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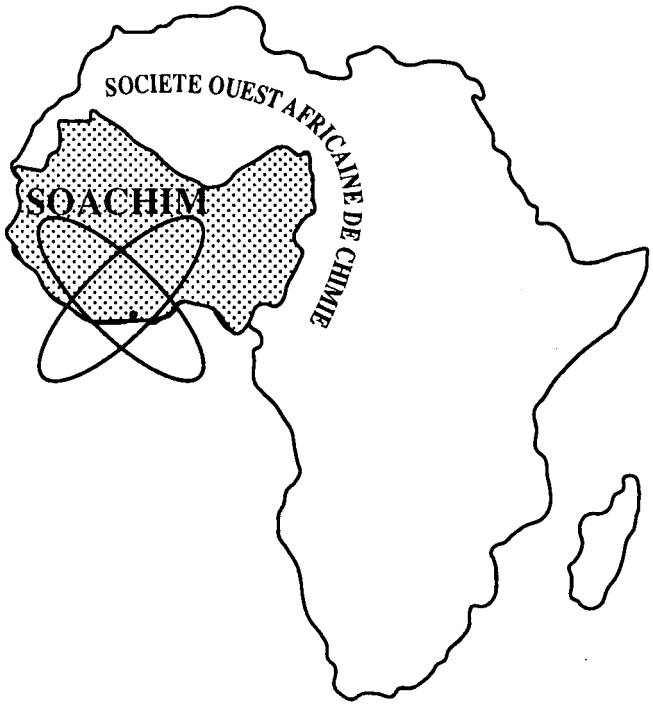

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Temporal variability of arsenic speciation in northern Burkina Faso groundwater

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Abstract: Inorganic arsenic species determination is important to measure health hazards and to interpret in the best possible way clinical signs within populations drinking exposed water. This study was performed on groundwater samples from northern Burkina Faso using a portable electroanalytical apparatus in order to assess the proportion of As (III) versus As (V) when analyzed on site and during conservation. Two different treatment methods of water samples were performed and analyzed for their ability to maintain the initial As species content. The samples conserved with HCl and EDTA in white non opaque bottles were subsequently analyzed at days 7 and 21 post sampling. The investigations showed that arsenic (V) species were the most predominant form in the twenty-one studied samples. In general, regardless of their treatment, arsenic (III) species were spontaneously converted into the arsenic (V) during conservation. The arsenic (III) form, however, was kept for three samples until day 7 and for two of them until day 21.

Key words: arsenic, speciation, voltammetry, groundwater

Variabilité temporelle des espèces d'arsenic dans les eaux souterraines de la Région Nord du Burkina Faso

Résumé : La détermination des espèces d'arsenic inorganique est importante pour mesurer les risques pour la santé et pour interpréter au mieux les signes cliniques chez les populations exposées à travers la consommation d'eau contaminée. Cette étude a été réalisée sur des échantillons d'eau souterraine du nord du Burkina Faso à l'aide d'un dispositif électroanalytique portable afin d'évaluer la proportion d'As (III) par rapport à As (V) lors de l'analyse sur site et pendant la conservation. Deux méthodes différentes de traitement des échantillons d'eau ont été appliquées et analysées pour déterminer leur capacité à maintenir la teneur initiale en espèces As. Les échantillons conservés avec du HCl et de l'EDTA dans des flacons blancs non opaques ont ensuite été analysés aux jours 7 et 21 suivant l'échantillonnage. Les recherches ont montré que l'espèce d'arsenic (V) était la forme la plus prédominante dans les vingt et un échantillons étudiés. En général, indépendamment de leur traitement, les espèces d'arsenic (III) ont été spontanément converties en arsenic (V) pendant la conservation. La forme d'arsenic (III) a toutefois été conservée pour trois échantillons jusqu'au jour 7 et pour deux d'entre eux jusqu'au jour 21.

