Original Research Article

Assessment of the level of contamination of groundwater found near -------pl ADD NAME OF REGION by glyphosate, aminomethylphosphonic acid, glufosinate and trace metal elements and health risks

Abstract

This study aims to determine the level of vulnerability of groundwater water to glyphosate, aminomethylphosphonic acid (AMPA), glufosinate and trace metal elements (ETM) as well as the physicochemical parameters of this water. The study covered water from thirteen boreholes APPROX DEPTH ?in the autonomous district of Abidjan. (PL ADD LATITUDE AND LONGITUDEIn situ measurements were made for temperature, pH and electrical conductivity. Chemical analyzes were carried out using chromatographic method with spectrophotometric detection. The average temperature values are above the standards, while the pH and conductivities are within the standards recommended by the WHO for drinking water. Regarding glyphosate, the results showed its presence in all the samples analyzed at average concentrations of: 0.12 ±0.02 µg/L (minimum) and 1.9 ±0.1 µg/L (maximum), all above the threshold value for drinking water (0.1 µg/L) defined by the WHO. As for ETM, they are present in these drillings at significant concentrations of: 39±2 µg/L (As), 130±3 µg/L (Pb), 80±1 µg/L (Cu), 73±3 µg /L (Ni), 200±3 µg/L (Zn) at FILTISSAC, 20±2 µg/L (Cr) at Vridi and 21000 ±200 µg/L (S) in the Koumassi borehole. The health risk linked to the consumption of groundwater by the population, according to the mathematical calculation model used, is not acceptable. This study deserves to be carried out across the entire national territory.

Keywords: Chromatography, trace metal elements, glyphosate, mathematical model, groundwater pollution, health risks, spectrophotometry.

1. INTRODUCTION

Glyphosate or its IUPAC name N-phosphonomethylglycine is an organophosphate herbicide with the chemical formula $C_3H_8NO_5P$ [1]. It is a synthetic molecule which was produced for the first time in 1970, inspired by glycine, a natural molecule (**Figure 1**). To date, it is found on the market in several commercial preparations. The commonly used product would contain 360 g of glyphosate/liter [2]. Used alone, glyphosate is not very effective and does not adhere to leaves or penetrate them easily. In order to increase its solubility, its herbicidal activity and to fix it on plants [3], it is prepared in the form of salt in the mining and agrochemical industries by adding additives or surfactants. Among these surfactants, metallic trace elements should be mentioned [4]. Glyphosate-based herbicide products are used on a large scale on agricultural soils. Which could be transported directly into the environment and reach groundwater through the phenomena of runoff, leaching and infiltration, thus creating risks of contamination and pollution. Studies have shown that more than 80% of drinking water comes from groundwater [5].

In Ivory Coast, hydraulic networks from groundwater are resources most exploited by the rural population for their daily needs [6]. These groundwater tables are constantly under pressure from pollution caused by population growth and human activities. This is the case of the autonomous district of Abidjan, which constitutes one of the large cities of West Africa faced with demographic growth, industrialization [6] and the modernization of agriculture. To meet food needs, farmers are increasingly turning to herbicide products based on glyphosate for rapid weeding of agricultural plots. These active substances act as protectors of plants from harmful agents.

Our study focused on glyphosate, aminomethylphosphonic acid (AMPA) and glufosinate for their persistence and toxicity and trace metal elements (ETM) for their non-biodegradable nature and their toxicity in the environment. Studies have shown that most phytosanitary products based on glyphosate appear as synthetic substances that persist after use. Glyphosate and its main metabolite, aminomethylphosphonic acid (AMPA) (**Figure 1**) as well as glufosinate (**Figure 1**) and residues of metallic trace elements would be suspected of being among the pollutants most detected in surface water and global underground [7]. In tropical zones, very few studies have been carried out on glyphosate, AMPA, glufosinate and ETMs in groundwater. In Ivory Coast, Soro et *al.* [8] quantified the concentrations of glyphosate residues in borehole, well and surface water at respective concentrations of 0.67 µg/L, 0.19 µg/L and 0.27 µg/L. The studies by Gokou et *al.* [9] showed the presence of glyphosate in surface water at an annual concentration of 1.26 µg/L. As for metallic trace elements, they have been detected at variable concentrations in surface and groundwater in Ivory Coast.Djadé et *al.* [10] detected Pb (3.10 µg/L), Cd (0.08 µg/L) and As (1.18 µg/L) in well water and Pb (4.08 µg/L), Cd (0.08 µg/L) and As (1.76 µg/L) in drilling waters in the Zouan-Hounien mining area. Kouadio's studies [6] made it possible to quantify As in the groundwater of San-Pedro and Abidjan at concentrations of 15 µg/L and 13.5 µg/L respectively. Studies carried out on groundwater in the city of Abidjan in 2012 made it possible to detect Cr, Co, Pb and Zn at respective concentrations of 613 µg/L, 361 µg/L, 4 µg/L. L and 77 µg/L [6].

This present work aims to know the concentrations of glyphosate, AMPA, glufosinate and ETM in the groundwater waters of the autonomous district of Abidjan and to evaluate the health risks linked to the consumption of this water by population.

