

Contribution to the Study of the Behaviour of Some MTEs in the Shallow Soils of Vegetable-growing Bottoms of the City of Duekoué (Côte d'Ivoire)

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To cite this article:

Sylla Tahiri, Koffi Akissi Lydie Chantal, Kouadio David Leonce, Yapi Yapo Hermann Aristide, Dibi Brou, Dongui Bini Kouame. Contribution to the Study of the Behaviour of Some MTEs in the Shallow Soils of Vegetable-growing Bottoms of the City of Duekoué (Côte d'Ivoire). *American Journal of Applied Chemistry*. Vol. 9, No. 6, 2021, pp. 207-212. doi: 10.11648/j.ajac.20210906.14

Received: December 6, 2021; Accepted: December 30, 2021; Published: December 31, 2021

Abstract: Metal pollutants constitute one of the major pollution risks in Côte d'Ivoire and in particular in the town of Duekoué. This pollution is problematic due to the non-biodegradability and the accumulation of Trace Metal Elements (TME) in the environment. Thus, the health risk assessment aims to preserve the health of populations in their consumption habits. Indeed, any study aimed at controlling and then monitoring the quality of drinking water and the environment is beneficial. In Duekoué, market garden products grown in the lowlands are consumed without prior treatment which could cause metal poisoning of the population. The objective of this work was to study the behavior of metallic trace elements in the vegetable gardens of the town of Duekoué. To achieve the objective of this work four samples were taken from the four sites at depths of (0 to 15 cm). These samples were analyzed in the laboratory by an atomic absorption spectrometer (AAS). For this purpose, the determination of the concentrations of metallic trace element, pH and the percentage of organic matter of the various samples was carried out. Also our study allowed us to show that soils 1 and 3 are basic while soils 2 and 4 are acidic. In addition, we noticed a richness in organic matter in site 1 with a percentage of 15.57. In addition, the analysis of the sediments showed that there are correlations between metallic trace elements and factors modifying the mobility of TME and a correlation between TME. In addition, analysis of the samples taken revealed the presence of TMEs including mercury, lead, magnesium and cadmium in the clay fraction of the sediments. Arsenic and chromium are linked to the organic fraction of sediments. From this study, it emerges that the behavior of TME in lowlands is influenced by certain physicochemical parameters such as the pH and the percentage of organic matter in the soil.

Keywords: Behavior, Metallic Trace Elements, Correlation, Shallows

1. Introduction

The development of urban and agricultural activities over the past decades has given rise to numerous pollution problems, particularly in Trace Metal Elements (TMEs) and organic pollutants. The notion of trace elements means that their average concentration in the earth's crust does not exceed 1 g.kg⁻¹ [1, 2]. In the environment, these TMEs can result from the weathering of naturally enriched rocks and /

or various anthropogenic sources. Because of its high retention capacities, the soil is an accumulator of various types of pollution resulting from the numerous human activities of which it is the support [3]. The contribution of TME can be direct (contaminated waste placed directly in contact with the soil) or indirect (atmospheric emissions in the form of aerosols). Soil is said to be "polluted" when it contains one or more pollutants or contaminants liable to cause biological, physical or chemical alterations within the

various environmental compartments (water, soil, biota, etc.). Human activities such as mining, agriculture or transportation are among the most polluting [4].

Once in the soil and depending on the physicochemical conditions, TMEs can either be “trapped” by the solid phase through different precipitation and / or sorption mechanisms on surface sites [5], or, if they are present in the soil solution, be redistributed to other environmental compartments such as surface water, groundwater, plants or living organisms.

It is accepted that the mobility, bioavailability and toxicity of TMEs depend more on their chemical forms rather than their total concentration [6-13]. Indeed, only a fraction of the total content of trace elements in the soil is available to living organisms. Speciation and mobility, i.e., the chemical forms of an TME, are thus intimately linked to its bioavailability and are therefore of fundamental importance in estimating the environmental risks associated with its presence. In the solid phase, determining the distribution of an TME between the different reactive phases allows their ability to release the TME in the soil solution to be evaluated. Determining the chemical forms of TME in the soil solution makes it possible to assess the fractions likely to be directly assimilated by living organisms, in particular market garden products grown in lowlands which are areas of accumulation of trace elements. metallic.