Mots clés: arsenic, speciation, voltampérométrie, eaux souterraines

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1. Introduction

It is well known that arsenic (III) is more toxic than arsenic (V) [1-3]. The oxidation state of arsenic has major toxicological issues and its speciation is important to assess the risk and impact on human health [2, 3]. Arsenic speciation studies are usually performed in central laboratories and less often on site. A rapid analysis of collected samples should ideally take place on site in order to prevent a change in the initial concentration of the studied species during sample storage [3, 4]. These changes can be due to several factors which include pH, redox potential, temperature, dissolved oxygen, iron and manganese content and biological activities due to micro-organism [1-3]. In the present work was examined the inorganic arsenic stability profile as a function of conservation time. A sample treatment by addition of stabilization agents was applied in order to try to avoid arsenic species transformation [3, 4]. HCl [5-8] and dibasic ethylene diamine tetra acetic acid (EDTA) [9, 10] are the most commonly used agents for this purpose. The former is often used for water samples studied by voltammetric methods [5-8]. Other acids have been reported with various effectiveness over days, weeks or months such as nitric acid [11-13] sulfuric acid [10], acetic acid [4], phosphoric acid [14], while ascorbic acid [15] has been used for water samples with high iron or manganese content [9, 10].

In Burkina Faso most reported data on arsenic groundwater determination concerned only total arsenic content. We report in this work speciation data during monitoring of arsenic inorganic species in groundwater from northern part of Burkina Faso (Ouahigouya district). The analyses were realized using a previously developed and validated voltammetric method using a gold modified carbon paste electrode [16].

2. Materials and methods

2.1. Reagents and solutions

Arsenious anhydride and sulfuric acid (85%) were from Chem Lab. Synthetic graphite powder (< 20 µm), sodium citrate and sodium borohydride were from Sigma-Aldrich. Gold salt ($HAuCl_4 \cdot xH_2O$) was from UCB Belgium. Glutathione, hydrochloric acid (37%) was from Fluka. Others reagents were: potassium iodide (Vel Leuven Belgium), ascorbic acid, EDTA (Acros Organics). The arsenic(III) standard solution ($1x10^{-2}$ M) was prepared by dissolving 0.09892 g of As_2O_3 powder in 25 mL of sodium hydroxide (2 M) and then acidified to a pH less than 2 with hydrochloric acid. This solution was stored at 4°C and all the standards and working solutions were prepared from this stock solution. All solutions were prepared with water of Milli-Q quality. Colloidal gold solution was prepared according to literature reports [17,18]. It consisted of mixing under stirring a gold solution at 1 mM (20 mL) and a solution of sodium citrate 38.8 mM (2 mL) during approximatively 5 min. Then, 50 mL of sodium tetraborate (75% m/v) was slowly added and the initial color changed passing from yellow to dark red indicating the formation of gold nanoparticles.

2.1 Working electrode preparation

The working electrode was prepared in the laboratory and used the next day for the on-site assays. The working electrode preparation consisted of filling the electrode cylinder wall with a carbon paste made which is a mixture of graphite powder and solid paraffin in proportion 60/40 (w/w). After smoothing the electrode surface with a Whatman paper and a glossy paper, it was covered with 10 µL of gold colloidal solution (1mM) and then left to dry at laboratory temperature. The electrode was modified electrochemically using a three-electrode cell configuration comprising the working electrode, a silver/silver chloride reference and a platinum wire auxiliary electrodes, respectively. A potential of -500 mV vs Ag/AgCl, KCl 3M was applied to the working electrode during 15 s in the gold salt solution ($HAuCl_4$ xH_2O 5 mg/50 mL) containing KI (5 mg/10 mL). The modified electrode was subsequently immersed in hydro-alcoholic solution (80/20 v/v) of glutathione (2.5 mM) during 2 hrs. The electrode preparation procedure was completed by thoroughly rinsing the electrode with Milli-Q water [16].

2.2 Selection of preservative agents

HCl and EDTA were chosen due to their reported effectiveness for maintaining the distribution of arsenic inorganic species in water samples. Both agents prevent the oxidation and the precipitation of iron and manganese ions which affect directly the distribution of arsenic species [19]. Although nitric acid has been very often used, it should be avoided in order to preserve the stability of species due to its inherent oxidant effect. Sulfuric acid is a good preservative for arsenic but it's not commonly used because due to the risk of barium salt precipitation ($BaSO_4$). Phosphoric acid has also been used but it can give rise to the formation of metallic phosphate compounds on which arsenic may adsorb [4]. Phosphoric acid also may promote microbial growth [19].