Figure 1. Chemical structures of glyphosate, AMPA and glufosinate

2. MATERIAL AND METHODS

2.1. Study area

The boreholes selected as part of our study are all installed in the municipalities of Abidjan and also in Agboville and Alépé, highly urbanized with significant agricultural activities. Our study area is characterized by a sub-equatorial, hot and humid climate with a long rainy season (May-July), a short rainy season (September-November) and two dry seasons. The long dry season begins from December and ends at the end of March. The average annual temperature is between 24°C and 28°C with an average annual precipitation of approximately 1544.7 mm and a relative humidity rate of 82.7% [11]. The Universal Transverse Mercator (UTM) coordinates and the depths of the sampling stations are grouped in **Table 1**. PL CHECK THAT DRILLING DEPTH WHICH IS NEARING 6-9 KM IS TOO MUCH AND IF SO THAN FOSSIL WATER IS AVAIABLE WHICH CANNOT BE CONTAMINATED WITH FIELD RUN OFFS

Table 1. UTM coordinates and depth of boreholes

locality	UTM coordinates	Drillingdepth (m)
ER	X=369 685E; Y=650 973N	63,58
AR	X=381 424E; Y=607 006N	68,47
FI	X=386 816E ; Y=596 516N	90
MC	X=380 287E; Y=598 163N	128,15
DK	X=388 575E; Y=595 409N	45,1
AC	X=387 131E; Y=597 146N	94,67
AS	X=386 267E; Y=597 740N	100,04

AK	X=396 412E; Y=592 465N	67,50
MB	X=391 132E; Y=590 465N	39,87
KM	X=395 116E; Y=585 048N	25
CR	X=391 104E; Y=605 756N	90,60
AP	X=392 155E; Y=602 914N	87,36
VR	X=389 101E; Y=581 999N	21,70

VR : VRIDI LDC ; **DK** : Abobo Dokui 2 ; **AC** : ABOBO COCO SERVICE ; **ER** : ERYMAKOUGUIE ; **CR** : 4.CROIX; **AP** : ALEPE 1 ; **AR** : ANYAMA REFERENCE ; **KM** : KOUMASSI zone industrielle ; **MC** : MACA CITE ADO ; **FI** : Château Filtisac ; **AK** : AKOUEDO ; **MB** : M'BADON ; **AS** : ABOBO SAGBE

2.2.Measurement of physicochemicalparameters

In situ measurements of temperature, pH and electrical conductivity were carried out in three tests on each sample taken using electrochemical probes (a WTW multi 3430 brand multi parameter, a METTLER brand pH meter TOLEDO).

2.3. Determination of glyphosate, AMPA and glufosinate concentrations

The method used in our study is that described by the Central Air Quality Monitoring Laboratory of France **[**12**].** Glyphosate, AMPA and glufosinate were analyzed after derivatization with FMOC-Cl ((9-fluorenylmethyl)-chloroformate). The analysis is carried out in LC/MS/MS on a WATERS, UPLC® Acquity and TQD Acquity coupling with an X-Bridge C18 -2.5µm (50 x 2.1 mm) -WATERS column. The chromatographic gradient conditions followed come from standard NF ISO 16308. The extraction was carried out on Quartz filters. Glyphosate standard solutions were prepared by dissolving pure glyphosate crystals in acid form in water. The calibration functions were determined from standard solutions with concentrations varying from 0.2 to 200 ng/mL. Chromatographic gradient conditions from standard NF ISO 16308 were used to identify and quantify glyphosate, glufosinate and AMPA.

2.4.Determination of ETM concentrations

The water sample was prepared after filtration by adding 3 mL of 65% concentrated nitric acid until a pH less than or equal to 2 was obtained. The dosage is carried out using spectroscopy mass with inductively coupled plasma (ICP-MS).

2.5.Assessment of health risks linked to the consumption of water from boreholes

The quantitative health risk assessment method consists of estimating by calculation the health risks from natural or anthropogenic sources to which a given population is exposed. The Exposure Assessment in this study is carried out by adopting a deterministic approach. It makes it possible to define the contaminated environments, the routes of passage of the chemical compound studied from the source to the human receptor, the exposed populations, the importance of exposure and the duration of exposure. This results in the calculation of a daily exposure dose (µg/kg/j).

Based on the WHO Drinking Water Quality Guidelines, the following exposure scenarios are considered:

- A 60 kg adult consumes 2 liters of water per day;
- A 10 kg child consumes 1 liter of water per day;
- A 5 kg infant consumes 0.75 liters of water per day.

The daily dose of exposure to chemical pollutants through water consumption is calculated according to the following equation: $\mathbf{DJE = (Ce \times Qe \times Te)/Pc}$(I)

With **DJE** :Daily exposure dose linked to consumption of polluted water (µg/kg/j);

Ce: Exposure concentration relative to polluted water expressed in µg/kg;

Qe: Quantity of water consumed per day expressed in kg/j;

Te: Exposure rate (water is consumed 7 days a week, Te = 1);

Pc : Body weight of the targeted individual (kg).

The risk characterization for threshold effects is determined by calculating the hazard quotient (QD) according to the following equation:$\mathbf{QD = DJE/\ VTR}$ (II)

With **VTR**: Toxicological reference value (µg/kg/j).

For $QD < 1$ the occurrence of a toxic effect is unlikely (or very unlikely).

For $QD > 1$ the appearance of a toxic effect is probable (or very probable).

Table 2. VTRs used in this study [13, 14]

	Composé organique	**Metal trace elements**							
	Glyphosate	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
VTR (µg/kg. j)	300	0,3	0,2	500	3	10	20	3,5	300

2.6.Principal component analysis

The quantities of materials of these different compounds were used by the statistical method of principal component analysis (ACP) using Statistica software, version 6.1-2014, to highlight the existing relationships between compounds and between variables. The values were centered and reduced for the realization of the standardized principal component analysis from all the values found using the following formula: $\mathbf{Vcr = (Ca\text{-}Mc)/E}$

With **Vcr** = Reduced centered values; **Ca** = Concentration analyzed; **Mc**= Average concentrations and **E** = Ecartype.

