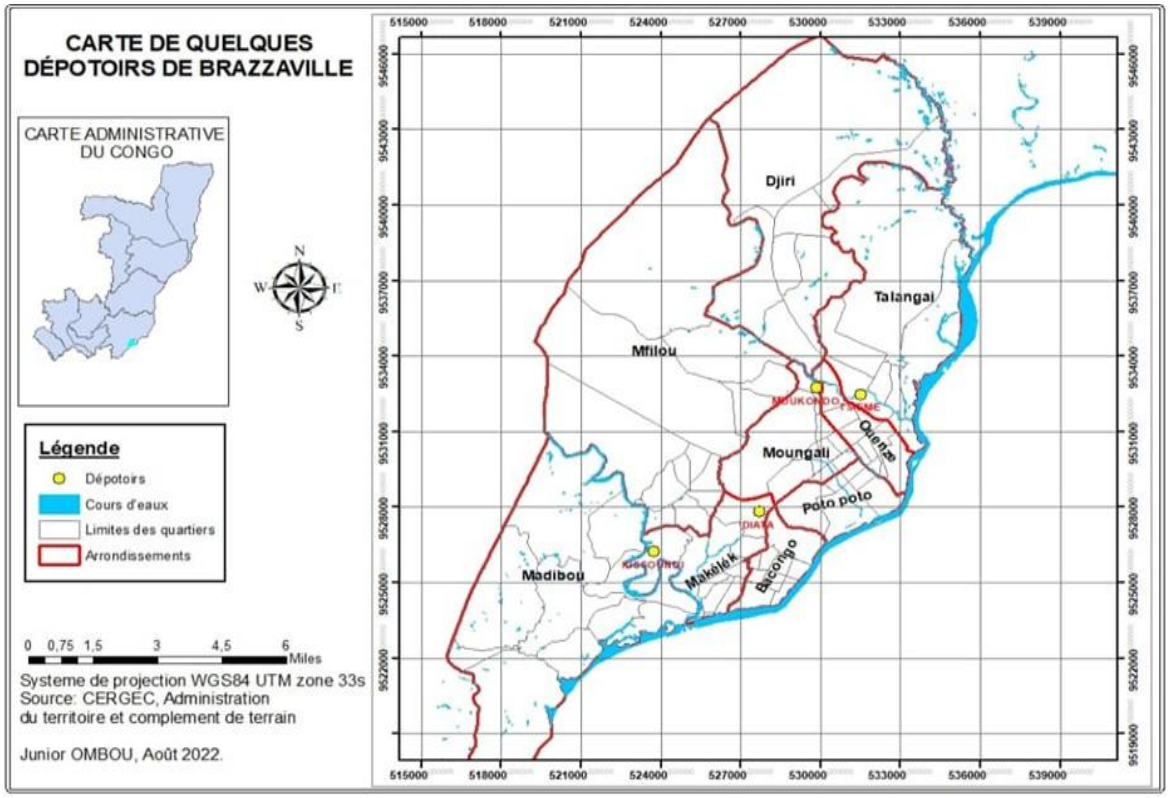

Figure 1: Location of landfills studied

Collection and preparation of samples

After visiting several landfills in the different districts of Brazzaville, three sampling sites were chosen according to several criteria: location, waste typology, age of the site, and anthropogenic activities carried out in the landfills. Three sampling campaigns were organized respectively in January, June and November of 2022. In each landfill, the samples were taken from five different points at a depth of 25 cm using an auger, then mixed to have composite samples that will undergo physicochemical analyses and determination of heavy metals. The samples were dried for ten days at room temperature, then sieved using a sieve of 2 mm porosity, crushed with an agate mortar and kept in plastic bags.

Determination of physicochemical parameters

A given amount of soil was dissolved in distilled water and then stirred for thirty minutes and after a fifteen-minute resting time, the pH and electrical conductivity of the supernatant solution were measured with a Dustgo multi-parameter (National Health Foundation, 2013) . The organic matter of the soil samples was determined by the Walkley and Black method, which is based on the oxidation of organic carbon by an excess of potassium dichromate ($K_2Cr_2O_7$) in an acidic medium, followed by an determination of this excess by ferrous ion (Wakley et al. 1934).

