Study of the Mobility of Some Metallic Trace Elements (MTEs) of Certain Lowlands of the City of Daloa (Côte d’Ivoire)

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Abstract: Metallic Trace Elements (ETM) are naturally transported to the shallows by runoff. As the lowlands are exploited for market gardening, ETM can be found in the products of these crops and present risks of contamination for the populations. It is with this in mind that we decided to study the mobility of metallic trace elements in the soils of the market garden lowlands of the city of Daloa. To achieve this goal, nine (9) soil samples were taken from 3 sites at different depths (0 - 15 cm, 15 to 30 cm and more than 30 cm). The determination of the water pH and of the organic fraction of the sediments were carried out according to ISO 10390 and NF ISO 10694 standards respectively. The ETM contents were obtained by an Atomic Absorption Spectrometer (AAS). The results obtained showed that the majority of the sediments studied are acidic. In addition, they contain a more or less large organic fraction of between 10 and 50%. In addition, our studies demonstrated a mobility of certain ETMs, in particular As, Cr, Hg and Zn, depending on the different sediment profiles studied. Also, Cd, Cr, Mg, Ni, Pb are linked to organic matter and to the clay fraction of the sediments. However, their mobility would be influenced by pH.

Keywords: Mobility, Metallic Trace Elements Organic Matter, Sediments, Lowlands, Vegetable Crops

1. Introduction

Since the end of the 20th century, Africa has experienced rapid population growth and urbanization. As food needs are growing, the rural world is no longer able to respond effectively to the food issue because of unfavorable bioclimatic conditions, rural exodus and land issues.

Intra-urban agriculture, and in particular market gardening, therefore presents itself as an important alternative to guarantee food security. Its proximity to the city, its accessibility at any time of the year, its responses adapted to the eating habits induced by urbanization and the westernization of African populations, make this market gardening the most important value chain favorable to nutrition [1].

In the Ivory Coast, and more particularly in Daloa, the population maintains more or less close relations with the lowlands. They are the subject of numerous hydro-agricultural developments throughout the year as the rice fields succeed market gardening. In addition, the shallows are used for household purposes (laundry, dishes) or for fun (swimming, fishing) [2].

In addition, certain districts of the city of Daloa directly discharge their waste water there, which contains metallic trace elements (MTE) without having previously treated it. Also, MTEs are naturally channeled to the lowlands by
runoff. Once in the soil, metallic trace elements are not very prone to migrations and often accumulate on the surface [3]. They can also change shape or migrate to other constituents of the soil or to the liquid phase depending on the physicochemical conditions. These changes make MTEs more or less mobile in soils and more or less available to the biosphere [4]. In addition, being exploited for market gardening, MTE can be found in the products of these crops and present risks of contamination for the populations.

Hence the object of this study, which is a contribution to the study of the mobility of MTE in the lowlands of the city of Daloa by highlighting factors including pH and organic matter that influence their mobility.

2. Materials and Methods

2.1. Sampling

The soil sampling consisted of taking a systematic sample from each plot using an auger. On each site, we took three samples at different depths for P1 (0 to 15 cm), for P2 (15 to 30 cm) and P3 (> to 30 cm). For each soil horizon.

For each depth, we mixed E1, E2 and E3.

E1: sample from salad cultures;
E2: sample from onion leaf cultures;
E3: sample from cabbage cultures.

Figure 1. Presentation of study sites Units.
2.2. Statistical Analysis

In our study, we carried out a principal component analysis (PCA), with a view to highlighting the relationships between variables on the one hand, the distribution of individuals taking into account all of their physicochemical characteristics (Belghiti, 2013) and to determine the possible vectors of pollution. PCA is a technique for representing data under certain algebraic and geometric criteria, its objective is to extract most of the information contained in the data tables and to provide a graphical representation that is easy to interpret given the data correlations. The statistical processing of the data is carried out by the STATISTICA version 7 software.