3. Results

3.1. Measurements of physico-chemical parameters of water sampled

The measurements of the physicochemical parameters of the samples were carried out in situ. The average values of temperatures, pH and conductivities of water from the different boreholes obtained in this study are recorded in **Table 3**.

For temperature, the average values vary from 27.3±1.1 to 31.8±1°C. The highest value is recorded at Dokui 2. The results show temperature values above the admissible (25°C) and acceptable (15°C) standards defined by the WHO. The high temperatures in these boreholes could be linked to the depth of these boreholes [6].

For pH, the values found oscillate between 4.23±0.01 and 6.56±0.1 with a maximum value obtained in the Vridi LDC borehole. The results show average values similar to those of the waters of the sedimentary basin of Côte d'Ivoire. The average pH values obtained as part of this study are less than 7 and are well below that of commercial mineral waters from the AWA company in Côte d'Ivoire (pH=8), for example. All water from these boreholes is acidic. These pH are within the Chemical Potability Standards (6.5-8.5) established by the WHO [14]. The acidity of the water collected from our various boreholes would be linked to the presence of CO_2 [6] resulting from the biodegradation of glyphosate [15] deposited at groundwater level by infiltration.

Regarding conductivities, the average values vary from 39.9±1.5 to 385±1.3 µS/Cm with a maximum average concentration recorded in the Koumassi 1 borehole. All the values obtained in our study are lower than the admissible (2000 µS/Cm) and acceptable (400 µS/Cm) standards of the WHO [14]. By observing these average values, it appears that the waters of the boreholes studied are poorly mineralized due to the presence of glyphosate in significant quantities in these waters.

The pH and conductivities of all groundwater samples analyzed are below the drinking water standards defined by the WHO, while the temperatures are higher.

Table 3. Physico-chemical parameters of water samples

parameter	**Locality**					
	VR	**DK**	**AC**	**ER**	**CR**	**AP**
T (°C)	31,8 ±1	27,3 ±1,1	27,5 ±1,1	29,7 ±0,4	27,6 ±0,2	27,7 ±0,2

pH	6,56 ±0,1	5,61 ±0,1	5,63 ±0,1	5,60 ±0,1	4,65 ±0,1	4,23 ±0,01
Cond (µS/Cm)	367 ±10	294 ±2	319 ±1,2	87,5 ±1	58,1 ±1	92,2 ±2

VR : VRIDI LDC ; **DK** : Dokui 2; **AC** : ABOBO COCO SERVICE ; **ER** : ERYMAKOUGUIE ; **CR** : 4. CROIX ;
AP : ALEPE 1 ;

Table 3. (Continue..)

parameter	**Locality**						
	AR	**KM**	**MC**	**FI**	**AK**	**MB**	**AS**
T (°C)	29,7 ±0,9	29,6 ±0,9	28,4 ±0,5	28,6 ±1,5	27,3 ±1,1	28,1 ±1,4	27,7 ±1,2
pH	5,39 ±0,8	4,69 ±0,6	4,76 ±0,4	6,06 ±1,03	4,98 ±0,7	5,70 ±0,9	4,36 ±0,5
Cond (µS/Cm)	39,9 ±1,5	385 ±1,3	49,3 ±2,2	259 ±1,5	66,8 ±1,3	86,3 ±1,8	168,9 ±2,3

AR : ANYAMA REFERENCE ; **KM** : KOUMASSI 1 ; **MC** : MACA CITE ADO ; **FI** : FILTISSAC ; **AK** : AKOUEDO ;
MB : M'BADON ; **AS** : ABOBO SAGBE ; **Cond** : Conductivité ; **T** : Température ; **pH** : Potentiel Hydrogène

3.2.Contamination of groundwater by glyphosate, AMPA and glufosinate

The concentrations measured in glufosinate, glyphosate and its metabolite (AMPA) in the water samples taken from the boreholes are represented in **Table 4**.

According to the results (**Table 4**), the determined glyphosate concentrations vary between 0.12 ±0.02 µg/L (Vridi site drilling) and 1.9 ±1 µg/L (AboboSagbé drilling). While an absence of AMPA and glufosinate was observed. The fact that the last two pollutants are absent in these groundwaters would be linked either to their presence at concentrations lower than the quantification limits (0.05 µg/L) of the method used in this study, or to the fact that they would be non-persistent in groundwater. The results of our study clearly show that all the boreholes from our study site are polluted by glyphosate. The presence of glyphosate in groundwater water samples at high concentrations attests to non-compliance with the regulatory value recommended by the WHO which is 0.01 µg/L for drinking water. The presence of this organic pollutant, considered toxic, in borehole waters would be linked to repeated use of weedkillers not in accordance with recommendations by farmers in these areas [16], the presence of industries, landfills and auto packs. It should also be noted that one of the sources of this pollution would be the abandonment of packaging of glyphosate-based herbicides in the environment and household waste. This is the case of the Akouédo landfill. The presence of glyphosate in the waters of boreholes which are protected and deep at very high concentrations could also be explained by its very soluble nature in water. Consequently, it would end up in solution after infiltration of treated soils, thus causing pollution of groundwater. The concentrations obtained in the M'badon and AboboSagbé boreholes are much higher than those detected in Ivorian borehole waters (0.67 µg/L) by Soro et *al.* [8]. The studies noted that groundwater pollution in market gardening sites would be intensified by the leaching of crop soils through runoff and infiltration [17]. On the other hand, studies carried out in Canada have shown that after application, it is impossible for glyphosate and AMPA to migrate into the groundwater supply [5].