In Duekoué, these products are consumed without prior treatment which could cause metal poisoning of the population.

Moreover, the free form of TMEs is a priori the most assimilable form. It is therefore essential to determine the speciation of TME in the soils of these lowlands [14].

It is in this perspective that this study, the general objective of which is the study of the behavior of metals in the shallow soils of the lowlands of vegetable crops in the town of Duekoué.

Specifically, in this work it will be:

- 1) Determine the percentage of organic matter in soils;
- 2) Determine the levels of metallic trace elements;
- 3) Determine the different chemical forms of metals.

2. Material and Methods

2.1. Presentation of Study Sites

In Duekoué, site 1 is located in the Kokoman district. Site 2 is located at the entrance to the city coming from Daloa. As for site 3, it is on the Duekoué-Guiglo axis not far from the Touré Mamadou private college. Finally, site 4 is in the Petit Duekoué district near the SODECI water treatment dam.

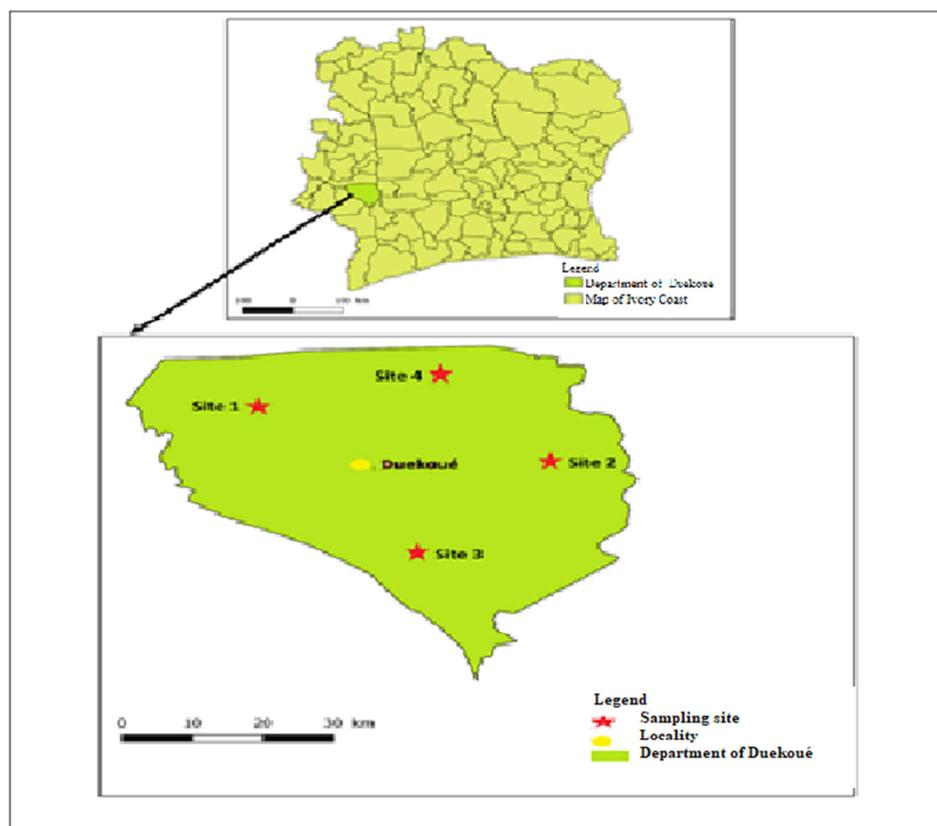


Figure 1. The different sampling sites.

2.2. Sampling Method

The soil sampling consisted of taking a systematic sample

from each plot using an auger. At each site, we collected sediments at a depth of 0 to 15 cm. The collected samples were placed in polyethylene plastic bags.