2.3. pH Determination

The pH was measured using a multimeter. The pH of the soil, or pHwater, 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-water is measured according to the ISO 10390 standard. 10 g of soil are suspended in 25 mL of ultra-pure water, stirred for 1 hour at 150 revolutions per minute on a standard. 10 g of soil are suspended in 25 mL of ultra-pure water, stirred for 1 hour at 150 revolutions per minute on a standard (determination of the loss on ignition of the sediments). The method applied is that of loss on ignition according to standard NF ISO 10694 (2000). It consists in weighing a sample of soil dried beforehand before its total calcination, taking into account all of their physicochemical characteristics (Belghiti, 2013) and to determine the possible vectors of pollution. PCA is a technique for representing data and to provide a graphical representation that is easy to extract most of the information contained in the data tables. 2.4. Organic Material

The organic matter content is evaluated by the loss of mass (m1) of 1 g of the dry sample after heating to 525°C (determination of the loss on ignition of the sediments). The percentages of organic matter obtained for the different sites 1, 2 and 3 vary respectively from 13.18 to 41.87%, from 1 to 45.05% and from 5.72 to 26.79% in site S1, the percentage is greater for profiles greater than 50 cm (P3 (41.87%)). Contrary to this, the basfond 2 (S2), with a more considerable organic fraction (P1 (45.05%)) for the surface profiles between 0 and 15 cm. The percentage of organic matter in the S3 site is substantially equal for the surface profiles (P1 (26.79%)) and greater than 50 cm (P3 (25.65%)).

In addition, the results of our study show that the trace elements studied are present in the sediments and in the various profiles. MTEs including aluminum, calcium and zinc are present in considerable quantities. On the other hand, low levels of cadmium, mercury and lead were noted, the contents of which in the various sediment profiles are less than 1 mg/Kg.

2.5. Determination of Trace Elements

Weigh 0.2 g of sediment into the Teflon flasks, add 5 ml of 65% nitric acid then 2 ml of hydrofluoric acid and leave to stand in the hood for 1 hour. Then add 2 ml of hydrogen peroxide (30-33%). Close the vials and place them on a hot plate for 3 hours at 120°C. After this heating time, lower the flasks and add 10 ml of 4% boric acid, close and heat for a further 1 hour. Let the vials cool under the hood. After cooling, put 10 ml of 4% boric acid in the 50 ml FALCON tubes and transfer the contents of the Teflon vials into them and make up the volume to 50 ml with distilled water. Make a blank under the same conditions but not containing a sample. The mineralized (liquid) thus obtained are ready to be injected into the device (AAS). Thus, aluminum, magnesium, calcium and zinc were determined by the flame method, lead, cadmium, arsenic, chromium and nickel by the furnace method and mercury by the hydride method.

3. Results and Discussion

3.1. Results

3.1.1. Physicochemical Parameters in Sediments

Table 1 gives the pH values measured for the different soil horizons of the three sites studied. We retain that this varies from 5.71 to 7.58 for the low bottom 1, from 5.70 to 6.88 for the low bottom 2 and from 6.63 to 7.04 for the site 3.

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Table 1. Physicochemical parameters in the lowlands of vegetable crops.