In view of these results, it should be noted that the waters in the boreholes located near plantations, auto packs, industries, landfills and market gardens in the autonomous district of Abidjan are exposed to diffuse pollution. This could create health risks for populations using this water for their daily needs. The presence of glyphosate in all the water samples taken from the boreholes allows us to validate the hypothesis of the solubility and stability of glyphosate in water.

Table 4. Concentrations (µg/L) of Glyphosate, AMPA and Glufosinate in groundwater

Chemical compound	**Locality**						
	VR	**DK**	**AC**	**ER**	**CR**	**AP**	**AR**
Glyphosate	0,12 ±0,02	0,21 ±0,04	0,22 ±0,02	0,27 ±0,03	0,28 ±0,01	0,31 ±0,04	0,32 ±0,02
AMPA	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
Glufosinate	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05

VR : VRIDI LDC ; **DK** : Dokui 2 ; **AC** : ABOBO COCO SERVICE ; **ER** : ERYMAKOUGUIE ; **CR** : 4. CROIX ;
AP : ALEPE 1 ; **AR** : ANYAMA REFERENCE ;

Table 4. (Continue..)

Chemical compound	**Locality**					
	KM	**MC**	**FI**	**AK**	**MB**	**AS**
Glyphosate	0,38	0,39	0,42	0,43	1,1	1,9

	±0,03	±0,02	±0,04	±0,02	±0,07	±1
AMPA	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05
Glufosinate	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05

KM : KOUMASSI 1 ; **MC** : MACA CITE ADO ; **FI** : FILTISSAC ; **AK** : AKOUEDO ; **MB** : M'BADON ; **AS** : ABOBO SAGBE

3.3.Contamination of groundwater by trace metal elements

The average concentrations of trace metal elements in the different waters from the boreholes of the study sites are reported in **Table 5**. The raw results show variable concentrations from one area to another. The concentrations obtained show the presence of the pollutants analyzed at concentrations higher than the value recommended by the WHO for drinking water. Cadmium and cobalt were not detected in all water samples taken from the boreholes. This could be linked to the fact that our study sites are not full of sources emitting these two elements or to the detection limits of the method used. For zinc, all concentrations detected in borehole water are within WHO standards (500 µg/L). Sulfur is present in all samples analyzed at very high concentrations. Concerning lead, it is present in the waters of the boreholes of Erymakouguie (Agboville), Anyama reference, MACA Cité ADO and M'badon at concentrations significantly higher than the WHO guideline value (10 µg/ L). It is also present in the Abobo Coco Service and Koumassi industrial zone boreholes at concentrations three times higher than the value recommended by the WHO (10 µg/L) and in the FILTISAC borehole at an average concentration thirteen times higher. to that of water potability defined by the WHO (10 µg/L). Arsenic is present only in water sampled at FILTISAC at an average concentration three times higher than the value recommended by the WHO for drinking water (10 µg/L). Likewise, copper is only detected in the water from the FILTISAC borehole but at a concentration lower than that recommended by the WHO (1000 µg/L). Chromium analysis showed its presence in the waters of VRIDI LD, Abobo Coco Service and FILTISAC boreholes at average concentrations lower than the threshold value recommended by the WHO (50 µg/L). Regarding nickel, it is present at concentrations consistent with that established by the WHO (70 µg/L) in the waters of the Erymakouguie (Agboville), MACA Cité ADO and Koumassi 1 boreholes. The presence of these metallic pollutants in significant quantities in groundwater would be linked to the presence of numerous anthropogenic activities such as artisanal, domestic, agricultural and industrial activities. This is the case, for example, in the areas of Erymakouguie (Agboville) and Anyama, which are full of agricultural activities requiring heavy use of herbicides. We also have the areas of Koumassi, VRIDI

LD and FILTISAC which are full of industrial activities near these drillings. Indeed, studies have shown that anthropogenic activities could have effects on metal pollution of groundwater in the city of Abidjan [6]. As for de Zhang et *al.* [18], they showed the impact of discharges from anthropogenic activities and soil erosion on the presence of certain metallic trace elements in well water.

Table 5. Average concentrations (µg/L) of ETM in groundwater

Chemical compound	**Locality**						
	VR	**DK**	**AC**	**ER**	**CR**	**AP**	**AR**
As	<15	<15	<15	<15	<15	<15	<15
Pb	<10	<10	31±1,3	12±1	<10	<10	12±0,5
Cd	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5
Cr	20±0,7	<5	5,8±0,9	<5	<5	<5	<5
Co	<5	<5	<5	<5	<5	<5	<5
Cu	<10	<10	<10	<10	<10	<10	<10
Ni	<10	<10	<10	11±0,7	<10	<10	<10
S	1700±10	1400±6,7	1700±11	230±8,8	140±0,7	1500±50	260±1,5
Zn	24±0,5	61±2	150±5	120±3	50±1	70±2,02	74±3

VR : VRIDI LDC ; **DK** : Dokui 2 ; **AC** : ABOBO COCO SERVICE ; **ER** : ERYMAKOUGUIE ; **CR** : 4. CROIX ; **AP** : ALEPE 1 ; **AR** : ANYAMA REFERENCE ;

Table 5. (Continue..**)**

Chemical compound	**Locality**					
	KM	**MC**	**FI**	**AK**	**MB**	**AS**
As	<15	<15	39±1,5	<15	<15	<15
Pb	37±2	13±1	130±3,3	<10	16±1,3	<10
Cd	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5
Cr	<5	<5	11±1,5	<5	<5	<5
Co	<5	<5	<5	<5	<5	<5
Cu	<10	<10	80±3	<10	<10	<10
Ni	11±1,7	18±1,7	73±1	<10	<10	<10
S	21000±120	9800±66,7	1700±33,7	1800±20	900±82,3	57±2

Zn	87±4	78±2	200±1,7	92±0,7	75±5	84±3

KM : KOUMASSI zone industrielle ; **MC** : MACA CITE ADO ; **FI** : FILTISSAC ; **AK** : AKOUEDO ; **MB** : M'BADON ; **AS** : ABOBO SAGBE

3.4.Health risks linked to the consumption of borehole water in adults, children and infants

The health risks linked to the ingestion of water from boreholes in the autonomous district of Abidjan estimated in this study concern elements whose concentrations are higher than the detection limits and having Toxicological Reference Values (VTR) available as well as the knowledge of their epidemiological effects on humans. The study focuses on chronic exposures because the water is supposed to be consumed orally.