Determination of heavy metals

The soil samples were first mineralized to dissolve the heavy metals before proceeding to their determination. A mass of 0.5 g of each composite sample was attacked by the mixture composed of 9 mL of concentrated hydrochloric acid and 3 mL of concentrated nitric acid. This step was carried out at 95 °C for 75 minutes on a heating block. The solution was diluted to 50 mL with deionized water and then the metals in the dissolved metals were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Nhari et al. 2014).

Speciation of heavy metals

The sequential extraction scheme was used to study heavy metal speciation in soil samples (Legret et al. 1988). The main steps are as follows.

- Step 1: exchangeable fraction: 1 g of soil sample is dissolved in 16 mL of $CaCl_2$ (1 M) and stirred for 2 hours at room temperature.
- Step 2: oxidizable fraction (organic fraction and sulphides): the pellet of step 1 is dissolved with a mixture composed of 10 mL H_2O_2 8.8 M and 6 mL of HNO_3 0.02 M and stirred for 5 hours at room temperature and 1 hour at 98 ° C. The extraction is done in 10 mL of CH_3COONH_4 3.5 M and stirred for 1 hour at room temperature.
- Step 3: acid-soluble fraction (carbonates): the pellet of step 2 is dissolved by a mixture composed of 17.5 mL of CH_3COOH 1 M and 17.5 mL of CH_3COONH_4 0.6 M and stirred for 5 hours at room temperature.
- Step 4: reducible fraction (oxide of Fe and Mn): the pellet of step 3 is dissolved by a mixture composed of 17.5 mL of $NH_2OH \cdot HCl$ 0.1 M and 17.5 mL CH_3COOH 25% and stirred for 4 hours at room temperature and for 1 hour at 98 °C. The extraction is done in 10 mL CH_3COONH_4 3.5 M and stirred for 1 hour at room temperature.
- Step 5: residual fraction: the pellet of step 4 is calcined for 2 hours at 550 ° C in a muffle oven then the residue is solubilized in a mixture composed of 10 mL of concentrated HCl (12 M) and 10 mL of HF 40%. Sequential extractions were performed in polyethylene centrifuge tubes. Between two stages, the suspensions

were centrifuged for 30 minutes. The heavy metals related to each phase were determined in the supernatant of each phase by inductively coupled plasma-optical emission spectrometry (ICP-OES).

Assessment of metal contamination in soil

Contamination factor (CF)

To assess metal contamination in landfill soils, the contamination factor (CF) was used. The contamination factor is calculated by the ratio of the determined concentration of the metal in the soil (Cn) to the background noise of the metal in the earth's crust (Bn) which is a reference value contained in the Wedephol concentrations (Hakanson et al. 1980).

$$CF = \frac{Cn}{Bn} \quad (1)$$

Based on the value of the contamination factor, the pollution intensity is estimated according to Table 1.

Table 1: Assessment of the intensity of soil contamination by heavy metals

Value of CF	Class	Pollution intensity
CF < 3	1	Uncontaminated
3 < CF < 10	2	Polluted
CF > 10	3	Presents a risk

Geo-accumulation Index (Igeo)

The geo-accumulation index is used to assess the degree of accumulation of a metal in soils. It is determined from the baseline level of metal content in soils (Ayantobo et al. 2005 ; Mohameden et al. 2022) according to the following relationship:

$$Igeo = \text{Log}_2 \frac{Cn}{1,5\ Bn} \quad (2)$$

Where Cn is the concentration of metal in the soil for element n, Bn the geochemical background noise for element n and 1.5 the correction factor.

