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SORPTION MECHANISMS STUDIES OF Pb (II), Cd (II) AND Cu (II) INTO SOIL OF PORT-AU-PRINCE.

ESTUDIOS DE MECANISMOS DE SORCIÓN SIMULTÁNEA DE Pb (II), Cd (II) Y Cu (II) EN EL SUELO DE PUERTO PRÍNCIPE

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Abstract

The aim of this study was to qualify and quantify the mechanisms of retention / release of some heavy metals (Pb, Cd and Cu) in a representative soil in Port-au-Prince. We have taken as hypothesis that chemical sorption is a key issue in assessing the mobility and retention of heavy metals in soils. The used porous matrix is from a sedimentary deposit of the Plain of Cul-de-Sac aquifer. Groundwater from this aquifer is the main source of drinking water for urban population of Port-au-Prince. Previous researches have showed an impact of waters quality due to the contribution of urban contaminants. Then, to assess the adsorption of Pb(II), Cd(II) and Cu(II), batch equilibrium tests were performed using single metal solutions in soil. Single-element equilibrium studies were carried out with 0.01 M $NaNO_3$ as background electrolyte. Soil characteristics have affected heavy metals sorption such as soil pH (8.26), cation-exchange capacity (CEC) [135 $meq.kg^{-1}$] and organic matter (58 $g.kg^{-1}$). In this case, it was impossible to carry out adsorption experiments with the metals due to precipitation of the metals as the hydroxides, which introduces uncertainty into the interpretation of the results. Cadmium ions have little tendency to hydrolyze at pH ≤ 8 but at pH > 11, all cadmium exist as the hydroxo-complex. The precipitation is very rapid for Cu (II) and Pb(II) at pH > 6.0, then the experiments was performed at pH = 6.0.The equilibrium sorption batch tests showed that the adsorption of heavy metals on the soil decreased in the order of $Cd^{2+} > Cu^{2+} > Pb^{2+}$. Indeed, column tests will be necessary to assess heavy metals progressive saturation on the soil.

Key words: heavy metals, equilibrium sorption, soil, pH.

Resumen

El objetivo de los trabajos presentados es de cualificar y de determinar en cantidad los mecanismos de retención de unos metales pesados (Pb, Cd, Cu) en un suelo representativo de Puerto Príncipe. Agarramos como hipótesis que el sorption químico es una llave para la evaluación de la movilidad y de la retención de los metales pesados en los suelos. La matriz porosa utilizada se deriva de un depósito sedimentario de la llanura del Cul de Sac. Las aguas subterraneas de este acuífero está el principal recurso en agua potable de la población urbana de Puerto Príncipe. Trabajos precedentes mostraron un impacto de la calidad de las aguas que parece debida a la aportación de contaminants urbano. En efecto, para evaluar la adsorción del Pb II), del Cd II) y del Cu II), ensayos de equilibrio batch han sido realizadas utilizando monosoluciones metálicas con NaNO3 a 0.01 M como electrólito. Las características del suelo han afectado la adsorción de los metales como el pH del suelo (8.26), la capacidad de intercambio catiónico (CEC) [135 Meq.kg-1] y la materia orgánica (58 g.kg-1). En este caso, era imposible realizar estudios de adsorción con los metales al pH del suelo a causa de la precipitación de los metales como los hidróxidos, que introducía una incertidumbre en la interpretación de los resultados. Los iones de cadmio tienen una tendencia débil a hidrolysarse a pH ≤ 8 pero a pH> 11, todo el cadmio existe bajo forma hydroxyle-compleja. La precipitación era muy rápida para el Cu (II) y el Pb (II) a pH> 6.0, es por eso que los ensayos han sido realizados a pH 6.0. El equilibrio de adsorción de los ensayos en batch mostró que la adsorción de los metales en el suelo disminuía en la orden de Cd2+> Cu2+>Pb2+. Es necesario proceder a ensayos en columnas con vistas a evaluar la saturación progresiva de metales en el suelo.