2.3 Arsenic (III) determination

As (III) electroanalysis was realized both on site and in the laboratory with the use of a portable 910 PSTAT mini potentiostat (Metrohm). Measurements were performed in a 10 mL measurement cell and with the help of a laptop for signal recording and analysis. Briefly, the method used Differential Pulse Anodic Stripping Voltammetry (DPASV) using the above described gold modified carbon paste electrode covered with a Self-Assembled Monolayer (SAM) of glutathione (GS-Au-NP/SCPE). All the analyzed samples were acidified with HCl (final concentration: 1.0 M) which served also as supporting electrolyte. More details about the developed method can be found elsewhere [16]. The main parameters of the measuring technique are summarized in **Table I**

As (III) was determined using an aliquot of 10 mL of sample acidified with HCl in order to adjust the total acidity at 1.0 M. Standard addition method was used for quantification. Total arsenic was determined after chemical reduction of As (V) to As (III) in acidic medium and using as reductant a solution composed of ascorbic acid and potassium iodide both at 750 µM.

2.4 Total arsenic and As (V) determination procedures

The total arsenic content determination required conversion of all the pentavalent form in trivalent form through a reduction step. As (V) reduction was achieved using 100 to 250 µL of KI and ascorbic acid solution (depending on As presumed level). This reducing solution was added to 10 mL of the studied water sample acidified at 1 M HCl. The mixture was put in an oven at 90°C and left to react during 45 min. Total arsenic was subsequently measured in its As (III) form. Arsenic (V) was estimated by the difference between total arsenic and the initial As (III) determined value [16].

2.5 Speciation study

The arsenic (III) content was also determined as a function of preservation time assuming that the total arsenic content remained unchanged. Analyses were performed on site immediately after sampling, and after a delayed time in the laboratory. The collected underground water was splitted into 3 samples, namely: one for on-site As (III) determination and the others containing HCl or EDTA as preservative for As (III) determination at days seven and twenty-one.

2.6 Iron content determination

Total iron content was determined due to its possible interference with arsenic speciation. Total iron was determined by flame atomic absorption spectrometry FAAS (AA240 FS Fast Sequential Atomic Spectrometer from Varian). For calibration, different standard iron concentrations were prepared from a commercial stock solution at 1000 ppm. The resulting working solutions were: 1.0; 2.0; 4.0; 8.0; 10 ppm. Iron hollow cathode lamp intensity was fixed at 5 mA. The width of the slit was 0.2 nm and the working wavelength was 248.3 nm. Operational conditions are summarized in **Table II**. A blank and a fixed iron standard solution were used for control.

Table I: Summary of main parameters of DPASV technique

Electroanalytical parameters	GS-Au-NP/SCPE
Measurement technique	DPASV
Preconcentration potential and time	-300 mV during 150 s
Equilibrium time	3 s
Scan rate	50 mV/s
Amplitude of the pulses	100 mV
Increments	5 mV
Duration of the pulse	10 ms
Scan windows	[-450 mV ; +500mV]
Supporting electrolyte	1.0 M HCl

Table II: Summary of Atomic Absorption Spectrometry operational conditions

Spectrophotometer	FAAS
Working wavelength (λ)	248.3 nm
Slot width	0.2 nm
Ultra-lamp (intensity)	5 mA
Signal measurement mode	Integration
Calibration	1.0 – 2.0 – 4.0 – 8.0 - 10 ppm
Flame	Air/acetylene
Acetylene flow	2 mL/min
Air flow	13.5 mL/min

2.7. Sampling

The selection of water sampling points and localities was based on results reported in a previous study devoted to total arsenic content in underground water from northern Burkina Faso [20]. Based on these data sampling areas with high, medium and low concentrations of arsenic were selected. It was reported that more than 50% of the investigated boreholes had arsenic content higher than the WHO recommended standard; 10 µg/L [20]. Twenty-one boreholes from different areas and different level of concentration were sampled. Sampling was made after a pumping time of 30 min. Two hundred mL of borehole water were sampled twice and stabilized, one with 1 mL HCl (37 %), and the other with 1 mL EDTA (200 mM). The samples collected in transparent white plastic bottle were held in an ice-box at the sampling area. After on-site analysis of an aliquot, they were carried out to the university and stored in a fridge in the laboratory for subsequently analyses.

3. Results and discussion

3.1 Arsenic (III) on-site determination

The advantage of on-site measurements is the possibility to determine the As (III) content and the distribution of different arsenic species in the original matrix at the moment of sampling. In case of delayed analysis, changes in oxidation state can take place during conservation. The device portability, low reagent consumption and relatively simple measuring conditions are some clear benefits of electroanalytical methods comparatively to other methods based on complex and heavy instrumentation.

The range of arsenic (III) concentration determined in the 21 studied samples varied from less than 0.9 µg/L ie., the Limit of Detection (LOD) of the method to 2561 (±106) µg/L (**Table III**). A typical voltammogram is presented in Figure 1.