The intensity of pollution as a function of the Igeo value is presented in Table 2: Table no 2 : Assessment of the heavy metals geo-accumulation index

Value of Igeo	Class	Pollution intensity
Igeo < 0	0	Unpolluted
0 < Igeo < 1	1	Unpolluted to moderately polluted
1 < Igeo < 2	2	Moderately polluted
2 < Igeo < 3	3	Moderately to severely polluted
3 < Igeo < 4	4	Severely polluted
4 < Igeo < 5	5	Severely polluted to very severely polluted
5 > Igeo	6	Very severely polluted

3. Results and Discussion

Physico-chemical parameters

pH

The pH values recorded in landfill soils are shown in Figure 2. The pH recorded in these soils indicates that these soils are neutral and therefore poor in carbonate since theoretically, at atmospheric pressure, the pH of soil solutions increases with the presence of excess carbonate. The pH values obtained in the soils of the landfills studied are similar to those found in the soil of the uncontrolled landfill in Tangier, Morocco (Ikram et al. 2016), but do not agree with those found in 2015 by Baghdadi in the soil solutions of the landfill in the city of Beni-Mellal in Morocco (Baghdadi et al. 2015) that recorded basic values. The average pH values obtained for our study at the different sites are acceptable and meet the growth standards of fish species (Waris et al. 2018).

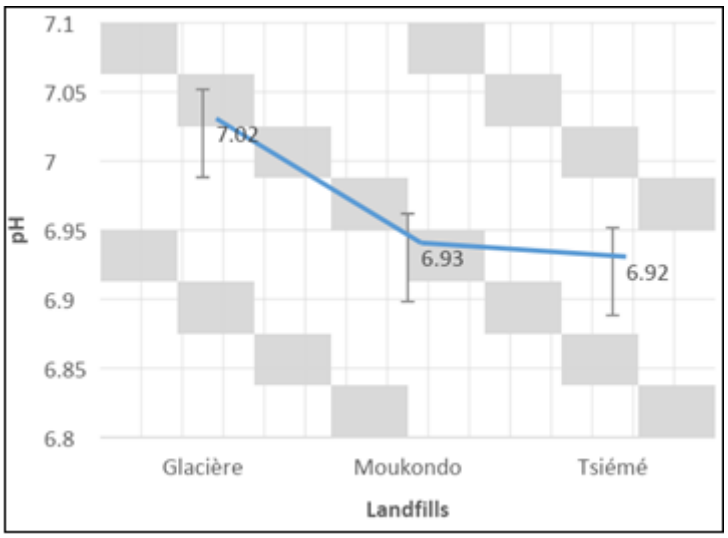

Figure 2: pH of soil solutions. From landfill

Electrical conductivity

Figure 3 shows the electrical conductivity values of the soils determined in the three discharges. The values are 348 µS/cm for the discharge of the Cooler, 476.33 µS/cm for the discharge of the tsiémé and finally 475.83 µS/cm for that of Moukondo. In the three landfills, the highest electrical conductivity values were measured during the third sampling campaign corresponding to the rainy season. These values are much lower than those obtained by Ikram in 2016 in the soils of the landfill in the city of Tangier in Morocco.

Compared to the measured electrical conductivity values, the soils of these three landfills are unsalted because the electrical conductivity of the soil extracts by water is used as a diagnosis of soil salinity.

