Speciation of Arsenic, Cadmium, Chrome and Lead in Gold Mining Environment (Côte d’Ivoire): Effect of pH and Redox Potential

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Abstract: To evaluate the different chemical forms of arsenic, cadmium, chromium and lead present in a mining environment, we determined the levels of metals in different compartments water-sediment by ICP-AES method, measured pH and redox potential of these different compartments. From these results, we note the presence of bioavailable forms of arsenic cadmium and lead in stations where agricultural exploitations at high contents are practiced and the groundwater stations (water consumption). It’s feared the risk of metal poisoning of the population live in our study area.

Keywords: Pollution, metallic, speciation, bioavailable, Côte d’Ivoire

1. Introduction

Metallic pollution is one of the environmental problems in the gold exploitation. In Côte d’Ivoire, the metallic contamination of ecosystems attracted the attention of many researchers [1, 2, 3]. In fact, the metallic contaminants accumulation in aquatic organisms points out the toxicological effects on species, ecosystems and sanitary risks through edible ingestion species [4]. In the environmental systems like soils and water, heavy metals can appear in many various chemical forms: free ones; mixed ones with a “simple” ligand, organic or inorganic; mixed ones with a colloidal or macromolecular ligand, adsorbed or blended into suspended particles, adsorbed or assimilated by a living organism [4]. Metals toxicity don’t depend only upon the concentration, but also upon the species [5]. Indeed, the total grade of an element just gives only a global indication of pollution rate, but this doesn’t permit to check the toxicity risk related to the element [6]. The development of this element, its transfer as well as its bioavailability and its toxicity in the environment are conditional upon the speciation [7]. The study of metals speciation is the identification task and that of the quantity measurement of one or several species in a sample [8, 9].

Thus, it permits to reduce the uncertainty about the bioavailability, that is the exposure, and therefore, to improve the actions of preventions and of risks management. This speciation analysis must take into account the characteristics related to metals or, the physicochemical features of the environment (pH, redox potential (Eh), Salinity and Cationic Exchange Capacity (CEC) [10].

PH and redox potential are the factors that really determine the action about the mobility and the speciation of metals [11, 12, 13, 14]. Moreover, the oxido reducing conditions of soils and water influence the pH. In fact, the reducing features generally tend to increase the pH while the oxidizing ones reduce it [14].

The speciation of elements in metallic traces will greatly be influenced by both effects of the pH and the redox potential (Eh) [13]. This research aims at studying the metals speciation, that is, arsenic (As), cadmium (Cd), chrome (Cr), and lead (Pb) in a mining environment in order to better evaluate their toxicity. To reach this goal, we determined the concentration of these trace elements in water compartment and sediments of different stations. The pH and the redox potential of different compartments have been measured. We also determined the different chemical forms under which metals appear in different compartments.
2. Method

2.1 Study area

Study area is located between latitude 06°15’08.6 and 06°10’ North and 05°23’44.8 and 05°16’32.1 longitude West (Figure 1).

Climate is equatorial with an average rainfall estimated at about 1200 mm. Pedology study shows many soils profiles: plinthosol; ferrasoil and geysoil [15]. All these soils result from a long and intense alteration, with a clayey part essentially composed with kaolinite [15].

2.2 Sampling design

Samplings have been occurred during two campaigns, in August and October 2013. August is the rainy season and October, is the dry season. Our objective here is to point out the temporal species aspect of metals. Water samples were cut off in seventeen (17) stations marked Pn, (n is the number of the station) (Figure 1). Moreover, sediments samples were collected in eight (8) stations marked Sm (m is the station number). The choice of different stations results from a compromise between the possibilities to reach there and the abilities to report metallic pollution of water. P1, P2, P8, P9, P10, P11, P12, P13, P15 and P16 are stations where water samples were collected. P1, P2, P9 and P16 are water samples from wells and P8, P10, P11, P12, P13, P15 and P17 are water samples from village pump water. P3, P4, P6 and P14 are stations where surface water samples were collected. These stations are located in the shallows where agriculture is practiced through rice and farming market cultures (okra, lettuce or salad vegetable, cabbages …). P3 and P4 are located in Hiré. P6 is close to gold panning sites, whereas P14 is at least one kilometer from the gold mining site of Bonikro. P14 could receive effluents from the park of the mine rocks scraps. P5 is a liquid effluent from gold panning sites which flows into the stations P6. P7 and P8 are located in the areas where gold panning water is thrown.