Palabras clave : metales pesados, equilibrio de adsorción, suelo, pH..

Résumé

L'objectif des travaux présentés est de qualifier et quantifier les mécanismes de rétention/relargage de quelques métaux lourds (Pb, Cd, Cu) dans un sol représentatif de Port-au-Prince. Nous avons pris comme hypothèse que la sorption chimique est une clé pour l'évaluation de la mobilité et de la rétention des métaux lourds dans les sols. La matrice poreuse utilisée est issue d'un dépôt sédimentaire de la plaine du Cul de Sac. Les eaux souterraines de cet aquifère est la principale ressource en eau potable de la population urbaine de Port au Prince. Des travaux précédents ont montrés un impact de la qualité des eaux qui semble due à l'apport de contaminants urbains. En effet, Pour évaluer l'adsorption du Pb (II), du Cd (II) et du Cu(II), des essais d'équilibre en batch ont été réalisés en utilisant des mono-solutions métalliques

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avec du $NaNO_3$ à 0.01 M comme électrolyte. Les caractéristiques du sol ont affecté l'adsorption des métaux comme le pH du sol (8.26), la capacité d'échange cationique (CEC)[135 Méq.kg^{-1}] et la matière organique (58 g.kg^{-1}). Dans ce cas, il était impossible de réaliser des études d'adsorption avec les métaux au pH du sol à cause de la précipitation des métaux comme les hydroxydes, qui introduisait une incertitude dans l'interprétation des résultats. Les ions de cadmium ont une faible tendance à hydrolyser à pH ≤ 8 mais à pH > 11, tout le cadmium existe sous forme hydroxyle-complexe. La précipitation était très rapide pour le Cu(II) et le Pb(II) à pH > 6.0, c'est pourquoi les essais ont été réalisés à pH 6.0. L'équilibre d'adsorption des essais en batch ont montré que l'adsorption des métaux dans le sol diminuait dans l'ordre de $Cd^{2+} > Cu^{2+} > Pb^{2+}$. Il est nécessaire de procéder à des essais en colonnes en vue d'évaluer la saturation progressive en métaux dans le sol.

Palabras clave : Métaux lourds, équilibre d'adsorption, sol, pH.

INTRODUCTION

Heavy metals release onto soils is a major concern today in both developed and developing countries. Their presence onto soils as a result of human activities may pose a serious threat to the environment and groundwater quality. Common anthropogenic sources include agricultural activities, atmospheric deposition, road run off, discharges from industrial plants and sewage works, acidic mine effluents and building of reservoirs (Sajidu *et al.*, 2006). Increased anthropogenic inputs of trace elements in soils may result in transport of these metals in the soil profile, leading to the increased concentrations of trace elements in the ground or surface waters (Hooda et Alloway, 1993; Jalali et Moharrami, 2007).

Problems of environmental pollution by heavy metals from industrial activity represent a serious threat to human health and have been widely described (Keane, 1998; Bliefert and Perraud, 2001; Alvarez-Ayuso et *al.*, 2003; Inglezakis and Grigoropoulou, 2003). In Port-au-Prince (Haiti), the presence of heavy metals has been reported in wastewater (Carré, 1997) and even in drinking water (Angerville et *al.*, 200; Emmanuel et *al.*, 2007). Important concentrations of lead (40 µg/L), chromium (470 µg/L) and nickel (250 µg/L) were measured in the drinking water of Port-au-Prince (Emmanuel et *al.*, 2004).