| Stations | pH     | %MO     | MTE Concentrations (mg/Kg) |
|----------|--------|---------|---------------------------|
|          |        |         | Al  | As  | Ca  | Cd  | Cr  | Hg  | Mg  | Ni  | Pb  | Zn  |
| shallows 1 |       |         |     |     |     |     |     |     |     |     |     |     |
| P1       | 5.78   | 13.18   | 12279.0 | 3.10 | 5008.1 | 0.33 | 16.43 | 0.16 | 185.8 | 21.86 | 0.61 | 499.15 |
| P2       | 5.71   | 15.94   | 12935.7 | 11.33 | 5432.3 | 0.47 | 20.91 | 1.34 | 198.8 | 22.08 | 0.79 | 601.7 |
| P3       | 7.37   | 41.87   | 11894.9 | 9.25 | 4928.6 | 0.15 | 24.90 | 1.04 | 98.66 | 9.32 | 0.59 | 570.1 |
| P1       | 5.37   | 45.05   | 11225.2 | 4.77 | 5482.8 | 0.59 | 25.09 | 0.21 | 324.63 | 22.77 | 0.57 | 83873 |
| shallows 2 |       |         |     |     |     |     |     |     |     |     |     |     |
| P2       | 6.88   | 1      | 9664.23 | 1.81 | 4994.22 | 0.30 | 18.84 | 0.15 | 283.20 | 19.14 | 0.68 | 596.5 |
| P1       | 5.94   | 5.62   | 8653.34 | 11.15 | 4922.73 | 0.25 | 20.76 | 0.31 | 172.71 | 19.77 | 0.59 | 550.65 |
| P1       | 6.71   | 26.79   | 7682.39 | 5.45 | 4991.85 | 0.28 | 23.11 | 0.51 | 143.70 | 23.85 | 0.56 | 588.71 |
| shallows 3 |       |         |     |     |     |     |     |     |     |     |     |     |
| P2       | 6.63   | 5.72   | 8723.85 | 1.82 | 4805.85 | 0.17 | 24.94 | 1.02 | 119.19 | 26.77 | 0.57 | 611.97 |
| P3       | 7.04   | 25.65   | 8055.68 | 3.09 | 4979.55 | 0.27 | 27.95 | 0.46 | 189.30 | 15.75 | 0.65 | 683.73 |
Table 2. Correlation between the parameters studied in the lowland 1.

|       | PR   | pH   | Al   | As   | Ca   | Cd   | Cr   | Hg   | Mg   | Ni   | Pb   | Zn   | %MO  |
|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| PR   | -0.80 | -0.36 | 0.72 | -0.15 | -0.53 | 0.99 | 0.72 | -0.80 | -0.86 | -0.09 | 0.68 | 0.91 |      |
| pH   | 1    | 0.85 | -0.16 | 0.71 | 0.93 | -0.78 | -0.16 | 1    | 0.99 | 0.67 | -0.10 | -0.97 |      |
| Al   | 1    | 0.38 | 0.97 | 0.98 | -0.33 | 0.39 | 0.85 | 0.79 | 0.96 | 0.44 | -0.72 |      |      |
| As   | 1    | 0.58 | 0.21 | 0.74 | 0.99 | -0.16 | -0.26 | 0.63 | 0.99 | 0.36 |      |      |      |
| Ca   | 1    | -0.92 | 0.58 | 0.71 | 0.63 | 0.99 | 0.63 |      |      |      |      |      |      |
| Cd   | 1    | -0.50 | -0.21 | 0.93 | 0.89 | 0.89 | 0.26 |      |      |      |      |      |      |
| Cr   | 1    | 0.74 | -0.78 | -0.84 | -0.06 | 0.69 | 0.89 |      |      |      |      |      |      |
| Hg   | 1    | -0.16 | -0.26 | 0.628 | 0.99 | 0.36 |      |      |      |      |      |      |      |
| Mg   | 1    | 0.99 | 0.67 | -0.10 | -0.98 |      |      |      |      |      |      |      |      |
| Ni   | 0.64 | 0.77 | 0.77 | 0.97 |      |      |      |      |      |      |      |      |      |
| Pb   | -0.13 | 0.99 |      |      |      |      |      |      |      |      |      |      |      |
| Zn   |      |      |      |      |      |      |      |      |      |      |      |      |      |
| %MO  |      |      |      |      |      |      |      |      |      |      |      |      |      |

3.1.2. Factor Analysis in the Lowlands 1

The factor extraction was performed by the principal component method. Two factors whose eigenvalues are greater than 1 were retained according to the criterion of KAISER [5]. They correspond to 100% of the total variance. The factor $F_1$ is the most important with an expressed variance of 78.48% and the factor $F_2$ with a variance of 21.52% (Table 3).