Among samples with undetectable content (samples 14-18), one of them (N° 18) had a red brick color likely due to a high Fe (III) content. It is well known that Fe (III) exerts a negative influence on arsenic (III) through an oxidizing action according to equation (1). Iron content measured for this sample was 0.274 mg/L.

$$H_3AsO_3 + H_2O + 2Fe^{3+} \rightarrow H_3AsO_4 + 2H^+ + 2Fe^{2+} \quad \text{(eq.1)}$$

It was inferred that in sample N°18 all As (III) was oxidized to As (V) by iron. This was confirmed by the determination of total arsenic (Table 3). Eleven samples had As (III) concentration in the range comprised between 10 and 50 µg/L (Table III, N°18). Two samples (N°2, 12) had a concentration comprised between 50 and 100 µg/L. Sample N°19 had dramatically high arsenic content namely, 2561 µg/L (**Table III**). Determination was difficult to conduct in two samples (N° 20, 21) due to a distortion of the As peak attributed to dissolved copper in the analyzed samples. This interference resulted in two peaks overlapping as also reported in the literature [16, 21]. For a Cu (II)/As (III) ratio below or equal to 9 there was no problem for measurement of the relative peak current (Ep = 30 mV) for arsenic as shown in Figure 2.

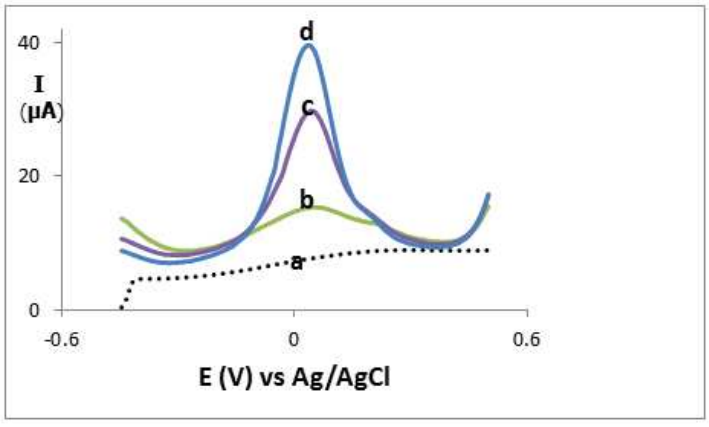


Figure 1: DPASV profiles recorded for the measurement of arsenic (III) in a water sample (Zana Sandoogo area); a: blank; b: sample; c: first standard addition of 40 µL As(III) ($1x10^{-3}$M); d) second standard addition of As(III) 40 µL ($1x10^{-3}$M) .

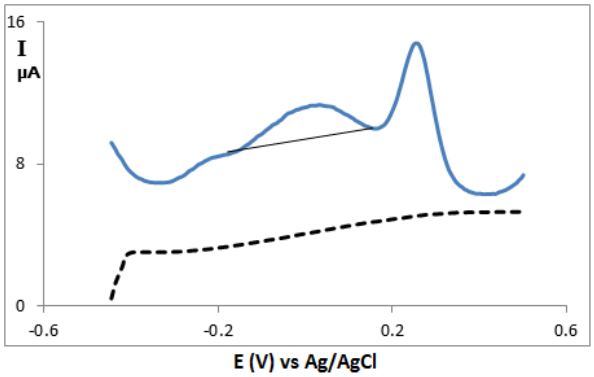


Figure 2: DPASV for water sample at Zana Ecole with a ratio Cu (II)/As (III) less than or equal to 9. Dotted line: reagent blank, full line: sample signal. Ip As at Ep = 0.030 V, Ip Cu at Ep = + 0.255 V vs Ag/AgCl, 3M KCl

Table III: Arsenic (III) content (µg/L) in borehole water samples in villages of the Ouahigouya district. Influence of time, preservation agent and storage.