3. Methods

3.1. Determination of pH (H_2O)

The pH and the redox potential are measured in situ using a multimeter. Soil pH, or water pH, is considered to be the equilibrium pH between the solid phase of a soil sample and the liquid phase represented by distilled water. It represents the acidity of the medium and reflects the concentration of H^+ ions in the soil. The pH of the water is measured according to the ISO 10390 standard. 10 g of sol are suspended in 25 mL of ultra-pure water, stirred for 1 hour at 150 revolutions per minute on a back-and-forth stirring table. comes Ping-Pong type 560, then left to stand for an hour. The pH is then measured using a pH meter.

3.2. Determination of Eh

10 g of sol are suspended in 25 mL of ultra-pure water, stirred for 1 h at 150 revolutions per minute on a back and forth stirring table of the Ping-Pong 560 type, then left to stand for one hour. The Eh is then measured using a multiparameter.

3.3. Percentage of Organic Matter (% MO)

The organic matter content is evaluated by the loss of mass of 1 g of the dry sample after heating to 525°C. Let M be the mass in grams taken. Dry the sediment by placing the capsule in an oven set at 105°C. Leave the capsule in the oven until a constant mass is obtained. Let M2 be the mass obtained. Then place the capsule in an oven, raise the temperature to 525°C, leave the capsule for 4 hours. Weigh after cooling the capsule in the desiccator. Let M3. Repeat until a constant mass is obtained:

$$\%MO = \frac{(M2-M3) \times 100}{M2-M} \quad (1)$$

3.4. Methods for the Determination of Heavy Metals in Target Matrices

Determination of TME

The solutions obtained after acid digestion of the plant samples were assayed with an atomic absorption spectrophotometer (AAS) at well-defined wavelengths at National Laboratory for Support to Agricultural Development of Ivory Coast.

Assay Methods

3.4.1. Flame Method (Zn)

The atomic absorption of flame is a method which makes it possible to determine essentially the metals in solution. This elemental analysis method requires that the measurement be made from an analyte (element to be determined) transformed into the state of free atoms. Each mineral is introduced into the apparatus by the capillary tube which aspirates approximately 2 mL / min of each sample which will be sprayed on the optical path of the apparatus. The sample is sprayed into the flame (atomic excitation source) while forming an atomic cloud which is traversed by

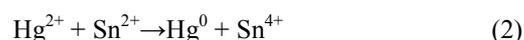
monochromatic light.

3.4.2. Four Method (Pb, Cd, As, Cr, Ni)

Between 10 and 20 μ L of solution are taken by the automatic injector to be injected into the graphics tube. Once deposited, this drop is dried and then sprayed onto the optical path of the device, forming an atomic cloud, which is crossed by the monochromatic light characteristic of the element to be quantified.

3.4.3. Hydride Method (Hg)

The water or mineralized sample is aspirated and mixed with tin chloride in a gas-liquid separator where the mercuric ion is reduced to gaseous elemental mercury according to the following reduction reaction:



The generated cold mercury vapors are entrained by a stream of nitrogen directly towards the detector to be quantified.

4. Results

4.1. pH, Eh and Percentage of Organic Matter (% MO) in Sediments

The study shows that the sediments of lowlands 1 and 3 are basic while those of lowlands 2 and 4 are acidic. In addition, it is retained that the most basic and acidic are respectively those of site 1 and 2. During this, it is noted that the soils of sites 2 and 3 are in oxidizing conditions while those of sites 1 and 4 are the reducing conditions.

In addition, the organic matter is more important in site 1 during our study. Indeed, the determined percentage of organic matter is 15.57%. Also, let us specify that this percentage in the sediments of the other sites is of the same order of magnitude as that of site 1.

Table 1. Table of pH and percentage of organic matter (% OM) in the sediments.

	pH	Eh (mV)	%MO
SITE 1	7.56	-37.2	15.57
SITE 2	5.60	10.3	12.33
SITE 3	7.25	20.5	15.17
SITE 4	6.71	-47.2	13.17

4.2. Levels of Trace Elements Studied in Sediments

From the results of the table, we note the presence of the trace elements studied in the sediments of our different study areas. The determined contents of aluminum, calcium and zinc are the most important.