In the present work, we have studied single-element adsorption systems of three divalent metals (Pb, Cd and Cu) from a sedimentary deposit of the Plain of Cul-de-Sac aquifer. Previous researches have showed an impact of waters quality due to the contribution of urban contaminants. Lead, copper, and cadmium belong to the group of serious hazardous heavy metals (Qin *et al.*, 2006). Cadmium is accumulated in the human body, causing erothrocyte destruction, nausea, salivation, diarrhea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity (Mohan et Singh, 2002); gastrointestinal distress is one of the reported health effects of Cu (II), and vomiting, nausea and abdominal pain are common symptoms of Cu(II) poisoning, particularly after drinking beverages stored in copper or untinned brass containers (ATSDR, 2002; Bhattacharyya et Gupta, 2007); low levels of Pb(II) have been identified with anemia, as it causes injury to the blood-forming system, while high levels cause severe dysfunction of the kidneys, the liver, and the central and peripheral nervous system and high blood pressure (ATSDR, 1999).

Chemical sorption is a key issue in assessing the mobility and retention of these heavy metals in soils. The solubility and bioavailability of heavy metals are controlled by the adsorption characteristics of soils (Krishnamurti *et al.*, 1999), such as pH, redox potential, clay minerals, soil organic matter, Fe and Mn oxides, and calcium carbonate (Mclean et Bledsoe, 1992; Rieuwerts *et al.*, 1998; Usman, 2008). The adsorption of heavy metal cations is often pH-dependent, whereas Fe and Mn oxide and hydroxide minerals as well as humic substances dominate (Usman, 2008). As soil pH increases, the retention of the heavy metal cations to soil surfaces increases via adsorption, inner-sphere surface complexation, and/or precipitation and multinuclear type reactions (Mcbride, 1994). For example, Cadmium ions have little tendency to hydrolyze at pH ≤ 8 but at pH > 11, all cadmium exist as the hydroxo-complex (Mohan et Singh, 2002) and at pH >6 precipitation can be very rapid for copper and lead adsorption.

The aim of this study was to qualify and quantify the mechanisms of retention / release of some heavy metals (Pb, Cd and Cu) in a representative soil in Port-au-Prince. Sorption isotherms and distribution coefficient (K_d) were developed to establish the selectivity sequences of these metals in the soil and to evaluate the capacity of the soil to sorb these metals.

MATERIALS AND METHODS

Soil samples and characteristics

Thee soil samples were collected from a sedimentary deposit of the Plain of Cul-de-Sac aquifer. To obtain a homogeneous sample of the study area, three approximately 3-kg samples from 2 m apart of the same site of each soil were combined prior to the experiments. All samples were air-dried at room temperature, passed through a 2 mm sieve, homogenized, and stored pending for physicochemical properties (Table 1) such as pH, organic carbon, clay, and $CaCO_3$ using standard analytical methods (Page, 1982; Adhikari et Singh, 2003). Soil pH were measured using a pH meter at a soil to solution ratio in both deionized water in 1:2.5 and 1 mol L^{-1} KCl. Soil organic matter (OM) was determined by calcinations at 550°C during 2

h. The inorganic carbon was determined using the calcimeter method and carbonate concentrations were calculating using Universal Gas Law (Usman, 2008).The cation exchange capacity of soil was determined using METSON method. Concentration of available Pb, Cd and Cu in soils samples was determined using DTA method (Lindsay et Norvell, 1978; Adhikari et Singh, 2003).

Table 1. physicochemical properties of the experimental soil

Parameters	Values
pH (H2O)	8.26
pH (1 mol L-1 KCl)	7.46
Organic matter (g kg-1)	58
Organic carbon (g kg-1)	100
CaCO3 (g kg-1)	343
Clay (g kg-1)	17
CEC (meq kg-1)	135
Total Pb (mg kg-1)	Ud
Total Cd (mg Kg-1)	Ud
Total Cu (mg kg-1)	61.4
Ud : undetected	