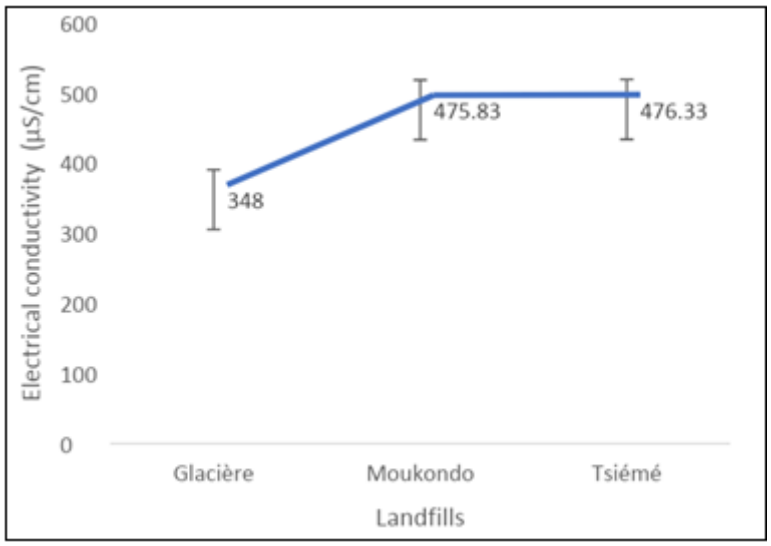

Figure 3: Electrical conductivity of soil solutions from landfills

Organic matter

Figure 4 shows organic matter levels in landfill soils. The content of organic matter in landfill soils ranges from 1.72% to 7.24%. The values of the organic matter content obtained in the soils of the Moukondo and Tsiémé landfills are higher than the guide value (1% to 2%) accepted for mineralized soils, and that found in the soil of Bé-Avetolandfill in Lomé, Togo (Akpaki et al. 2014). However, these levels are lower than those recorded in the soils of the Tangier landfill in Morocco (Ikram et al. 2016). The high organic matter content in landfill soils can be justified by the fact that fermentable materials represent a significant part of the physical composition of household waste.

It can therefore be claimed that the soils of the Moukondo and Tsiémé landfills are potentially rich in organic pollutants. Organic matter content is the parameter that correlates very well with the retention power of organic and metallic pollutants by soil.

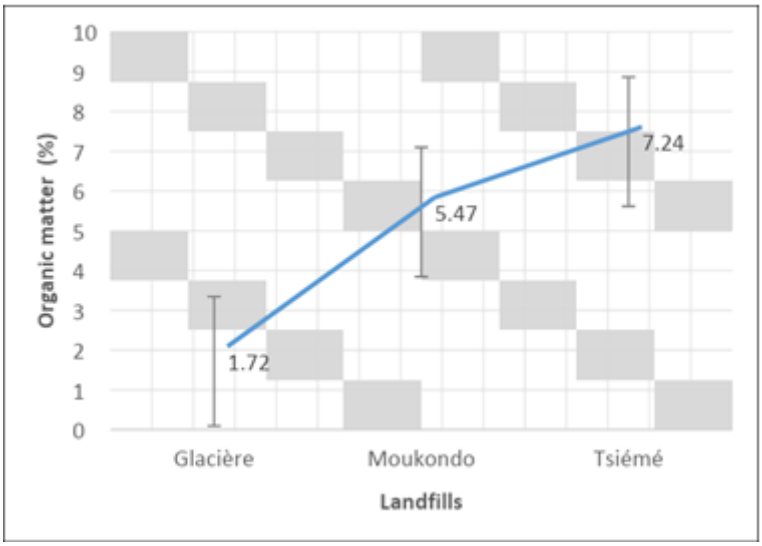

Figure 4: Soil organic matter from landfills

Determination of heavy metals

Chrome

Chromium concentrations in landfill soils are shown in Figure 4. The lowest chromium content is recorded in the soil of the Glacière landfill (15 mg/kg) while the highest is recorded in the soil of the Tsiémé landfill (1900 mg/kg). The results show that the content obtained in the Tsiémé landfill is higher than the AFNOR NF U 44-041 standard (150mg/kg). In comparison with the contents of the indoor studies, the content of chromium obtained in the Tsiémé landfill is much higher than those recorded in 2020 in the soils of the Bobo-Dioulasso landfills in Burkina Faso by Lambiénou (Lambiénou et al. 2020). The high presence of chromium in the Tsiémé landfill and the low concentration in the other two landfills can be explained, among other things, by the type of waste, which is not the same from one landfill to another.