Indeed, they are all greater than 500 mg / Kg. Also, the maximum concentrations determined are respectively 6976.11 mg / Kg (S4), 4696.54 mg / Kg (S4), 571.56 mg / Kg (S4). Then, we have the metallic trace elements whose concentrations determined in the lowlands of the town of Duekoué are greater than 1 mg / L. We have nickel, chromium and magnesium in particular.

On the other hand, for cadmium the contents obtained during our study are all relatively very low. In fact, they are less than 1 mg / L in the various sediments covered by our study.

On the other hand, for arsenic, only the S1 station at

relatively low concentrations.

The lowest concentrations were obtained for mercury, lead, cadmium and arsenic, in particular in the lowlands of site 1. In addition to station S1, station S4 at very low concentrations of mercury and lead.

Table 2. Levels of trace elements studied in the sediments.

	Al (mg/Kg)	As (mg/Kg)	Ca (mg/Kg)	Cd (mg/Kg)	Cr (mg/Kg)	Hg (mg/Kg)	Mg (mg/Kg)	Ni (mg/Kg)	Pb (mg/Kg)	Zn (mg/Kg)
SITE 1	5941.02	0.55	4429.51	0.06	4.86	0.29	76.2	8.85	0.64	566.01
SITE 2	6418.78	5.05	4696.54	0.01	17.56	1.70	85.58	18.5	1.14	569.15
SITE 3	6944.46	2.35	3625.43	0.17	11.81	1.97	655.42	5.94	1.74	122.74
SITE 4	6976.11	2.12	4725.3	0.03	16.54	0.37	78.66	19.29	0.58	571.86

4.3. Study of the Correlation Between the Studied Parameters

This matrix highlights important associations between the parameters object of our study. Thus, we have correlations between the physicochemical parameters of the soil, in particular the pH and Eh, and the trace elements studied.

As/Eh,
Cd/Eh, Cd/pH, Cd/%MO,
Pb/Eh,
Hg/Eh,

Mg/Eh

In addition, there are associations between the metallic trace elements studied, in particular between:

Al/Cr, Al/Mg
Mg/Pb
As/Cr, As/Hg, As/Ni
Ca/Ni, Ca/Zn
Cd/Hg, Cd/Mg, Cd/Pb
Cr/Ni
Hg/Pb

Table 3. Correlation matrix between the different parameters studied.

	Al	As	Ca	Cd	Cr	Hg	Mg	Ni	Pb	Zn	Eh	%MO	pH
Al	1	0.23	-0.29	0.35	0.64	0.35	0.51	0.17	0.39	-0.50	0.21	-0.28	-0.13
As		1	0.24	-0.33	0.81	0.66	-0.05	0.58	0.37	0.06	0.61	-0.82	-0.95
Ca			1	-0.99	0.35	-0.56	-0.96	0.87	-0.81	0.97	-0.59	-0.67	-0.54
Cd				1	-0.37	0.47	0.95	-0.86	0.75	-0.96	0.50	0.71	0.61
Cr					1	0.37	-0.09	0.76	0.13	0.11	0.24	-0.91	-0.84
Hg						1	0.68	-0.23	0.94	-0.67	0.99	-0.16	-0.39
Mg							1	-0.70	0.89	-0.99	0.68	0.46	0.35
Ni								1	-0.51	0.72	-0.33	-0.92	-0.77
Pb									1	-0.88	0.94	0.16	-0.05
Zn										1	-0.67	-0.48	-0.36
Eh											1	-0.06	-0.32
%MO												1	0.94
pH													1

4.4. Principal Component Analysis

The Principal Component Analysis performed resulted in a circle of correlation. The factor extraction was performed by the principal components method. Two factors whose eigenvalues are greater than 1 were retained according to the criterion of Kaiser [15]. They correspond to 90.11% of the total variance. Factor F1 is the most important with an expressed variance of 59.40%. The factor F2 has a variance of 30.70%.

Table 4. Eigenvalues and percentage of cumulative expressed variance.