Equilibrium sorption experiments

Batch adsorption studies were conducted to determine the relationship between adsorbent and adsorbate bt varying the amounts of adsorbate (Aziz *et al.*, 2001; Tran *et al.*, 2002; Markiewicz-Patkowska *et al.*, 2005). The retention/release of heavy metal on soil was performed by equilibrating 5-g soil with 50 mL solutions of Pb, Cu or Cd nitrates containing concentrations range 2 - 400 mg L^{-1}, with 0.01 M $NaNO_3$ as background electrolyte. All experiments were performed with suspension were shaken for 24 h at room temperature. Later, the batches were taken from the shaker and filtered though a 0.45 µm membrane, and finally the samples were carefully dispensed to 50mL PE sample cups, acidified to pH 1.5–2 using strong HNO_3 and stored at 4°C until the heavy metal measurements. The amount of the trace elements sorbed by soil was calculated with the equation 1 (Benguella et Benaissa, 2002; Chaturvedi *et al.*, 2006; Sevil et Bilge, 2007) :

$$q_e = \frac{(C_0 - C_e) \times V}{W} \qquad (1)$$

Where q_e is the amount of Pb^{2+}, Cd^{2+} or Cu^{2+} sorbed by the soil(mg g^{-1}), Ce is the concentration of Pb^{2+}, Cd^{2+} or Cu^{2+} in equilibrium solution (mg L^{-1}), C_0 is the initial concentration of Pb^{2+}, Cd^{2+} or Cu^{2+} in solution (mg L^{-1}), V is the solution volume (L), and W is the weight of air-dried soil (g). In order to estimate the maximum adsorption onto the soil, simple linear relationship between solution and adsorbed phases by the equation 2:

$$q_e = k_d \times C_e \qquad (2)$$

Where k_d is the slope (L g^{-1}) of the isotherm, often referred to as distribution coefficient.

Effect of pH

In order to investigate the effect of pH on Pb (II),Cu (II) and Cd (II) adsorption, 5-g soil with 50 mL of metal solutions containing 2 mM, respectively 810, 455 and 575 mg.L^{-1} for Pb, Cu and Cd, were equilibrated in the same conditions as described above. The influence of pH on metal adsorption on the selected soil was studied at varying pH values (2 – Soil pH). These experiments were carried out by adjusting pH with NaOH or HNO_3. These experiments were performed in order to select an optimum pH for heavy metal sorption isotherms. Therefore, the others soil characteristics especially clay content was kept constant.

RESULTS AND DISCUSSION

Soil physicochemical characteristics

Table 1 summarizes the main physicochemical characteristics of the studied soil. Soil pH was 8.26, due to the presence of the free $CaCO_3$ in the soil. The high value of CEC (135 g kg^{-1}) could be generally determined by the clay content (17 g kg^{-1}).

Data indicate that the studied soil had high value of calcium carbonate (343 g kg^{-1}). Therefore, initial concentrations of Pb and Cd were undetected, but for Cu we have obtained 61.4 mg kg^{-1}.

Sorption experiments

Effect of pH

Sorption processes and the leaching potential of trace elements by soil depend on factors such as soil pH, the nature of the mineral and organic constituents, the nature of the metal, the ionic strength of the soil solution and the simultaneous presence of competing metals (Msaky et Calvet, 1990; Kookama et Naidu, 1998; Harter et Naidu, 2001; Jalali et Moharrami, 2007). Then, the pH of the aqueous solution is an important controlling parameter in the adsorption process (Ajmal *et al.*, 1998; Nuhoglu et Oguz, 2003; Pérez-Marìn *et al.*, 2007). **Fig. 1** shows the effect of pH on Cu (II), Pb(II) and Cd (II) in experiments carried out at different pH values.

According to Fig. 1, we can observe that for lows pH values (2-4), retention efficiency is relatively small. However, in the other range of pH values the rate of retention increases considerably. Moreover the increase in pH favours often precipitation, then Pb, Cu and Cd could probably be eliminated though precipitation as well (Bellir *et al.*, 2005). This is why that our experiment was carried out at pH value 6.0.