Locality	N°	pH	As (III) on-site initial content n=3	As (III) (J_0+7) (HCl) n=3	As (III) (J_0+7) (EDTA) n=3	As (III) (J_0+21) (HCl) n=3	As (III) (J_0+21) (EDTA) n =3	Total As n=3
Bougodogo 1	01	6.41	13.6 (0.48)	10.9 (4.2)	6.1 (0.6)	<LOD	<LOD	99.5 (18.7)
Lilgomde bagarin	02	7.75	88.5 (11.9)	21.0 (1.7)	32.6 (6.3)	23.0 (3.3)	26.9 (1.4)	191 (34)
Lilgomde Ecole	03	7.53	34.0 (5.8)	20.1 (4.6)	25.1 (3.2)	<LOD	<LOD	189 (6)
Ouattinooma	04	7.76	47.8 (3.2)	<LOD	<LOD	<LOD	<LOD	47.7 (2.9)
Youba Ecole 1	05	7.86	12.7 (1.1)	12.9 (2.0)	13.0 (1.3)	<LOD	<LOD	54.5 (2.8)
Zana Ecole	06	7.36	35.7 (3.5)	22.3 (0.3)	LOD	<LOD	<LOD	69.2 (2.1)
Zana sandoogo	07	7.66	24.8 (2.8)	<LOD	<LOD	<LOD	<LOD	55.8 (11.8)
Pelle gonkè	08	7.95	27.6 (3.4)	<LOD	31.0 (3.1)	<LOD	<LOD	35.9 (6.6)
Margo Koego	09	7.38	27.3 (2.6)	<LOD	<LOD	<LOD	<LOD	55.8 (4.6)
Rapougma Ecole	10	7.76	19.9 (0)	20.3 (4.3)	22.0 (3.4)	21.3 (0.1)	22.8 (1.8)	47.7 (4.0)
Kononga	11	7.23	39.0 (3.4)	28.9 (3.2)	18.9 (2.2)	<LOD	<LOD	44.2 (4.5)
Nogo	12	7.21	59.1 (4.2)	29.8 (3.5)	<LOD	<LOD	<LOD	84.0 (7.3)
Yaoguin Namissiguima	13	6.43	23.3 (0.8)	19.4 (2.1)	<LOD	<LOD	<LOD	91.7 (9.5)
Lilgomde Ipaala	14	7.43	<LOD					<LOD
Youba Ecole 2	15	7.96	<LOD					<LOD
Bonsomnore Kioloye	16	6.93	<LOD					<LOD
Mogombouli Yonbo	17	6.78	<LOD					<LOD
Rapougma Bagarin	18	-	<LOD	<LOD	<LOD	<LOD	<LOD	61.7 (5.1)
Tanlili Bougodogo 2	19	8.15	2561 (106)	2529 (50)	2575 (198)	2078 (307)	2510 (295)	4512 (162)
Tanlili signonguin	20	5.94	-	24.9 (0.4)	14.7 (2.4)	12.72 (1.9)	<LOD	112 (13)
Pelle Bougodogo	21	7.96	-	<LOD	<LOD	<LOD	<LOD	58.9 (2.2)

(..)= standard deviation; $LOD_{As(III)}$ (0.9µg/L) ; - not determined

3.2 Arsenic (III) content as a function of time and preservation agent

3.2.1 Day J_0+7

Regarding the samples treated with HCl, 4 of them had their concentration unchanged (Table III, N° 1, 5, 10, 19). Statistical significance tests gave respectively p value of 0.4190, 0.9212, 0.9177, 0.3148. We noticed a content decreased between 10 and 25 % for 1 sample (p-value,0.03509, table 3, N°,13), between 25 and 50% for 4 samples (p-value < 0.05, table III, N°3, 6, 11, 12), and a decrease between 75 and 100% for 5 samples (p-value < 0.05, table 3, N°2, 4, 7, 8, 9). Concerning the samples treated with EDTA, 3 samples had their concentration unchanged (p value respectively, 0.1216, 0.5158, 0.3148, table III, N°5, 10, 19). It was noticed that the content decreased between 25 and 50% for 1 sample (p-value 0.003328, table 3, N°2), and between 50 and 75% for 3 samples (p-value < 0.05, table 3, N°1, 2, 11). Six samples had a content below the LOD (table III, N°4, 6, 7, 9, 12, 13).

Samples N° 5, 10, and 19 had their content unchanged either treated with HCl or EDTA. For the other samples a slight drop in As (III) was generally noted. The decrease of As (III) content could likely be explained by arsenic (III) oxidation due to several oxidants such as iron (III) and /or nitrate [13]. Dissolved oxygen was present in all collected samples and the nitrate concentration ranged between 1.1 and 2.1 mg/L [23, 24]. Van den Berg et al. showed that arsenic content decreased by approximately 70% in samples exposed to the sun after 2 hrs and was no longer detectable after 5 hrs [22]. The decrease of As (III) content to different levels seemed to be linked to the intrinsic nature of the matrix of each sample [2]. During a compared efficacy trials for several acids (hydrochloric, orthophosphoric, acetic, nitrolotriacetic) it was reported that As (III) decreased by 100 % after 9 days in all the samples except those treated with phosphoric acid [4]. Only the latter allowed the limitation of arsenic content falling to 10% of its initial value.