Table 3. Eigenvalues and percentage of cumulative expressed variance for the lowland 1.

|       | Own values | % total variance expressed | Cumulation of eigenvalues | Cumulative % |
|-------|------------|---------------------------|--------------------------|--------------|
| F_1   | 6.39       | 63.89                     | 6.39                     | 63.89        |
| F_2   | 3.61       | 36.11                     | 10.00                    | 100.00       |

Table 4. Coordinates of the various factors in the lowland 1.

|       | F_1 | F_2 |
|-------|-----|-----|
| PR    | 0.82 | -0.57 |
| pH    | -0.99 | -0.04 |
| Al    | -0.83 | -0.56 |
| As    | 0.19 | -0.98 |
| Ca    | -0.69 | -0.73 |
| Cd    | -0.92 | -0.39 |
| Cr    | 0.80 | -0.60 |
| Hg    | 0.19 | -0.98 |
| Mg    | -0.99 | -0.04 |
| Ni    | -0.99 | 0.07 |
| Pb    | 0.64 | 0.77 |
| Zn    | -0.13 | 0.99 |
| %MO   | -0.99 | 0.17 |

However, the variation in depth (PR) is opposed to this group.

The factorial weights of the variables (Table 4) reflect their correlations with the extracted factors. The first factor $F_1$ contains the PR depth, chromium (Cr), and lead (Pb). The second factor is in association with lead (Pb) and zinc (Zn).

The projection of the variables in the factorial plane ($F_1$-$F_2$) highlights a single group of parameters which notably contains %MO, Ni, pH, Mg, As, Cd, Al and Ca (Figure 2).

Table 5. Correlation between the parameters studied in the lowland 2.

|       | pH | %MO | Hg | Pb | Cd | As | Cr | Ni | Ca | Mg | Al | Zn | PR |
|-------|----|-----|----|----|----|----|----|----|----|----|----|----|----|
| pH    | 1  | 0.5 | -0.39 | 0.23 | 0.24 | 0.83 | 0.63 | 0.51 | 0.36 | -0.39 | -0.39 | 0.23 | 0.14 |
| %MO   | 1  | 1   | 0.64 | 0.97 | 0.97 | -0.11 | 0.97 | 0.99 | 0.99 | 0.64 | 0.64 | 0.97 | -0.81 |
| Hg    | 1  | 0.80 | 0.80 | -0.83 | 0.47 | 0.58 | 0.71 | 0.99 | 0.99 | 0.81 | 0.81 | 0.11 | -0.93 |
| Pb    | 1  | 0.99 | -0.35 | 0.89 | 0.95 | 0.98 | 0.81 | 0.81 | 1   | 0   | 0   | 0   | -0.92 |
| Cd    | 1  | -0.34 | 0.90 | 0.95 | 0.90 | 0.80 | 0.80 | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 | -0.81 |
| As    | 1  | 0.10 | -0.04 | -0.21 | -0.83 | -0.83 | -0.34 | 0.67 |      |      |      |      |      |
| Cr    | 1  | 0.99 | 0.95 | 0.47 | 0.47 | 0.89 | 0.89 | 0.89 | 0.89 | 0.89 | 0.89 | 0.89 | 0.89 |
| Ni    | 1  | 0.98 | 0.58 | 0.58 | 0.95 | 0.95 | 0.95 | 0.95 | 0.95 | 0.95 | 0.95 | 0.95 | 0.95 |
| Ca    | 1  | 0.71 | 0.71 | 0.98 | 0.98 | 0.86 | 0.86 | 0.86 | 0.86 | 0.86 | 0.86 | 0.86 | 0.86 |
| Mg    | 1  | 0.8  | 0.8  | 0.8  | 0.8  | 0.8  | 0.8  | 0.8  | 0.8  | 0.8  | 0.8  | 0.8  | 0.8  |

![Figure 2. Principal component analysis of lowland sediments 1 in the factorial plane $F_1$-$F_2$.](image-url)
Table 6. Eigenvalues and cumulative expressed percentage variance for lowland sediments 2.

|        | Own values | % total variance expressed | Cumulation of eigenvalues | Cumulative% |
|--------|------------|----------------------------|---------------------------|-------------|
| F₁     | 7.11       | 71.11                      | 7.1                       | 71.11       |
| F₂     | 2.89       | 28.89                      | 10.00                     | 100.00      |

Table 7. Coordinates of the various factors in the lowland 2.