At very low pH, the number of H_3O+ ions exceeds that of metal ions by several times and the metal ions can hardly compete with H_3O+ ions for the binding sites on the clay adsorbents. With an increase in pH, the concentration of H_3O^+ ions decreases and some of the sites become available to the metal ions (Bhattacharyya et Gupta, 2007). As the acidity decreases, more and more H_3O^+ ions on the clay surface are replaced by metal ions and metal species (such as Cd^{2+}, $Cd(OH)^{+,}$ and $Cd(OH)_2$ (Lai *et al.*, 2002); Cu^{2+}, $Cu(OH)^+$, and $Cu_2(OH)_2^{2+}$ (Bosso et Enzweiler, 2002); Pb^{2+}, $Pb(OH)^+$, $Pb(OH)_2$, $Pb(OH)_3^-$, and $Pb(OH)_4^{2\square}$ (Taty-Costodes *et al.*, 2003). This happens at a comparatively lower pH (~6.0) for Cu(II) (Nuhoglu et Oguz, 2003) and Pb(II) (Jain et Ram, 1997) while the adsorption could be safely carried out to pH ~10.0 for Cd(II) (Mathialagan et Viraraghavan, 2002). Therefore, Heavy metal sorption was carried out at pH value 6.0 to avoid precipitation of the metals as the hydroxides, which introduces uncertainty into the interpretation of the results.

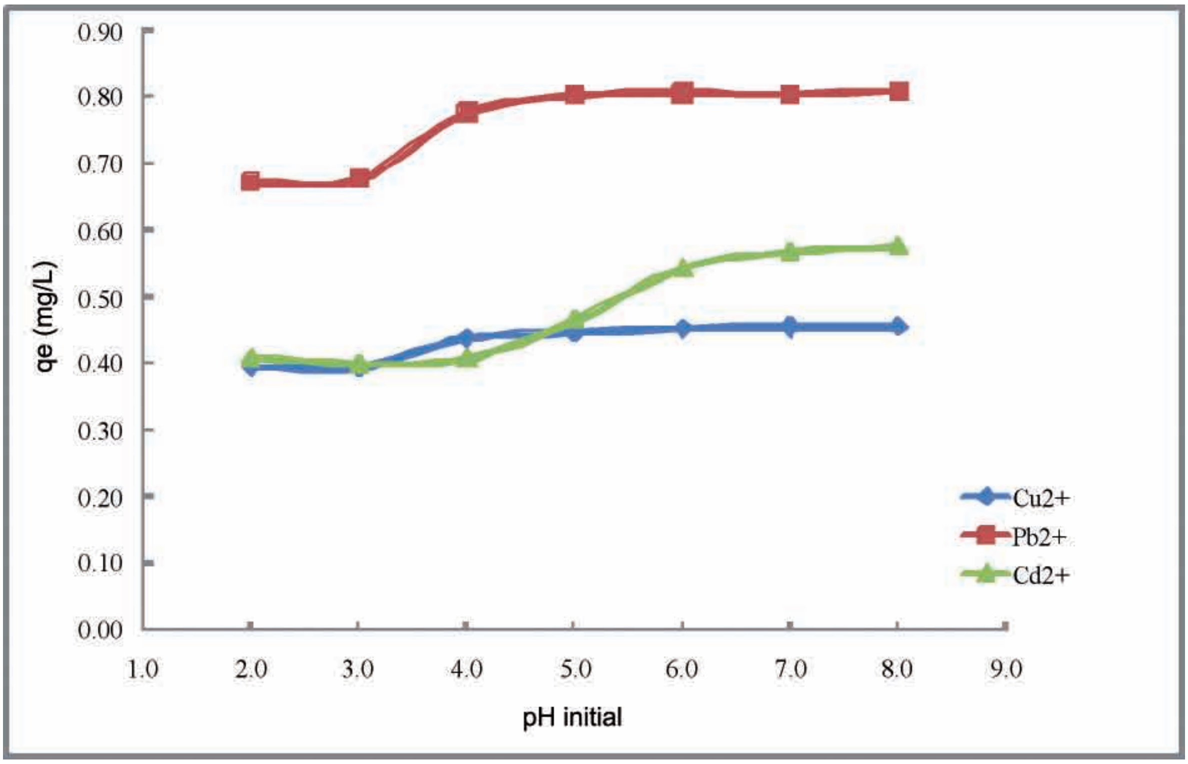

Figure 1. Effect of pH on adsorption of Cu2+, Pb2+ and Cd2+ by selected soil (metal concentrations 2 mM and background 0.01 M $NaNO_3$).