3.4.1. Estimated level of exposure of the population

The estimate of the level of exposure to glyphosate, sulfur and ETMs linked to the consumption of water from boreholes in the autonomous district of Abidjan in infants weighing 5 kg, children weighing 10 kg and adults weighing 60 kg is shown. in **Tables 6-8**.

By observing the results obtained (**Table 6-8**), it appears that the daily exposure doses (DJE) are approximately four times higher in infants weighing 5 kg and three times higher in children weighing 10 kg than in children weighing 10 kg. adults weighing 60 kg regardless of the area considered.

For glyphosate, the maximum DJE are: 0.286 µg/kg/j (in infants weighing 5 kg), 0.19 µg/kg/j (in children weighing 10 kg) and 0.063 µg/kg/j (in adults weighing 60 kg). The maximum DJE are observed in the locality of AboboSagbé (AS).

For sulfur, the maximum DJE are obtained in the Koumassi 1 (KM) with respective values of 3158.4 µg/kg/j (infants weighing 5 kg), 2100 µg/kg/j (children weighing 10 kg) and 700 µg/kg/j (adults weighing 60 kg).

Concerning zinc, the highest DJE are obtained at the population level of the FILTISAC (FI) zone with values of 30.08 µg/kg/j (5 kg infants), 20 µg/kg/j (children weighing 10 kg) and 6.67 µg/kg/j (adults weighing 60 kg) respectively.

Concerning lead, the calculated DJE are higher for the FILTISAC population with respective maximum values of 19.552 µg/kg/j (infants weighing 5 kg), 13 µg/kg/j (children weighing 10 kg) and 4.3333 µg/kg/j (adults weighing 60 kg).

For nickel, the highest DJE are for infants weighing 5 kg (10.98 µg/kg/j), children weighing 10 kg (7.3 µg/kg/j) and adults weighing 60 kg (2 .4333 µg/kg/j) all alive in the FILTISAC area.

As for chromium, the highest DJE are in infants weighing 5 kg (3.0008 µg/kg/j), children weighing 10 kg (2 µg/kg/j) and adults weighing 60 kg (0.67 µg/kg/j) residents in the Vridi area.

The only DJE values obtained for copper and arsenic are obtained within the population of the FILTISAC area with respective values of 12.032 µg/kg/j (5 kg infants), 8 µg/kg/j (children of 10 kg) and 2.67 µg/kg/j (adults of 60 kg) for copper and 5.9 µg/kg/j (infants of 5 kg), 3.9 µg/kg/j (children of 10 kg) and 1.3 µg/kg/j (adults) for arsenic.

Table 6. Daily exposure doses (µg/kg/j) for a 60 kg adult consuming 2 L/day

Chemical compound	Locality												
	VR	**DK**	**AC**	**ER**	**CR**	**AP**	**AR**	**KM**	**MC**	**FI**	**AK**	**MB**	**AS**
Glyphosate	0,004	0,007	0,007	0,009	0,009	0,01	0,011	0,013	0,013	0,014	0,014	0,037	0,063
S	56,67	46,67	56,67	7,67	4,67	50	8,67	700	326,67	56,67	60	30	1,9
Zn	0,8	2,03	5	4	1,67	2,33	2,47	2,9	2,6	6,67	3,067	2,5	2,8
Pb			1,033	0,4			0,4	1,2333	0,4333	4,3333		0,5333	
Ni				0,3667				0,3667	0,6	2,4333			
Cr	0,67		0,19							0,37			
Cu										2,67			
As										1,3			

Table 7. Daily exposure doses (µg/kg/j) for a child weighing 10 kg consuming 1L/day

Chemical compound	**Locality**												
	VR	**DK**	**AC**	**ER**	**CR**	**AP**	**AR**	**KM**	**MC**	**FI**	**AK**	**MB**	**AS**
Glyphosate	0,012	0,021	0,022	0,027	0,028	0,031	0,032	0,038	0,039	0,042	0,043	0,11	0,19
S	170	140	170	23	14	150	26	2100	980	170	180	90	5,7
Zn	2,4	6,1	15	12	5	7	7,4	8,7	7,8	20	9,2	7,5	8,4
Pb			3,1	1,2			1,2	3,7	1,3	13		1,6	
Ni				1,1				1,1	1,8	7,3			
Cr	2		0,58							1,1			
Cu										8			
As										3,9			

Table 8. Daily exposure doses (µg/kg/j) for a 5 kg infant consuming 0.75 L/day

Chemical compound	**Locality**												
	VR	**DK**	**AC**	**ER**	**CR**	**AP**	**AR**	**KM**	**MC**	**FI**	**AK**	**MB**	**AS**
Glyphosate	0,018	0,032	0,033	0,041	0,042	0,0467	0,048	0,057	0,059	0,063	0,065	0,165	0,286
S	255,68	210,56	255,68	34,592	21,056	225,6	39,104	3158,4	1473,92	255,68	270,72	135,36	8,573
Zn	3,61	9,17	22,56	18,05	7,52	10,53	11,13	5,56	13,08	30,08	13,84	11,28	12,63
Pb			4,6624	1,8048			1,8048	5,5648	1,9552	19,552		2,4064	
Ni				1,654				1,654	2,707	10,98			
Cr	3,008		0,8723							1,6544			
Cu										12,032			
As										5,9			