The decrease in As (III) content for samples preserved with EDTA was difficult to explain because previous studies showed that addition of this complexing agent allowed maintaining arsenic original redox state [22]. The EDTA concentration, however, used in our study was 10 to 500 times less than that reported by other authors who stored the samples in opaque bottles [10, 25]. EDTA content was determined taking account the mean iron levels found previously in the underground water from northern Burkina Faso (between 0.005 – 0.69 mg/L) [24]. From the stoichiometric perspective, EDTA content used, would be quite sufficient for complexation reactions with iron. In samples N° 5, 10 and 19, HCl and EDTA proved to be effective for As (III) conservation. Arsenic (III) content measured 1 week later was similar to its content at J_0 taken on the site. A shelf life of 1 week, for arsenic species in groundwater samples with iron high content and acidified with HCl, was reported [26]. It was also reported that synthetic samples of As (III) standard solutions stabilized with HCl, subjected to dark or exposed to light, showed arsenic (III) stability and total arsenic during 45 days[19].

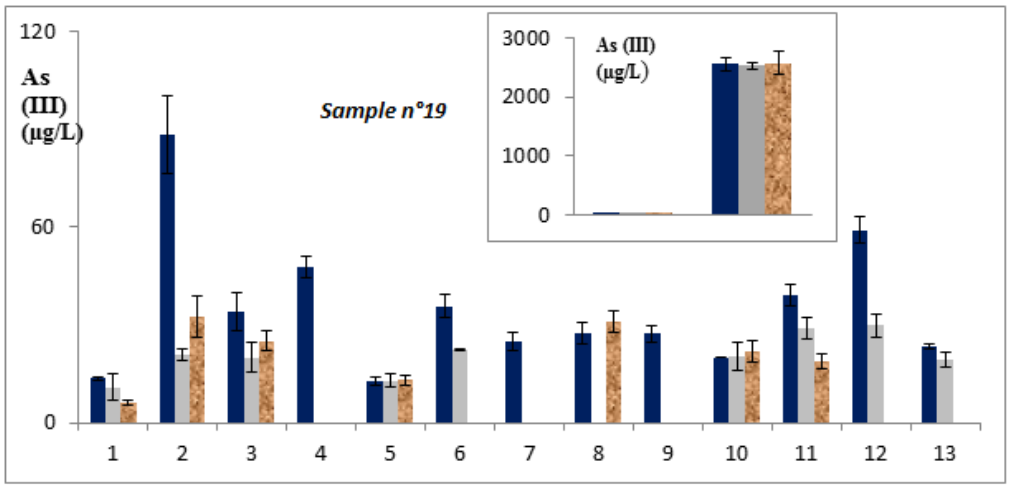


Figure 3: On-site arsenic (III) measurements and seven days later:
Initial content (J_0) ; : Content at J_0 + 7 in EDTA , Content at J_0 + 7 in HCl

3.2.2 Day J_0+21

Twenty one days later, eighteen samples (Table 3), all the samples except N°2, 10, 19 had their arsenic (III) content below the LOD. Three samples had detectable As (III) content (Figure 4, N° 19, 10, 2). Sample N°10 had already a stable content at J_0+7 and this stability was maintained at J_0+21 for sample preserved both with HCl or EDTA. Sample N° 19 preserved with EDTA showed a net stable As (III) content (p-value, 0.6862). However, in this sample preserved with HCl, the stability was relatively less good (p-value, 0.05316), and a decrease of 19% was observed. Although the iron level was high in sample N° 10 (0.47 mg/L) and sample N° 19 (4.96 mg/L), EDTA enabled to stabilize arsenic species distribution in these two samples likely by interaction with iron and formation of a stable chemical complex. The efficacy of EDTA as preservative in these two samples was in agreement with literature data [9, 10]. In sample N° 2 the level decreased to 74% and 70% of the initial value in HCl and EDTA, respectively (p-values 0.005697 and 0.001518).