Heavy metal sorption isotherms

A sedimentary deposit such Cul-de-Sac plain deposit is a heterogeneous mixture of several minerals, several retention processes such as precipitation, co-precipitation, diffusion and surface sorption may contribute metal sorption. Sorption isotherm of Cu, Pb and Cd are shown in **Fig. 2** at pH 6.0. These isotherms represent the sorption behavior of metals on soil as a function of increasing aqueous metal ion concentration after equilibrium.

The sorption capacity of these three metals increased as the equilibrium concentration of the metals increased. The sorption behavior of Pb^{2+} was significantly higher than Cd^{2+} and Cu^{2+} sorption. The equilibrium sorption batch tests showed that the adsorption of heavy metals on the soil decreased in the order of Cd^{2+}> Cu^{2+}>Pb^{2+}.

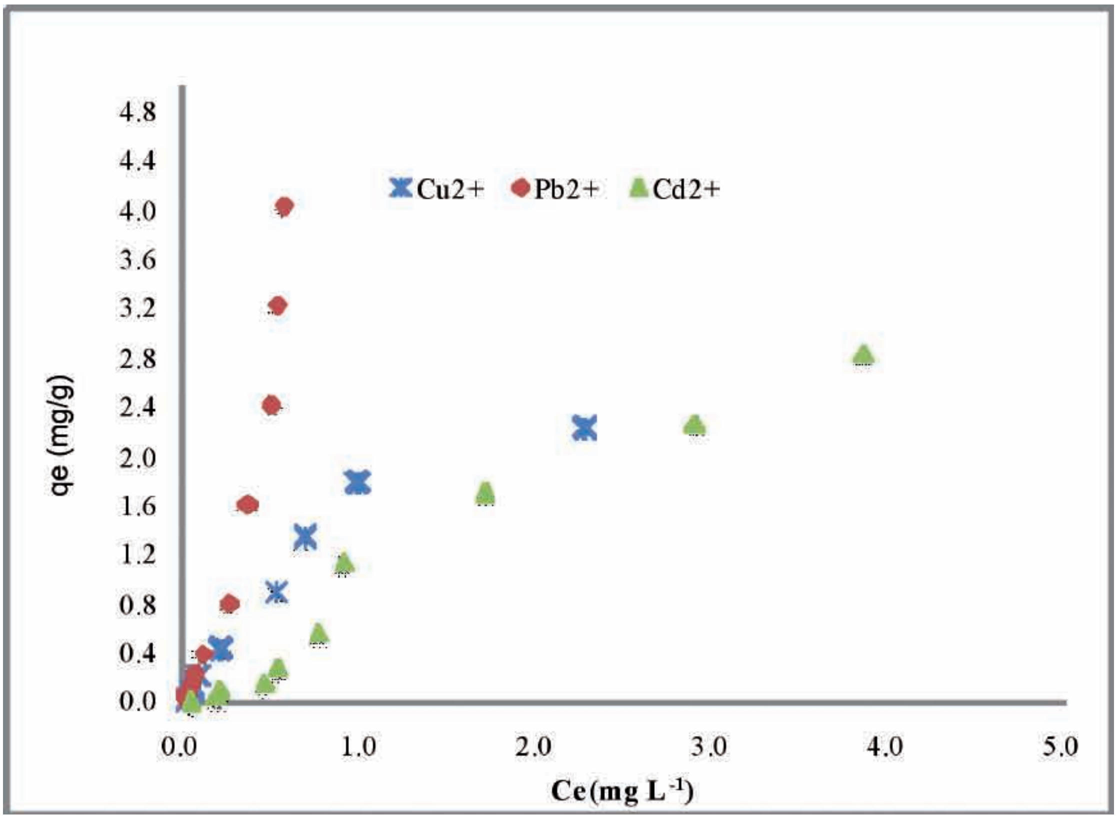

Figure 2. Sorption isotherms of Pb2+, Cd2+ and Cu2+ on the soil at pH 6.0.