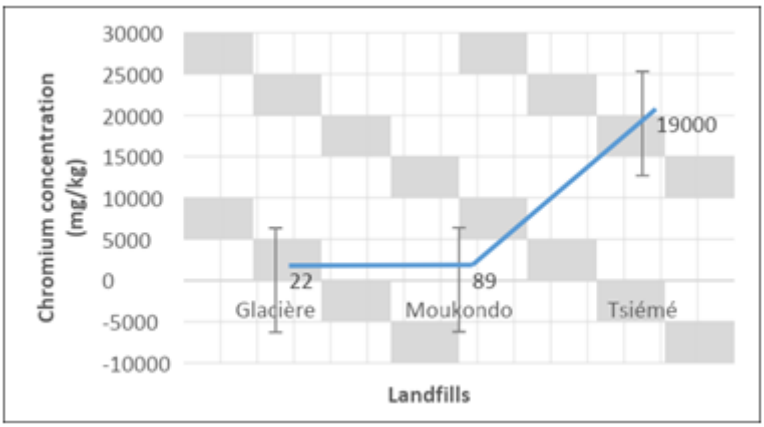

Figure 5: Chromium concentrations in landfill soils

Zinc

Figure 6 shows the levels of zinc in soils collected from landfills. The results of the analyses indicate that the presence of zinc in landfill soils is not homogeneous, this may be due to the heterogeneous nature of the waste or to non-uniform degradation of the waste. In comparison with the results of indoor studies, the average concentrations of zinc in the different soils of the landfills are all higher than the average concentration recorded in the soils of the Agoé landfill (Lomé-Togo) (401 mg/kg) (Magnoudéwa et al. 2012).

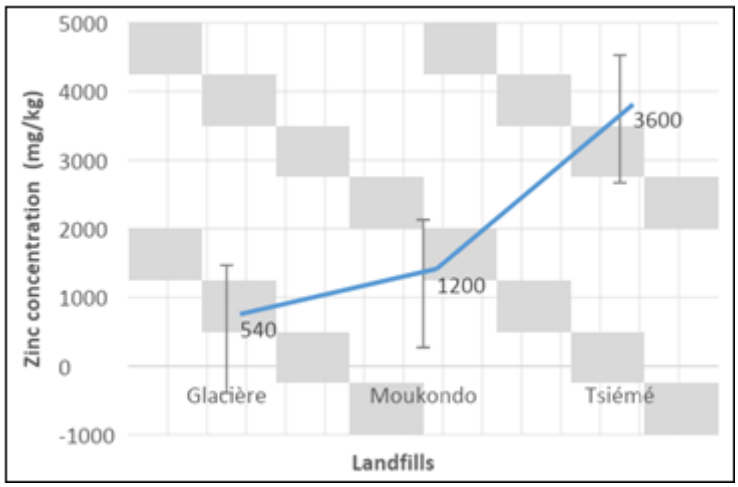

Figure 6: Zinc concentrations in landfill soils.

Sequential extraction

Chrome

Figures 7a, 7b and 7c show the results of sequential chromium extractions in landfill soil samples. The results show that at the soil level of the Glaciè landfill, chromium has a high affinity with acid-soluble (34%), reducible (28%) and oxidizable (23%) fractions. It is the same in the soils of the Moukondo landfill, in fact, it is bound to 38% in the reducible fraction, 31% in the acid-soluble fraction and 19% in the oxidizable fraction.

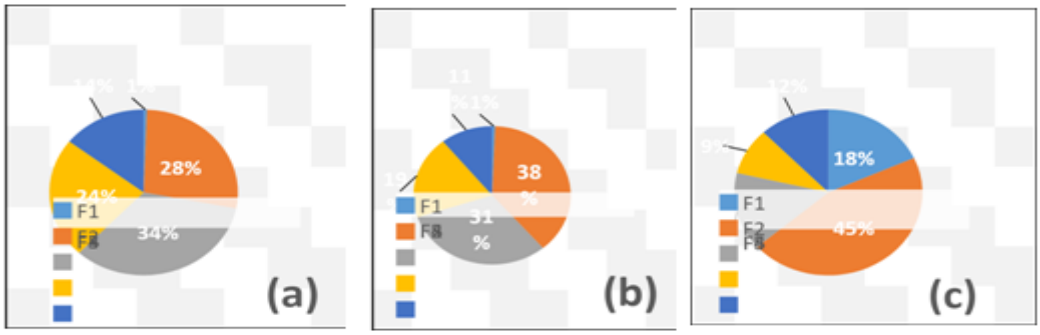

Figure 7: Chromium speciation in the landfills of Glacière (a), Moukondo (b) and Tsiémé (c)