VR : VRIDI LDC ; **DK** : Dokui 2 ; **AC** : ABOBO COCO SERVICE ; **ER** : ERYMAKOUGUIE ; **CR** : 4. CROIX ; **AP** : ALEPE 1 ; **AR** : ANYAMA REFERENCE ; **KM** : KOUMASSI zone industrielle ; **MC** : MACA CITE ADO ; **FI** : FILTISSAC ; **AK** : AKOUEDO ; **MB** : M'BADON ; **AS** : ABOBO SAGBE

3.4.2. Risk characterization

Risk characterization was carried out by calculating danger quotients. For glyphosate (**Table 9-11**), the minimum danger quotients (QD) are recorded in the locality of Vridi and the maximums in the locality of AboboSagbé. They vary from 0.00006 to 0.001 in infants weighing 5 kg, from 0.00004 to 0.0006 in children weighing 10 kg and from 0.000013 to 0.0002 in adults weighing 60 kg.

For zinc (**Table 9-11**), the minimum QD are obtained in the Vridi zone and the maximums in the FILTISAC zone. In infants, they vary from 0.012 to 1.55 (QD>1). In children weighing 10 kg, they range between 0.008 and 0.067. In adults weighing 60 kg, they range between 0.003 and 0.022 (QD<1).

Concerning lead (**Table 9-11**), the minimum QD are obtained in the Erymakouguie and Anyama reference zone and the maximums in the FILTISAC zone. In infants, they vary from 0.5156 to 5.5862 (QD>1). Also, the QD obtained in the areas of Koumassi (QD= 1.5899) and Abobo Coco Service (QD= 1.3321) are greater than 1. Among children, they oscillate between 0.3429 and 3.7143 (QD>1). The QD obtained in the Koumassi area (QD= 1.0571) is greater than 1. In the population of adults weighing 60 kg, they vary from 0.1143 to 1.2381 (QD>1).

Concerning nickel (**Table 9-11**), the minimums are observed in the localities of Erymakouguie and Koumassi industrial zone, on the other hand the maximums come from the FILTISAC zone. The QD obtained in 5 kg infants from these localities range between 0.0827 and 0.5490 (QD<1). In children weighing 10 kg, they vary from 0.055 to 0.365 (QD<1). In adults, QDs varying from 0.0183 to 0.1217 (QD<1) were detected.

The QD obtained for chromium (**Table 9-11**) have minimums observed in the Anyama Reference location, on the other hand the maximums were found in the Vridi area. They vary from 0.2908 to 1.0027 (QD>1) in infants weighing 5 kg, from 0.1933 to 0.6667 (QD<1) in children weighing 10 kg and from 0.0644 to 0.2222 (QD<1) in adults weighing 60 kg.

The QD for copper (**Table 9-11**) were found only in the FILTISAC area with respective values of 1.2032 (QD>1) in infants weighing 5 kg, 0.8 (QD<1) in children weighing 10 kg and 0.27 (QD<1) in adults weighing 60 kg.

As for arsenic (**Table 9-11**), QD of 19.6 (well above 1) were detected in infants weighing 5 kg, 13 (well above 1) in children weighing 10 kg and of 4.33 (QD>1) also higher than the normal danger quotient in adults weighing 60 kg.

Although the daily consumption of water from boreholes is low in infants and children, the danger quotients calculated in relation to daily exposure doses reveal that the QD in infants and children are higher than in adults consuming more water (**Table 9-11**). This could be linked to their low body weight and physiological fragility. Studies have shown that in the bodies of infants and children, contaminants are easily absorbed [19].

The level of population exposure to glyphosate due to ingestion of borehole water is very littleprobable (QD < 1) in infants weighing 5 kg, children weighing 10 kg and adults weighing 60 kg. Glyphosate is an organic compound with proven toxicity. The level of exposure to glyphosate among the entire population of the autonomous district of Abidjan is very little probable. However, glyphosate has been shown to be mutagenic, genotoxic, carcinogenic and to have cellular, reproductive, cardiovascular, cerebral, cellular, digestive effects for humans [20] and congenital malformations in children [21].

The level of population exposure to zinc linked to the ingestion of borehole water is little probable (QD < 1) in infants weighing 5 kg, children weighing 10 kg and adults weighing 60 kg. But probable in infants (QD = 1.55>1) in the Koumassi area. Indeed, studies have shown that acute zinc poisoning linked to the ingestion of water would cause gastrointestinal disorders and diarrhea in exposed populations [22].

The level of population exposure to nickel linked to the ingestion of borehole water is little probable among infants, children and adults in all localities consuming borehole water. However, a study showed the case of death of a child after ingestion of 570 mg of nickel/kg orally [23] as well as cases of intestinal disorders such as nausea, abdominal cramps and diarrhea within the population [24]. The literature noted that depending on the route of penetration into the body, immunological, hematological, hepatic, renal, genotoxic effects on embryonic development and reproduction of nickel were possible [25, 26]. According to epidemiological studies, nickel taken in small quantities is relatively essential for human nutrition, but could be dangerous by exceeding the tolerated dose. At a low and prolonged level of exposure, nausea, vomiting and dizziness have been observed. For the WHO [27], the effects linked to nickel toxicity are pulmonary embolisms, respiratory failures, birth failures, asthma and chronic bronchitis, allergic reactions such as skin rashes and heart problems.