The sediments of stations S3, S4, S7, S8, S10 and S12 were cut off in the same waterspout as respectively stations tides P3, P8, P5, P7 and P14. It is important to notice that S3, S4, S7 and S12 are located in agricultural exploitations. SB and SB1 are stations where we cut off sediments samples only. These stations are mining effluents accumulation area.

2.3 Measurement of physical parameters

In both sites, temperature, pH and redox potential, of water samples are measured in situ with a multimeter HACH HQ 40 d. Water pH, and the redox potential (Eh), deposits are determined at the laboratory.

2.3.1 Determination of the water pH and the redox potential (Eh)

We used a multimeter HACH HQ 40 d to measure the redox potential (Eh) and the neat or active acidity (water pH) after mixing up 20 g of dried soil at 40°C with 50ml of distilled water during 2 hours [16].

2.3.2 Determination of the pHKCl

The acidity reserve also called the pHKCl was measured with a multimeter HACH HQ 40 d after mixing up 20 g of dried soil at 40°C with 50 ml of KCl solution during a period which varies from 2 hours to 24 hours.

We also cut off some water samples by means of plastic bottles of 1L filled to the brim and rinsed beforehand with water of the station. These samples were turned sour in the field with nitric acid (HNO3), conserved at 4°C for metals analysis (arsenic, cadmium, chrome, nickel and lead) to the laboratory. We cut off the sediments intended to analysis in the same waterspout like the surface waters. These samples were collected with plastic sacks.

2.3.3 Measurement of Chemical parameters

Water samples that have to be analyzed were already filtered through a GFC Wattman filter of 0, 45µm diameter. Concerning sediments samples, they were dried in the oven during 2 days at 80°C, ground in a mortar and screened through a mesh screen inferior to 100µm. Selected dry
sediment was mineralized at 120°C during 4 hours in 4ml of hydrofluoric acid and a mixture of hydrochloric acid and nitric acid v/v [17, 18]. The solution is allowed to stand for cooling. The concentrations of As, Cd, Cr and Pb in water and sediments were analyzed by the ICP-AES (Inductively Coupled – Plasma / Atomic – Emission – Spectrometry).

3. Results

3.1 Waters compartment

The mean temperature of water in different stations in October (27.5°C) is roughly high to that in August (26.3°C). The pH of studied sites during both campaigns and of most of the stations is lightly acid or basic. However, the acidity of some sites is too high, namely stations P9 (5.78); P11 (5.81); P12 (4.77) and P16 (4.96) in August and P3 (5.91); P8 (5.38); P12 (4.68) and P16 (4.74) in October (Table 1).

<table>
<thead>
<tr>
<th>T° (°C)</th>
<th>pH</th>
<th>Eh (mV)</th>
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</thead>
<tbody>
<tr>
<td>P1</td>
<td>27</td>
<td>28.3</td>
</tr>
<tr>
<td>P2</td>
<td>27.3</td>
<td>27.3</td>
</tr>
<tr>
<td>P3</td>
<td>27.3</td>
<td>24.9</td>
</tr>
<tr>
<td>P4</td>
<td>25.9</td>
<td>27.9</td>
</tr>
<tr>
<td>P5</td>
<td>25.5</td>
<td>27.2</td>
</tr>
<tr>
<td>P6</td>
<td>25.6</td>
<td>28.7</td>
</tr>
<tr>
<td>P7</td>
<td>24.2</td>
<td>30</td>
</tr>
<tr>
<td>P8</td>
<td>24.7</td>
<td>29.5</td>
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<tr>
<td>P9</td>
<td>27.5</td>
<td>28.7</td>
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<tr>
<td>P10</td>
<td>26.3</td>
<td>28</td>
</tr>
<tr>
<td>P11</td>
<td>26.3</td>
<td>27</td>
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<tr>
<td>P12</td>
<td>26.9</td>
<td>28.1</td>
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<td>25.7</td>
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<tr>
<td>P14</td>
<td>25.2</td>
<td>24.8</td>
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<tr>
<td>P15</td>
<td>26.7</td>
<td>28</td>
</tr>
<tr>
<td>P16</td>
<td>27.5</td>
<td>28.9</td>
</tr>
<tr>
<td>P17</td>
<td>27.2</td>
<td>27.9</td>
</tr>
</tbody>
</table>

Moreover, only the pH of station P9 is higher than 8. Then, during the two campaigns, most of water samples don’t change their acido-basic nature and keep their oxido-reduction conditions. Nevertheless, concerning some stations (P2; P5; P7 and P9), |ΔpH| is higher than 0.5 and for the most stations, |ΔEh| is higher than 50 mV (Table 1). On the contrary, water samples of stations P1, P5 and P14 which were in reducing conditions in August turn into oxidizing conditions in October.