Distribution coefficient (K_d)

The distribution coefficient (K_d) is a useful index for comparing the sorptive capacities of different soils or materials for a particular ion under the same experimental (Alloway, 1995; Usman, 2008). Distribution coefficients have previously been used in studies of mobility and retention of trace elements in the soils (Katou *et al.*, 2001; Martin-Garin *et al.*, 2002; Magesan *et al.*, 2003; Voegelin et Kretzschmar, 2003; Jalali et Moharrami, 2007). This coefficient represents the sorption affinity of metal cations in solution for the soil solid phase and can be used as a valuable tool to study metal-cation mobility and retention in soils system (Gomes *et al.*, 2001). Table 2 shows the distribution coefficients (K_d).

A high K_d value indicates a high metal retention by the solid phase through sorption and chemical reactions, leading to a low potential bioavailability of the metal. However, a low K_d value indicates a high amount of the metal remains in the solution (Anderson et Christensen, 1988; Gomes *et al.*, 2001; Usman, 2008). Overall initial concentrations of heavy metals, the highest K_d values were found for Pb (6.66 $L.g^{-1}$) and followed by Cu (2.83 $L.g^{-1}$) and Cd (1.25 $L.g^{-1}$) (Table 2). According those results, the highest values obtained for Pb shows that it was the most retained cation. Therefore, Cu presented the lowest k_d values. These results strongly suggest why (Berti et Jacobs, 1996) found that soil loading of Cd, Ni, and Zn appeared to be of greater environmental concern than Cr, Cu, and Pb and that the first group could accumulate in the tissue of plants grown on sludge-treated plots (Gomes *et al.*, 2001). Then, Cd and Cu may pose a risk to groundwater of Cul-de-Sac plain and plants more than Pb.

CONCLUSION

The results obtained in this study show that Pb sorption is significantly higher than those Cd^{2+} and Cu^{2+}. Single equilibrium sorption batch tests show that the adsorption these three metals onto the selected soil decreased in the order of Cd^{2+}> Cu^{2+}>Pb^{2+}. Heavy metals adsorption in the sedimentary deposit of Cul-de-sac Plain is strongly affected by pH and the equilibrium concentration of the metals. In the future, it will be necessary to: (i) evaluate the competitive adsorption of these metals in multi-elements and modeling these process using classic models such as Langmuir and Freundlich model; (ii) to carry out some column tests in order to assess heavy metals progressive saturation on the soil. The results will be useful to sanity authorities of Port-au-Prince to protect water resources.

Table 2. Distribution coefficients (K_d) calculated for each added metal concentration for the soil.

Metal	Concentration added (mg L-1)	kd (L g-1)
Pb	405.00	7.13
	324.00	6.10
	243.00	4.89
	162.00	4.50
	81.00	3.18
	40.50	3.76
	24.30	4.38
	16.20	4.76
	8.10	4.52
	4.05	6.66
Cd	287.50	0.73
	230.00	0.78
	172.50	1.00
	115.00	1.25
	57.50	0.74
	28.75	0.53
	17.25	0.37
	11.50	0.56
	5.75	0.31
	2.88	0.77
Cu	227.50	0.99
	182.00	1.83
	136.50	1.97
	91.00	1.71
	45.50	2.15
	22.75	2.83
	13.65	2.47
	9.10	2.32
	4.55	1.56
	2.28	1.74

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