The level of population exposure to chromium linked to the ingestion of borehole water is little probable in infants, children and adults in most study areas. However, it is probable in infants (QD= 1.0027>1) in the Vridi zone. Indeed, studies have shown negative effects after ingesting chromium. These are disorders of the digestive tract such as bloody diarrhea, vomiting, spasms, methemoglobin malformations, liver and kidney damage [28].

The level of population exposure to arsenic linked to the consumption of water from boreholes in the FILTISAC area is probable among adults weighing 60 kg (QD = 4.33>1). It is very probable in children weighing 10 kg (QD= 13) and in infants weighing 5 kg (QD= 19.6>1). Studies have demonstrated that the negative effects linked to exposure to arsenic could manifest themselves in the form of more or less pronounced gastrointestinal, hepatic and renal disorders, cardiovascular manifestations, hypertension and tachycardia [6].

The level of population exposure to lead linked to the ingestion of borehole water is little probable in infants, children and adults (QD < 1) in several localities but probable in some places. In adults (QD= 1.2381>1) from the FILTISAC area, it is probable. In children, it is very probable in the FILTISAC zone (QD= 3.7143>1) and probable in the Koumassi zone (QD= 1.0571>1). In infants, it is very probable in the FILTISAC zones (QD= 5.5862>1), probable in Koumassi (QD=1.5899>1) and Abobo Coco Service (QD= 1.3321>1). Pb is a metallic element that is not essential for metabolism in humans [6]. The work revealed its very toxic nature for humans [29]. Exposure to Pb through ingestion of water has the toxicological consequences on human health of damage to the cardiovascular system, the central and peripheral nervous system and the kidney. The fetus and young children under 2 years of age are declared by Health Canada [30] sensitive to the neurobehavioral toxic effect of lead.

The level of population exposure to copper linked to the consumption of borehole water is little probable among infants, children and adults in the study areas. However, it is probable in infants (QD= 1.2032>1) in the FILTISAC area. Indeed, the studies carried out by Pizarro et *al.* [31] on 60 women who received doses of 0, 1, 3 or 5 mg of copper sulfate/L through drinking water for 2 weeks showed a significant increase in the incidence of gastrointestinal disorders such as diarrhea, nausea, abdominal pain and vomiting. In Togo, studies have shown that children consuming surface and groundwater from the phosphate mining area were more exposed to the toxic effects of Cd, Pb and Cu than adults [6].

Considering the results obtained during this study, it appears that the consumption of water from boreholes in the autonomous district of Abidjan containing glyphosate and ETMs does not present any health risk within the population in certain areas consuming this water given that danger quotients are less than 1. For reference institutions in toxicological studies such as the US EPA, INERIS and INVS, MENTION FULL FORMS the populations of these localities are theoretically out of danger. On the other hand, the consumption of this water containing ETMs such as Zn, Pb, Cr, Cu and As in other localities is very risky because of danger quotients greater than 1. For QD > 1, the health of the population of these localities is affected, that is to say they are exposed to danger.

Table 9. Danger quotients for a 60 kg adult consuming 2 L/day

Chemical compound	**Locality**												
	VR	**DK**	**AC**	**ER**	**CR**	**AP**	**AR**	**KM**	**MC**	**FI**	**AK**	**MB**	**AS**
Glyphosate	$1,33.10^{-5}$	$2,33.10^{-5}$	$2,44.10^{-5}$	0,00003	$3,11.10^{-5}$	$3,44.10^{-5}$	$3,56.10^{-5}$	$4,22.10^{-5}$	$4,33.10^{-5}$	$4,67.10^{-5}$	$4,78.10^{-5}$	0,0001	0,0002
Zn	0,003	0,007	0,017	0,013	0,006	0,008	0,008	0,01	0,009	0,022	0,01	0,008	0,009
Pb			0,295	0,1143			0,1143	0,3524	0,1238	**1,2381**		0,1524	
Ni				0,0183				0,0183	0,03	0,1217			
Cr	0,2222		0,0644							0,1222			
Cu										0,27			
As										**4,33**			

Table 10. Danger quotients for a child weighing 10 kg consuming 1L/day

Chemical compound	**Locality**												
	VR	**DK**	**AC**	**ER**	**CR**	**AP**	**AR**	**KM**	**MC**	**FI**	**AK**	**MB**	**AS**
Glyphosate	0,00004	0,00007	0,000073	0,00009	0,000093	0,0001	0,0001	0,0001	0,0001	0,0001	0,0001	0,0004	0,0006
Zn	0,008	0,02	0,05	0,04	0,017	0,023	0,025	0,03	0,026	0,067	0,031	0,025	0,028
Pb			0,8857	0,3429		0,3429		**1,0571**	0,3714	**3,7143**		0,4571	
Ni				0,055				0,055	0,09	0,365			
Cr	0,6667		0,1933							0,3667			
Cu										0,8			
As										**13**			

Table 11. Danger quotients for a 5 kg infant consuming 0.75 L/day

Chemical compound	**Locality**												
	VR	**DK**	**AC**	**ER**	**CR**	**AP**	**AR**	**KM**	**MC**	**FI**	**AK**	**MB**	**AS**
Glyphosate	0,00006	0,00011	0,00011	0,00014	0,00014	0,00016	0,00016	0,0002	0,0002	0,0002	0,0002	0,0006	0,001
Zn	0,012	0,031	0,075	0,06	0,025	0,035	0,037	1,55	0,044	0,1	0,046	0,038	0,042
Pb			**1,3321**	0,5156			0,5156	1,5899	0,5586	5,5862		0,6875	
Ni				0,0827				0,0827	0,1354	0,5490			
Cr	**1,0027**		0,2908							0,5515			
Cu										1,2032			
As										19,6			