Zinc

Figures 8a, 8b and 8c show the results from sequential zinc extractions in the soils of three landfills studied. Zinc is unevenly distributed in the different soil phases of landfills. At the soil level of the Glacière landfill, zinc has more affinity with the exchangeable (36%), reducible (33%) and

oxidizable (25%) fractions. In the soil of the Moukondo landfills, more than half of the zinc is bound to the exchangeable fraction (53%). The reducible, residual, acid-soluble and oxidizable fractions represent less than 20% of the percentage of zinc. In the soils of the Tsiémé landfill, more than half of the zinc is bound with the exchangeable fraction (53%) followed by the acid-soluble (28%) and reducible (15%) fractions, the oxidizable and residual fractions have 2% of zinc percentage. Overall, zinc is very much related to the exchangeable fraction. This explains the high mobility of zinc in soils from landfills to groundwater. Indeed, the exchangeable fraction is the most mobile and toxic fraction.

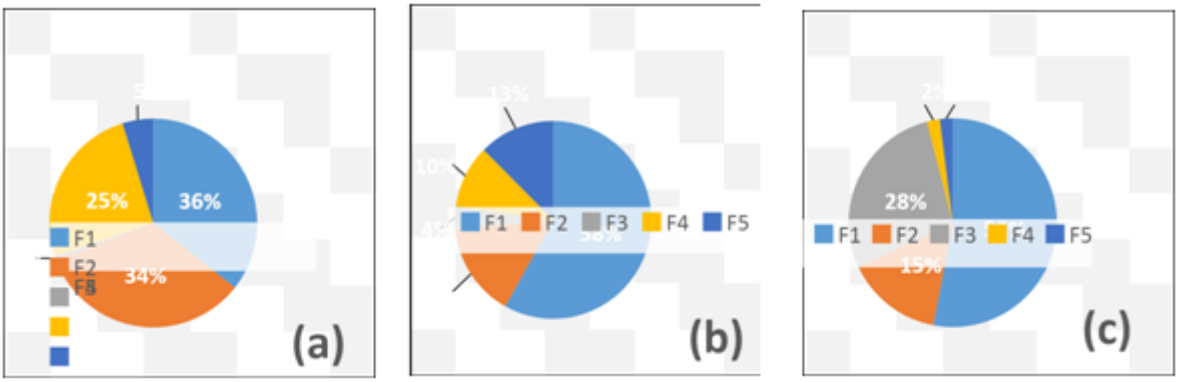

Figure 8: Zinc speciation in Glacière (a), Moukondo (b) and Tsiémé (c) landfills

Assessment of metal contamination

Contamination factor (CF)

Chromium contamination factor: CF(Cr)

Figure 9 shows the factors of chromium contamination in landfill soils. The contamination factor varies from one landfill to another. In the soils of the Glacière and Moukondo landfills, the values of the contamination factors are less than 3, which means that these soils are class 1 and therefore not polluted by chromium. On the other hand, in the Tsiémé landfill the contamination factor is well above 10, which makes it possible to deduce that the soils of the Tsiémé landfill are class 3, they present a great risk, in fact, they are greatly polluted by chromium.