3.3 Distribution of inorganic arsenic (III) and arsenic (V).

Total inorganic arsenic was determined in the 21 groundwater samples studied. The level ranged from undetectable (ie. below LOD for 4 samples) to 4512 µg/L measured in Tanlili Bougodogo (Table III). Four samples (Table III, N°4, 8, 10, 11) had a content comprised between 10 and 50 µg/L, 9 samples (Table III, N°1, 5, 6, 7, 9, 12, 13, 18, 21) were between 50 and 100 µg/L, 3 samples (Table 3, N°2, 3, 20) were between 100 µg/L and 200 µg/L and 1 sample (Table III, N°19) had a content excessively high of 4512 µg/L. Arsenic (V) estimation along with As (III) and total As are reported in Table IV. The total iron content is also reported in Table IV. The different As species content is presented comparatively in the histogram of figure 5. Relative frequencies for inorganic arsenic species are also presented in Table 4. Taking into account the samples with positive detection of arsenic, 9 out of 15 samples had As (III) ratio less than 50% (Table IV, N°1, 2, 3, 5, 7, 9, 10, 13,18) and 6 out of 15 had As (III) ratio higher than 50% (Table IV, N°, 4, 6, 8, 11, 12, 19). Arsenic (V) was thus the most frequently encountered form. This was already mentioned by other authors [23, 24]. Furthermore two samples differed by their specific composition in arsenic species namely samples N°18 (that had a particular red color) which contained 100% of As(V) and sample N° 4 which contained 100% of As(III). These distinct As(III)/As(V) ratios are comparable to those previously reported in several other countries around the world. In West Bengal in India the As(III) form was found high in 78 % of studied water samples [22]. In Bangladesh, As (III) ratio extended to a wide range between 30 and 98 [8]. In Mexico, however, As (V) was largely dominant in water with a ratio above 90 % [27]. These results are linked to hydro geochemical features of the aquifer environment [28].

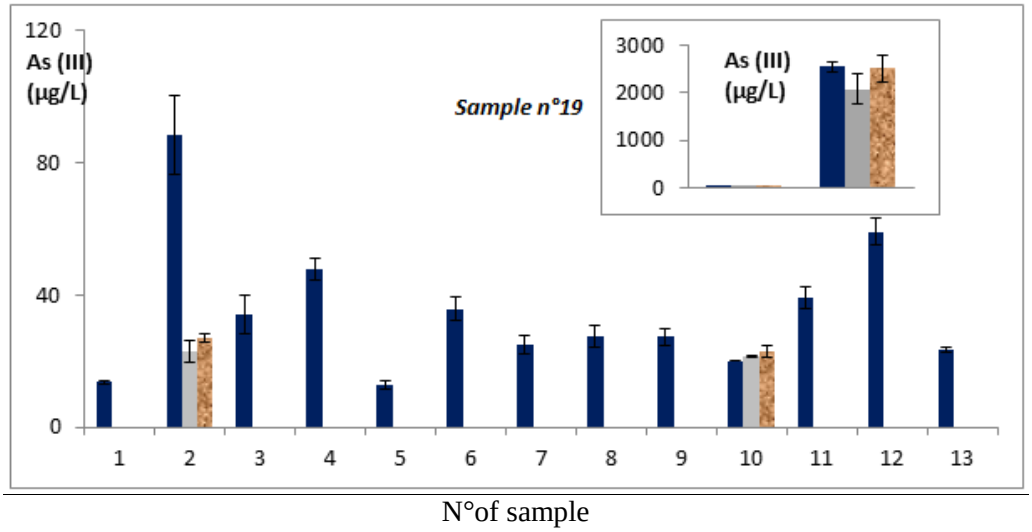
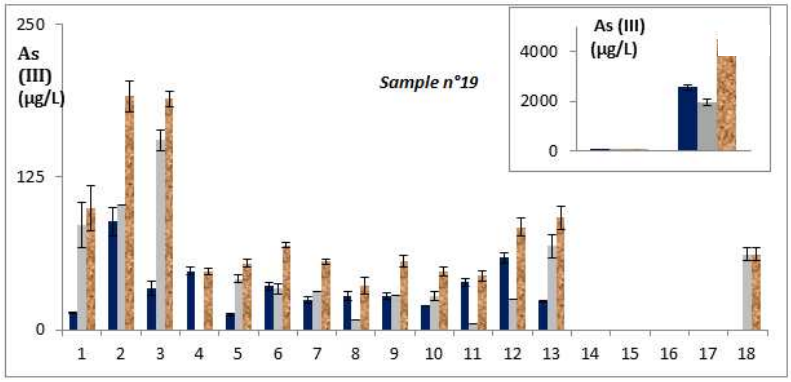