|        | F₁     | F₂     |
|--------|--------|--------|
| pH     | -0.23  | -0.97  |
| %MO    | -0.97  | 0.24   |
| Hg     | -0.80  | 0.59   |
| Pb     | -0.99  | 0.01   |
| Cd     | -0.99  | -0.01  |
| As     | 0.34   | -0.94  |
| Cr     | -0.90  | -0.43  |
| Ni     | -0.95  | -0.30  |
| Ca     | -0.98  | -0.14  |
| Mg     | -0.80  | 0.59   |
| Al     | 0.80   | -0.59  |
| Zn     | 0.99   | -0.01  |
| PR     | -0.92  | 0.37   |

Figure 3. Principal component analysis of lowland sediments 2 in the factorial plane F₁ - F₂.

The projection of the variables in the factorial plane (F₁-F₂) highlights a single group of parameters which notably contains Mg, PR, Pb, Cd, Ni, Cr, %MO, Ca, Hg.

Table 8. Eigenvalues and percentage of cumulative expressed variance for the sediments of the Lowland 3.

|        | Own values | % total variance expressed | Cumulation of eigenvalues | Cumulative% |
|--------|------------|----------------------------|---------------------------|-------------|
| F₁     | 6.93       | 69.30                      | 6.93                      | 69.30       |
| F₂     | 3.07       | 30.70                      | 10.000000                 | 100.00      |

Figure 4. Principal component analysis of lowland sediments 3 in the factorial plane F₁ - F₂.

The projection of the variables in the factorial plane (F₁-F₂) reveals three groups of parameters. The first group contains %MO, Al, As, Cd, PR and the second pH, Pb, Mg, Cr.

3.1.3. Study of the Mobility of Metals in the Lowlands 3

From the study of the correlation, we note an association between organic matter and Chromium. Also, there is an association between pH and Aluminum, Calcium, Cadmium, Nickel and Lead. Interestingly, there is a positive and significant correlation between Arsenic and Chromium with depth. We see that Aluminum and Calcium are correlated...
with the same elements which are Cadmium and Lead.

3.2. Discussion

The soil pH is a very influential parameter, which plays a major role in many physicochemical reactions such as precipitation/solubilization reactions or adsorption/desorption on the solid phases of the soil and the speciation of metals in aqueous solution. Our study has shown that the sediments from the different sites have a pH that varies between 5 and 8. These different pH values obtained will have a notable influence on the solubility or even the mobility of certain MTEs studied during our study. Indeed, the solubility of chemically stable elements in the form of cations such as Cd, Pb and Zn decreases when the pH increases. Conversely for chemically stable elements in the form of anions such as Cr (VI), As and Se, solubility increases with pH [6]. In lowlands 1, 2 and 3, the strong correlations observed at the level of pH values and metallic trace elements testify to the fact that the pH of the soil has a very strong influence on the soil's capacity to retain metals, but also to release them. Lowering the pH would therefore have favored the mobility of metals. These results are in agreement with those obtained by Kouassi in the soil of the Akouédo landfill (Abidjan) [7].

In addition, no correlations were noted between the pH and the percentage of organic matter in lowlands 2 and 3 (Table 7 and 8). For all the organic constituents, two groups are generally recognized as being the most reactive: humic substances (HS): humic acids, fulvic acids and humin [8]. and organic acids of low molecular masses [9, 10]. From the results of our study, we will have a solubility of the fraction of humic acids in the different sediments. On the other hand, fulvic acids are soluble in the shallow sediments 3 and those obtained at a depth greater than 50 cm.

In addition, during our study, we note the presence of MTEs studied in the various sediments at varying concentrations. Also, the statistical processing of different data including their correlations allows us to make several observations.

In lowland sediments 3, in addition to the correlation between the pH and %MO, we note associations between it and the arsenic As, Cd, Hg. This suggests that the acidity of the medium at a notable influence on the reactivity of the substances which constitute the organic matter by consequence the mobility of the MTE which are bound to this one in particular arsenic, cadmium and mercury. Cd preferentially accumulates in horizons rich in organic matter [11] and can migrate with the organo metallic complex. In addition, we have noted associations between pH and calcium, which is one of the constituents of calcium carbonate. However, this is involved in the fixation of metallic trace elements, either by adsorption or by precipitation of hydroxides or carbonates or even by insertion into the CaCO$_3$ network [12]. In addition, we have associations between calcium, cadmium and mercury. It could be deduced from this that these trace elements would be linked to carbonates and the pH would influence their various reactions with them.