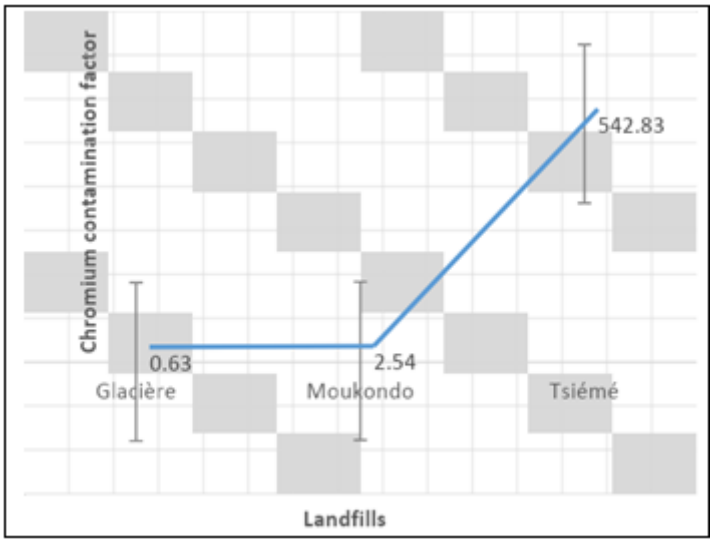

Figure 9: Chromium contamination factor in landfill soils

Zinc contamination factor: CF (Zn)

Zinc contamination factors in landfill soils are shown in Figure 10. The contamination factor values obtained in landfill soils are all greater than 10. These soils are class 3, they present a great risk, in fact, they are greatly polluted by zinc.

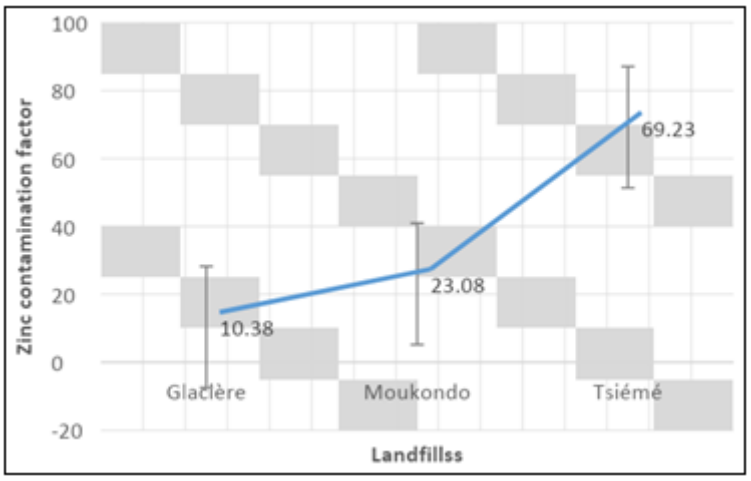

Figure 10: Zinc contamination factor in landfill soils

Geoaccumulation index (Igeo)

Geoaccumulation index of chromium: Igeo (Cr)

The results of the geoaccumulation index of chromium in landfill soils are presented in Figure 11. The intensity of chromium pollution indicates that the soils of the Glacière landfill are not polluted, since the Igeo value is less than zero. The intensity of chromium pollution indicates that the soils of the Moukondo landfill are characteristic of unpolluted to moderately polluted soils, they are class 1, in fact, in the soils of the Tsiémé landfill, the Igeo is between 0 and 1. The igeo (Cr) recorded in the soils of the Tsiémé landfill being greater than 6, these soils are characterized as class 6, they are severely polluted by chromium.

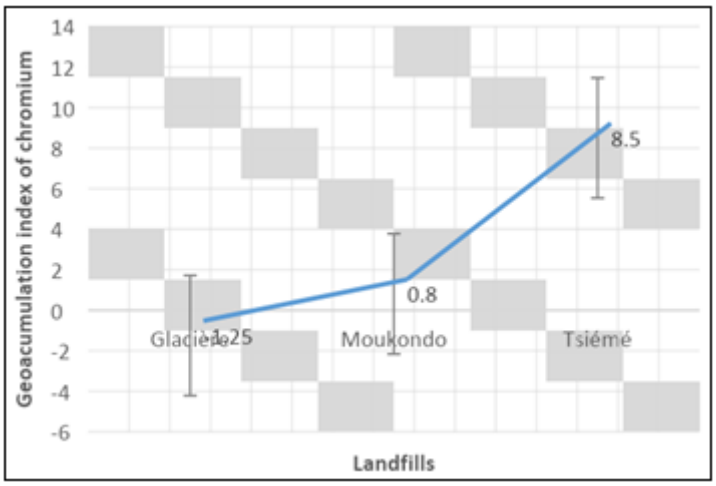

Figure 11: Geoaccumulation index of chromium in landfill soils

Zinc geoaccumulation index: Igeo (Zn)