We note about the chemical analysis of water samples that arsenic, cadmium, chrome and lead exist in most of the studied sites. However, some parameters (As and Pb) can’t be quantized in certain stations, namely the Lead in the stations P6, P8, P9, P16 and P17 (Figure 2 and 3) in August.

During the 2nd campaign, arsenic concentrations and those of lead respectively in stations P2, P7, P6, P12 and P16 can’t be quantized. Also chrome shows some relatively small concentrations, inferior to 10μg/L, for all stations and during the two campaigns (Figure 4). Arsenic, cadmium and lead with respectively average concentration of 113μg/L; 196μg/L and 74μg/L have a relatively high content in most of stations where they can be quantized. Indeed, during the first campaign, arsenic content in all the stations of underground water (consumption water) is superior to 100μg/L except the station P2 (5μg/L). Furthermore, cadmium contents (≥ 100μg/L) in the underground water were determined in the stations P1, P9, P12, P13, and P16 (Figure2). Only the concentration in the station P10 has a high concentration (>100μg/L) during the 1st campaign. Arsenic and cadmium concentrations are significant in the stations of surface water, with a maximal concentration of arsenic and cadmium respectively for the stations P6 (As 890μg/L) and P7 (Cd 533μg/L) (Figure5).
During the 2nd campaign, we notice a significant decrease of concentrations of arsenic, cadmium and lead in most of the stations of underground water and surface water. Nevertheless, in the stations of surface water P3 and P8, the arsenic content increases as well as the cadmium content in the stations P1, P2, P6, P8 and P7. From our results, we note an increase of the lead concentration during the campaign, apart from stations P3 and P7 (Figure 3).

3.2 Soils compartments

The conditions of some sediments (S3, S4, SB et SB1) change from oxidizing to reducing ones. From the sediments S3, S7, S10 and S12, only S3 remains in reducing conditions while the others remain in oxidizing conditions. Most of the sediments samples keep their acido-basic nature during the two campaigns, except the stations SB and SB1 which become basic after appearing slightly acid. About the sediments, S12 (5.20; 6.58) is the most acidic; S3 (7.71; 7.64) and S4 (7.11; 7.20) are the most basic (Table 2).

Table 2: Measurements results of $pH_{\text{water}}$, $pH_{\text{KCl}}$, Redox potential of sediments (August and October 2013)

<table>
<thead>
<tr>
<th></th>
<th>$pH_{\text{water}}$</th>
<th>$pH_{\text{KCl}}$</th>
<th>Eh (mV)</th>
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<tbody>
<tr>
<td>S3</td>
<td>7.71</td>
<td>7.64</td>
<td>-32.9</td>
</tr>
<tr>
<td>S4</td>
<td>7.11</td>
<td>7.5</td>
<td>6.9</td>
</tr>
<tr>
<td>S7</td>
<td>6.1</td>
<td>6.82</td>
<td>5.84</td>
</tr>
<tr>
<td>S8</td>
<td>6.46</td>
<td>7.34</td>
<td>6.2</td>
</tr>
<tr>
<td>S10</td>
<td>5.96</td>
<td>6.73</td>
<td>4.69</td>
</tr>
<tr>
<td>S12</td>
<td>5.2</td>
<td>6.58</td>
<td>4.4</td>
</tr>
<tr>
<td>SB</td>
<td>6.65</td>
<td>7.81</td>
<td>6.4</td>
</tr>
<tr>
<td>SB1</td>
<td>6.72</td>
<td>7.45</td>
<td>6.5</td>
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<td></td>
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</tr>
</tbody>
</table>

We observe the concentrations in arsenic, cadmium, chrome and lead are noticeable in the different sediments during the 1st campaign. During the 2nd one, this content decrease in cadmium and chrome in most of the stations (Figure 6 and 7).

Moreover, during the 2nd campaign we notice the concentration increase of the arsenic in most stations. Concerning the lead, we see its concentration increase in the stations S4, S7, S12 and Sb while it decreases in the stations S3, S8, S10 and Sb1 (Figure 9).