	Own values	% total variance Expressed	Cumulation of eigenvalues	Cumulative %
F1	5.941	59.41	5.941	59.41
F2	3.07	30.71	9.01	90.12
F3	0.988	9.88	10.00	100.00

Table 5. Coordinates of the different variables.

	F1	F2
Al	-0.40	-0.59
As	0.07	-0.92
Ca	0.98	-0.18
Cd	-0.96	0.22
Cr	0.19	-0.96
Hg	-0.69	-0.61
Mg	-0.99	-0.08
Ni	0.78	-0.61
Pb	-0.90	-0.37
Zn	0.99	0.06
Eh	0.70	0.50
%MO	0.53	-0.85
pH	0.40	-0.86

Table 4 gives us the eigenvalues and percentages of variance of the various factors.

In Table 5, the coordinates of the various physicochemical

parameters studied as a function of each factor (main component) F1 and F2. Thus, factor F1 is in association with calcium, nickel, zinc, redox potential and percentage of organic matter. As for the factor F2, it is only in association with the redox potential.

The figure below gives us the projection of the variables in the factorial plane (F1, F2). From this figure, we can see two groups of parameters. The first group contains in particular As, Cr, Ni, % MO and pH. In the second group we have Cd, Mg, Pb and Hg.

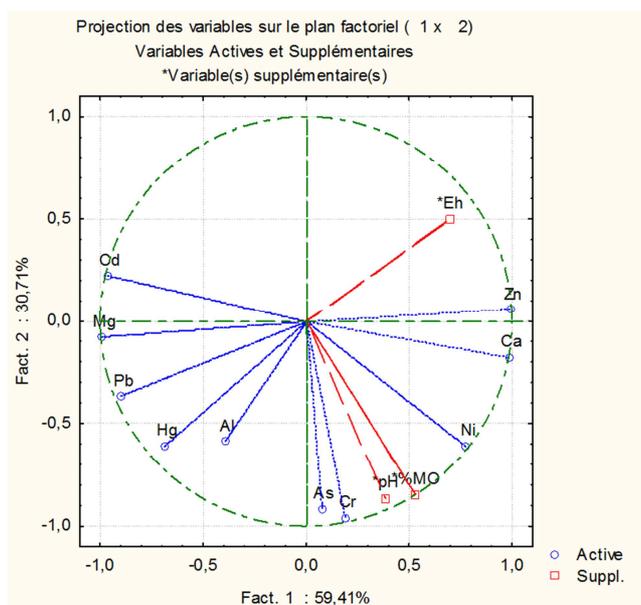


Figure 2. Principal component analysis in the factorial plane F1 - F2.

5. Discussion

The study showed that the trace elements studied are present in the various lowlands of the study area. However, the concentrations determined are all lower than those obtained for these TMEs during the evaluation of the metal pollution of the Hiré gold prospect [16]. This could be due to the particular mining character of the sub-prefecture of Hiré.

In addition, our study has shown that the levels of arsenic, cadmium, chromium and lead obtained in the sediments are all lower than the various established WHO standards which are respectively 40; 1.4; 64 and 50mg / L for arsenic, cadmium, chromium and lead. On the other hand, the levels determined for mercury (site 2 and 3) and zinc (site 1, 2 and 4) are higher than the various WHO standards which are for mercury and zinc respectively 0.5 and 300 mg / L. This could cause risks of metallic bioaccumulation in the vegetable crops cultivated in these lowlands and thus contaminate the population of the city of Duékoué who consume these products.

The acidic nature of the sediments at site 2 shows that we have peaty soils rich in organic matter [17]. When the soil is cultivated continuously, it quickly leads to acidification, due to the decomposition of organic matter in the soil by the effect of microbial activity and the respiration of the roots [17]. In addition, a correlation was noted between pH and percentage

organic matter. This suggests that the acidity of the environment has an influence on the substances that constitute organic matter and consequently the mobility of TMEs which are linked to it, in particular cadmium and magnesium.