Figure 4: On-site As(III) measurements and 21 days later.
: Initial content (J_0); : Content at J_0+21 in EDTA; : Content at J_0+21 in HCl



N° of sample

Figure 5 : Total arsenic, arsenic (III), and arsenic (V) content

: Arsenic (III), : Total arsenic, : Arsenic (V)

Table IV : Arsenic (III) and (V) and iron content (µg/L) and arsenic species relative frequency (in %) in groundwater measured on site

Locality	N°	As (III) on-site initial content. n=3	Total As n=3	As V	As (V) %	As (III) %	Iron content
Bougodogo 1	01	13.6 (0.48)	99.5 (18.7)	85.9 (18.7)	86	14	746 (15)
Lilgomde bagarin	02	88.5 (11.9)	191 (34)	102 (36)	54	46	<LOD
Lilgomde Ecole	03	34.0 (5.8)	189 (6)	155 (8)	82	18	<LOD
Ouattinooma	04	47.8 (3.2)	47.7 (2.9)	LOD	0	100	8.0 (1.2)
Youba Ecole 1	05	12.7 (1.1)	54.5 (2.8)	41.8 (3.0)	77	23	21 (0.6)
Zana Ecole	06	35.7 (3.5)	69.2 (2.1)	33.5 (4.1)	48	52	26 (1)
Zana sandoogo	07	24.8 (2.8)	55.8 (11.8)	31	56	44	12 (2)
Pelle gonkè	08	27.6 (3.4)	35.9 (6.6)	8.3	23	77	13 (1)
Margo Koego	09	27.3 (2.6)	55.8 (4.6)	28.5	52	48	18 (1)
Rapougma Ecole	10	19.9 (0)	47.7 (4.0)	27.8 (4.0)	58	42	470 (9)
Kononga	11	39.0 (3.4)	44.2 (4.5)	5.2	12	88	28 (3)
Nogo	12	59.1 (4.2)	84.0 (7.3)	24.9	30	70	15 (0.7)
Yaoguin Namissiguima	13	23.3 (0.8)	91.7 (9.5)	68.4 (9.5)	75	25	23 (2)
Lilgomde Ipaala	14	<LOD	<LOD	<LOD			<LOD
Youba Ecole 2	15	<LOD	<LOD	<LOD			11 (1)
Bonsomnore Kioloye	16	<LOD	<LOD	<LOD	<LOD		20 (1)
Mogombouli Yonbo	17	<LOD	<LOD	<LOD	<LOD		39 (2)
Rapougma Bagarin	18	<LOD	61.7 (5.1)	61.7 (5.1)	100	0	274 (14)
Tanlili Bougodogo 2	19	2561 (106)	4512 (162)	1951 (149)	43	57	4968 (10)
Tanlili signonguin	20	-	112 (13)				50 (3)
Pelle Bougodogo	21	-	58.9 (2.2)				<LOD

LOD_{Fe} (Limit of Detection: 6 µg/L); $LOD_{As(III)}$ (0.9µg/L); - not determined

4. Conclusion

In this work, different inorganic arsenic species were determined at the sampling site and according to a delay period and the nature of the preservative agent used. For most samples preserved in white bottles and treated with HCl or EDTA, initial content decreased to different levels after one week or three weeks of storage. This decrease has been inferred to be due to the oxidation of arsenic (III) by the presence of dissolved iron (III). Additional studies would be needed, though, in order to further characterize the parameters affecting the As(III)/As(V) ratio in the collected samples. For the fifteen samples with positive detection of arsenic, three samples showed stable arsenic content distribution one week later, regardless of their treatment with HCl or EDTA. This stability extended until day 21 for two of them preserved with EDTA. In one sample with relatively high iron content, EDTA has been shown to be more effective than HCl to ensure arsenic species stability. These results showed that priority should be given to on-site analyses given the marked difference in toxicity of the two inorganic As species. The high amount of As (III) found in samples N° 19 and 8 likely permitted to explain the arsenicosis clinical signs pointed out earlier in the studied areas namely, Tanlili and Pellé Gonkè. Ulcerative and necrotic tumor and palmoplantar hyperkeratosis have been highlighted in Tanlili after two or five years of lifetime exposure, while in Pellé Gonkè, hyperpigmentation was identified within the two-thirds of the population only after one month exposure to contaminated drinking water with total arsenic content of 1.300 µg/L [24].

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