4. Discussion

4.1 Water compartment

This study pointed out metals could exist in different forms at diverse oxidation degrees in waters. Indeed, during the two campaigns we encountered the following types of Arsenic: $\text{H}_2\text{AsO}_4^-$; $\text{As(OH)}_3$; $\text{AsO}_2^-$. Arsenite $\text{As(III)}$ which is the most toxical appears in a slightly acidic environment to a basic one in a highly reducing conditions. Thus, during the 1st campaign, we could find arsenite in most of...
underground water and surface water stations, apart from water samples in stations P5, P11, P12, P14 and P16 which are acidic and in oxidizing conditions. The oxyanions H2AsO4− could exist in stations P9, P11, P12 and P16. According to [19], Arseniates H2AsO4− and HAsO42− are the species main existing in an aqueous environment in oxidizing conditions. During the 2nd campaign, the changing of physicochemical conditions, namely about, redox potential increase, oxydoreductions conditions, a light variation of the environment pH engenders arsenite oxidation. Thus, H2AsO4− form appears respectively in the stations P1, P5, P14 and P17 where there was arsenite before. Furthermore, we could add that arsenic speciation is linked with bacterial activities. Some bacteria which modify the oxidation status of the Arsenic were highlighted these last years in most of aquatic compartments [20, 21]. So the oxidizing As(III) oxidises As(III) in As(V).

Also, the studies about underground waters done by [22] in Burkina Faso [23] in Argentina showed that these waters were in oxidizing conditions and that the arsenic existed in the form of As(V). Concerning cadmium, the free Cd2+ and the hydrolyzed species Cd(OH)+, Cd(OH)2 are the main species found in waters. The carbonated and sulphated species were characterized by a light contribution. In a gold mining environment where there are a high rate of sulphur batteries minerals such as the pyrite (FeS) [24], some cadmium sulphurated compounds Cd(HS)2 could be found. The analyses of [25] showed that the sulphurous species existing in solution are S2−, HS− and H2S. In fact, the sulfures in waters are not only determining for its aqueous speciation. The sulfur ions which are the reduction products of the sulphures could prevent from the harmful effect of metals by making them precipitate according to the following equation:

\[
Cd^{2+} + 2HS^{-} \rightarrow Cd(HS)_{2}
\]

This phenomenon is called «protection by sulfures» [26]. Thus, these precipitated species, that is the sulphures of cadmium, could exist in most of underground waters stations, except the stations P9 (Cd(7 μg/l)), P12 (Cd(496 μg/l)), P16 (Cd(347 μg/l)) where we could find the free bioavailable cadmium, [5]. The basic pH and the reducer environments could contribute to the formation of cadmium sulfate [25] while the free cadmium could exist in an oxidizing environment. During the 2nd campaign, the passage from reducing conditions to oxidizing ones of underground water stations (consumption water) P1(Cd(434 μg/l)) and surface water stations P9(Cd(421 μg/l)) and P14(Cd(143 μg/l)) could engender the presence of free cadmium in these stations. Besides, this dissolution reaction could provoke an increase of cadmium concentration in these stations.

According to [27], the free cadmium Cd2+ is the main specie existing in waters in oxidizing conditions or when the sulfures formation doesn’t occur in reducing conditions; the carbonated species contribute lightly. We knows about the case of lead that its aqueous chemistry is controlled by carbonated and hydrolysed species. And, we have to indicate the presence of the galena, (PbS), because of the presence of sulfureous minerals.

These complexioned species by the inorganic ligands (OH− and CO32−) [10, 28] could undergo some dissolution reactions to result in free lead (Pb2+). During the 1st campaign the free lead bioavailable exists, in the surface waters stations P1 (24 μg/l), P5 (30 μg/l), P9 (12 μg/l) and P14 (92 μg/l) and in underground waters P10 and P13. We can notice that the pH of these different samples of water is between 5.9 and 7.5. During the 2nd campaign, the changing of physicochemical conditions, is that the passage to the oxidizing conditions the free lead could precipitate in order to result in carbonated species in the station P1, P5, P14 and P17. Moreover, these precipitation reactions could provoke the decreasing of the lead content in surface waters in the stations P9, a non quantized one, and P14 (3 μg/l) [24]. Nevertheless, according to [29], the prevailing specie of lead remains the free Lead (Pb2+), in the presence of carbonated species of lead, with a pH<6.6 and Pb(OH)2 (S) with pH >6.6. Therefore, the appearance of hydroxide lead is noticeable in most of stations, except those of P5, P9, P11, P14 and P16.