The behavior of cadmium in soil is strongly controlled by pH [18]. The sediments of Site 2 which are in acidic conditions, their solubilities will increase and a slight adsorption of cadmium by organic matter. This justifies its association with organic matter. In addition, the correlations observed between Cd / pH, Cd / Eh suggest that the free forms Cd^{2+} , $CdCO_3$ (c), CdS (c) in the sediments of the various sites studied [18].

Arsines and arsenates are believed to be present in the sediments of the study area. Indeed, according to Burnol [18], arsenic exists mainly in the trivalent, arsenite As (III) or pentavalent, arsenate As (V) form in soils.

The distribution of mercury species in soils, elemental mercury (Hg^0), mercury ions (Hg_2^{2+}) and mercury ions (Hg^{2+}) depends on soil pH and redox potential. Mercury mercury and mercury mercury are adsorbed by clay minerals, oxides and organic matter. The adsorption of this TME therefore depends on the pH and increases with increasing pH [19].

The results of our study showed an association between Hg / Mg, which shows that a significant fraction of mercury is adsorbed by oxides, especially magnesium oxides. In alkaline soils (S_1 , S_3), mercury mercury precipitates with carbonates and hydroxides to form a stable secondary solid phase [20].

Nickel does not generally form insoluble precipitates in soils and the retention of Ni is therefore controlled by the mechanisms of secondary solid phase precipitation and adsorption. Nickel adsorbs to clays, oxides of iron and manganese, and to organic matter. The formation of complexes of Ni with organic and inorganic ligands increases the mobility of nickel in soils.

Although nickel is not an element sensitive to redox conditions, which justifies its non-association with Eh. However, under reducing conditions, the formation of stable aqueous sulfides and solid nickel sulfides cannot be ruled out. Thus, the formation of solid sulphide phases in equilibrium with aqueous sulphide species occurs in reducing environments although the formation of this solid phase is limited by the presence of sulphate-reducing bacteria, capable of degrading sulphates in water. underground.

Lead exists in two valence states: +2 and +4. Due to its basic character, this element hydrolyzes only at neutral or alkaline pHs [18]. Therefore, it will have the hydrolyzed species of lead ($Pb(OH)_2$, $Pb(OH)_4^{2-}$, $Pb(OH)_3^-$ in sites 1 and 3.

Zinc is easily adsorbed by clay minerals, carbonates or hydroxides. [21, 22] have shown that the greater proportion of zinc in contaminated soils and sediments is associated with oxides of iron and manganese.

Although zinc is not an element sensitive to variations in redox potential, in reducing media, the formation of sulphides in the aqueous phase or in the solid phase is the process controlling the availability of this metal in the environment.

From factor analysis, we have the factor F2 which is associated with Eh. This factor therefore reflects the

physicochemical conditions of the studied soils, in particular the oxyo-reducing conditions.

The factor F1, for its part, highlights the geochemical characteristics specific to the sediments studied, in particular an argillaceous fraction composed of calcium carbonates.

Factor analysis shows that the group consisting of Hg, Pb, Mg, Cd highlights common sources of pollution of these trace elements. We can cite among others wastewater from households and runoff. The second reflects the mobility of arsenic and chromium. Indeed, it shows that these metallic trace elements are linked to the organic fraction of the soil. However, the pH is an important factor in the mechanisms that govern their behavior, in particular their speciations and their mobility.

6. Conclusion

The present study made it possible to study the behavior of metallic trace elements in the sediments of four lowlands of the town of Duekoué. For this reason we determined the physico-chemical parameters and the contents of the ETM in the sediments of the sampled soils. In addition, it has shown that the levels of arsenic, cadmium, chromium and lead obtained in the sediments are all below the various WHO standards established. On the other hand, the levels determined for mercury (site 2 and 3) and Zinc (site 1, 2 and 4) are higher than the various WHO standards which are for mercury and Zinc respectively 0.5 and 300 mg / L. This could cause risks of metallic bioaccumulation in market gardening cultivated in these lowlands and thus contaminate the population of the town of Duekoué who consumes these products. Also, the analysis of the samples taken revealed the presence of TMEs, in particular mercury, lead, magnesium and cadmium in the clay fraction of the sediments. Arsenic and chromium are related to the organic fraction of sediments.

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