In the sediments of the lowland 2, we have the same information as those of the lowland1. However, organic matter is associated with most of the trace elements studied. These elements are either linked to the organic matter or incorporated into it. In addition, the associations observed between calcium, aluminum, magnesium, mercury and lead suggest the presence of an argillaceous fraction in lowland sediments 2 composed of carbonates bound to these MTEs either by adsorption by precipitation or incorporated therein.

Site 1, on the other hand, does not show an association between pH and organic matter. However, we note correlations between pH and aluminum and calcium which are the building blocks of the clay fraction of the soil. Also, they are associated with cadmium, magnesium, nickel, lead, mercury and lead. This suggests that these MTEs are not only linked to the clay fraction of the soil but the physicochemical parameters of the soil, in particular the pH, govern their mobility.

A pH greater than 5 and a soil with an organic matter content of at least 5% favor the accumulation of metals [13]. In this case, oxidation state II lead, which exists in a given environment, is slowly incorporated into clay minerals and organic matter [14].

In the soil, the concentration of MTE varies with depth. Microelements from external inputs will accumulate on the surface. Their concentration will therefore decrease with depth and, in cultivated soils, mark a clear discontinuity above the cultivated layer [15]. We observed this discontinuity in the MTE contents in the sediments of the various sites studied. Indeed, the study of the correlation showed that only Arsenic and Chromium are in association with the variation of the depth in the shallows 2 and 3. However in the sediments of the shallows, Arsenic, Chromium, Mercury and Zinc correlate with soil depth.

Factor analysis

The projection of the various parameters studied in the factorial plane $F_1$-$F_2$ for the sediments of the various sites made it possible to highlight a single group of parameters which contains % MO, Ni, pH, Cd, Al and Mg. This demonstrates that nickel, cadmium, and magnesium are not only linked to the clayey and organic fraction of the sediments, but their mobility is influenced by the pH. In addition, the factor $F_1$ expresses the vertical dynamics of the MTEs of Cr and Pb.

In site 2, factors $F_1$ and $F_2$ respectively demonstrate the clayey and organic fraction of the sediments. Indeed, $F_1$ and $F_2$ are respectively associated and aluminum Al with magnesium which is a constituent element of the clay and organic fraction of the sediments.

The projection in the $F_1$-$F_2$ plane highlights a single class. This class contains organic matter and aluminum. Therefore, the trace elements of this group including cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb) are bound to organic matter and to the clay fraction of the sediments.

Factorial analysis of data obtained for lowland 3 reveals two distinct classes. The first class which contains the percentage of organic matter, depth, aluminum, arsenic and
cadmium. This class reflects a vertical dynamism of MTEs in the profiles. In addition, they could be fixed by organic matter through complexation reactions.

The second class shows that the mobility of chromium, magnesium, and lead is influenced by pH.

4. Conclusion

At the end of this study, we note that the majority of the sediments studied are acidic with a more or less important organic fraction in the different sediment profiles. In addition, the trace metal elements studied including aluminum, arsenic, calcium, chromium, mercury, magnesium, nickel, lead and zinc are present in these lowlands of vegetable crops. Consequently, there are risks of metallic bioaccumulation of its MTEs in market garden products that can cause health risks to the populations who consume its products.

In addition, our study showed Arsenic, Chromium, Mercury and Zinc have a mobility function of different sediment profiles influenced in particular by pH. In addition, it is noted that Cd, Cr, Mg, Ni, Pb are linked to organic matter and to the clay fraction of the sediments. However, their mobility would be influenced by pH.

To deepen our research, we would like to study the influence of other physicochemical parameters such as redox potential, particle size, CEC, CEA on the mobility of ETM in soils. Also study the bioavailability of ETMs in plants in order to assess their health risks on populations.

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