For the study of chrome, literature indicates that as an ageneous solution, this substance mainly exists under its trivalent form (CrIII) and its hexavalent one (CrVI). According to [30], the most toxical one that is, the hexavalent form is generally found in the nature under some forms, namely CrO42− ; HCrO4− ; Cr2O72− whose presence depends on pH. Thus, our results show that we could find the form known as HCrO4− in the stations Pb, P12, P16 whose pH is less than 6 and in oxidizing conditions. According [31], this form is found in acidic environment, precisely, in underground water station (consumption water).

Chrome could be found in the other stations under its trivalent form (Cr(OH)3). The pH of these different stations is lightly acidic to basic one in some greatly reducing conditions. However, Cr(OH)3+ and the Cr(OH)4− could be found in neutral and basic environments [31]. Stations P5, P9 and P14 change from conditions to oxidizing ones creating, thus, the oxidizing of the Cr(III) in Cr(V).

4.2 Study of Soil Compartment

The toxicity and the ecotoxicity of metals in the soils are closely linked with the speciation. In the soil, the arsenic mainly exists in a trivalent form, particularly, Arsenite As(III) or pentavalent, arsenite As(V) [27]. However, our results revealed the presence of the As(III), the metallic form of arsenic As(S), and some arsenites, that’s (H2AsO4− ; HAsO42−). During the 1st campaign, apart from the station S3, we could find arsenate in the other stations. This type of arsenic could result in insoluble precipitates with iron, aluminum and calcium by complexation [27, 32]. Let’s note that iron is the most influential substance in the arsenates mobility control [27]. Rarely, arsenic is controlled by solubility; it’s only in a reducing environment that arsenic exists under its metallic form As(S) making it bioavailable. This form of arsenic could be found in the stations S1 during the two campaigns and in stations S3 and Sb during the 2nd campaign. It is important to emphasize that the stations S1 and S4 are where there are some agricultural exploitations.
With cadmium, we can note that this substance is adsorbed at the surface in most of clayey minerals, of carbonates or iron hydroxides or of manganese. Some studies showed that adsorption mechanisms are considered as the most important process of cadmium retention in soils [33, 34]. Thus, during the 1st campaign, cadmium could be precipitated in carbonated species (S3) and sulfurous one. Let’s underline that S3 and S4 are agricultural exploitations. The bioavailable specie Cd²⁺ could exist in the other stations. During the 2nd campaign, the changing of reducing conditions and the environment basicity could favour the precipitation reactions of free cadmium in sulfurous species concerning the stations (S1, SB and SB1). Concerning lead, it is either adsorbed at the clays surface or under carbonate lead form [27, 35]. Our results show during the 1st campaign, we could notice some carbonated species of lead (PbCO₃) exist in most of the sedimentary compartments, except agricultural exploitation station S1 where metallic lead could be found (Pb(S)). Moreover, in October the changing of oxydoreduction conditions, namely the passage to reducing conditions, could create some reduction effects of carbonated composites of lead (PbCO₃). This results in metallic lead (Pb(S)) in the agricultural exploitation station S1 and of the stations S8 and (SB, SB1). Those latter are respectively rejection and sedimentation areas of mining effluents. These physiochemical conditions could also engender the reduction of the hexavalent chrome (CrVI) into trivalent chrome (CrIII) in the stations mentioned above. Indeed, during the 1st campaign, the dichromate ion could be in most of the stations apart from the stations S4 and S1. At last, the bioavailable species of arsenic (As(S)), of lead (Pb(S)) of cadmium (Cd²⁺) could exist in the stations S3, S4, S7, S12 where there are some agricultural exploitation.

Some sanitary risks about the population could occur because of the adsorption capacities of plants. Moreover, the small difference between the neat acidity and the potential acidity involves that the soil is organic; therefore, the harmful effect of metals that we studied will be more noticeable [11]. This difference has also a positive aspect; this means that the neat charge of particles surfaces of the soil is negative. The metals adsorption on the particular surfaces will be made easier by coulombian attractions [11].

5. Conclusion

Through this task, results permit us to deal with the analysis of different chemical forms of arsenic, cadmium, chrome and lead existing in waters compartments and sediment compartments in a gold mining environment. These results also show that these quoted elements can appear under different chemical forms and can appear at different oxidation rates in surface waters, underground waters and the sediments. Moreover, in sediments, chemical forms As(S), Cd²⁺ and Pb(S) which are bioavailable forms could exist in stations S3, S4, S12 where agricultural exploitations are practiced. Therefore, the consumption of agricultural products from these exploitations could be considered as risks of metallic bioaccumulation. The use of water in our study area for consumption or agricultural irrigation could engender the some toxicity risks.

References


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