Figure 12 shows the geochemical accumulation index of zinc in the soils of the various landfills. The Igeo (Zn) values in the landfill soils are as follows: 2.8 in the Glacière landfill, 3.94 in the Moukondo landfill and 5.53 in the Tsiémé landfill. Zinc geoaccumulation indices recorded in landfill soils indicate that zinc accumulation is not homogeneous, but there is a large accumulation of zinc in these soils. In the soils of the Tsiémé landfill, the geoaccumulation index of zinc is between 5 and 6, the soils of the Tsiémé landfill are therefore class 6, they are severely polluted to very severely polluted. In the Glacière landfill, the Igeo (Zn) being between 2 and 3 the soils of the Glacière landfill are characteristic of moderately to severely polluted soils. In the Moukondo landfills the Igeo (Zn) being between 3 and 4, the soils of the Moukondo landfill is class 4, they are severely polluted. The high accumulation of zinc in landfills shows that zinc pollution in landfill soils is anthropogenic (Ekengele et al. 2016).

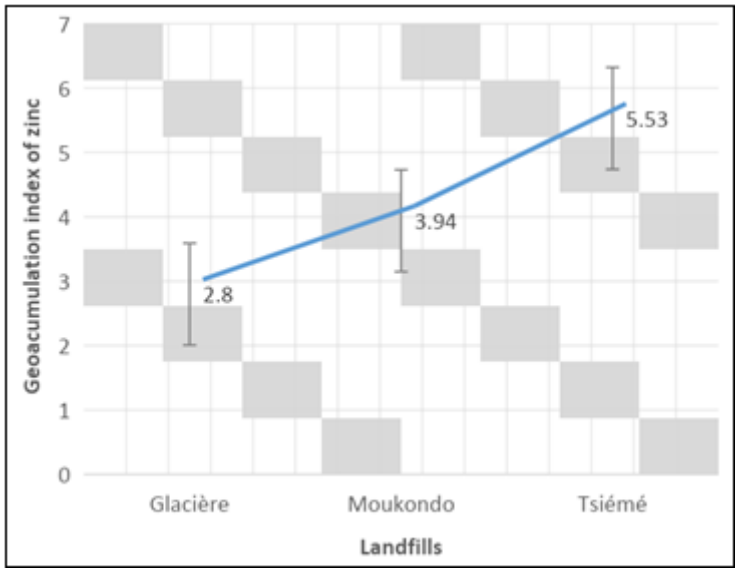

Figure 12: Geoaccumulation index of zinc in landfill soils.

4. Conclusion

The objective of this study is to study the speciation of chromium and zinc, and then to assess the soil pollution of two landfills by these two metals. The results of the analyses revealed that the pH varies between 6.92 and 7.02, indicating that these soils are slightly acidic. The electrical conductivity measured in these soils varies between 348 and 476.33 µS/cm, so these soils are unsalted. The organic matter content varies between 1.72 and 7.24%, these soils are potentially rich in organic matter. The concentration of chromium in landfill soils varies between 22 and 19000 mg/kg and the Tsiémé landfill has a chromium concentration higher than the threshold value recommended by the AFNOR NF U 44-041 standard. The concentration of zinc recorded in landfill soils varies between 540 and 3600 mg/kg, all landfills have a zinc concentration higher than the threshold value recommended by the AFNOR NF U 44-041 standard. Sequential extractions carried out for the study of chromium speciation show that chromium is more bound to the reducible and acid-soluble fractions. In the soils of the Moukondo and Tsiémé landfills, more than half of the zinc is bound to the residual fraction, while in the soils of the Glacière landfill, zinc is more bound to the exchangeable and reducible fractions, which implies contamination of anthropogenic origin. The results on the measurement of contamination factor and geoaccumulation index, only indicate that the soils of the Moukondo and La Glacière landfills have not been polluted by chromium, while the soils of all landfills are polluted by zinc.

Conflict of interest

The authors declare no conflict of interest

Acknowledgment

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