VR : VRIDI LDC ; **DK** : Dokui 2 ; **AC** : ABOBO COCO SERVICE ; **ER** : ERYMAKOUGUIE ; **CR** : 4. CROIX ; **AP** : ALEPE 1 ; **AR** : ANYAMA REFERENCE ; **KM** : KOUMASSI 1 ; **MC** : MACA CITE ADO ; **FI** : FILTISSAC ; **AK** : AKOUEDO ; **MB** : M'BADON ; **AS** : ABOBO SAGBE

3.5. Principal component analysis (ACP) of chemical compounds in water and drilling parameters

ACP was carried out on 13 water samples and applied to 9 variables. The correlation matrix of glyphosate, sulfur, lead, arsenic, zinc, pH, temperature, depth and conductivity (**Table 12**) shows that there is a good correlation between the 9 variables (p= 0.05000) used to carry out our ACP.

Compared to Factor 1 (axis 1), a group formed by arsenic (-0.875604), lead (-0.926540) and zinc (-0.742363) emerges. Which means that these three ETM are strongly correlated to the axis. Studies carried out on the origin of these ETM have shown that their presence in groundwater is linked to discharges from human activities but also from soil erosion.

Compared to Factor 2 (axis 2), a group formed by the variables depth (-0.842222) and temperature (0.744007) stands out. Which means that these two parameters are strongly correlated to the axis in an inverse way.

Compared to Factor 3 (axis 3), a group formed by the Sulfur variable (-0.904595) stands out. Sulfur is an element naturally present in soils. Studies have shown that the presence of sulfate ions (SO_4^{2-}) in the waters of the aquifer comes from the dissolution of gypsum and the oxidation of pyrite.

Compared to Factor 4 (axis 4), a group formed by glyphosate (-0.847445) stands out. Indeed, glyphosate is a synthetic molecule whose presence in the environmental environment comes from human activities.

Considering these results, it appears that the presence of glyphosate in these waters is independent of ETM, sulfur, pH, temperature and conductivity.

Table 12. Correlation matrix of variables and factors for glyphosate, sulfur, ETM, pH, temperature, depth and electrical conductivity

	Factor-variable correlations (factor loadings) based on correlations (Standardized ACP)								
Variable	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**	**Factor 6**	**Factor 7**	**Factor 8**	**Factor 9**
Depth	0,106866	**-0,842222**	-0,019558	0,273435	0,141529	0,408975	0,094397	-0,088808	0,001983
Glyphosate	0,257704	-0,410583	-0,098134	**-0,847445**	0,174209	0,047065	-0,047764	-0,048695	0,000044
Arsenic	**-0,875604**	-0,365154	0,051205	-0,035326	0,146818	-0,155279	0,218865	-0,013528	-0,048567
Lead	**-0,926540**	-0,298829	-0,130582	-0,029461	0,084192	-0,116034	0,101284	-0,006530	0,058762
Sulfur	-0,082761	0,304257	**-0,904595**	0,137955	0,158083	-0,050892	-0,103163	-0,157978	-0,008661
Zinc	**-0,742363**	-0,528855	-0,074418	0,039243	-0,073505	0,066697	-0,371168	0,119929	-0,011429
Temperature	-0,261283	**0,744007**	0,113652	-0,002050	0,566536	0,174236	-0,016201	0,116957	0,001025

pH	-0,620991	0,477777	0,543938	-0,069206	-0,076116	0,087723	-0,124500	-0,237596	-0,000469
Conductivity	-0,530570	0,522312	-0,355448	-0,241210	-0,387920	0,290266	0,146864	0,069521	-0,004659

No. of active vars: **9** No. of supplementary vars: **0**
No. of active cases: **13** No. of supplementary cases: **0**
Eigenvalues : **2,99634 2,52744 1,28864 , 878594 , 586656 …**

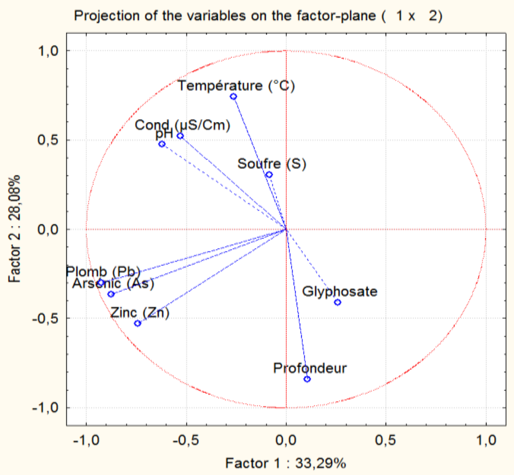

Figure 2. ACP of glyphosate, S, Pb, As, Zn, pH, Temperature, depth and conductivity

4. Conclusions

This study aimed to study the level of contamination of groundwater water in the autonomous district of Abidjan by glyphosate and trace metal elements in order to assess the health risks to which the population of these areas are exposed by consuming this water. The study was carried out on water taken from thirteen boreholes installed in strategic locations in this area. The average temperature values are above the standards, while the pH and conductivities are within the standards recommended by the WHO for drinking water. The results from the analyzes of chemical compounds show concentrations of glyphosate, lead and arsenic higher than that defined by the WHO for drinking water. Cadmium and cobalt were not detected in all water samples taken. All concentrations of zinc, copper, chromium and nickel detected in the borehole waters comply with those established by the WHO. Sulfur is present in all samples analyzed at very high concentrations. The assessment of health risks in infants, children and adults linked to the consumption of these polluted waters shows danger quotients greater than 1 in certain localities. Which suggests a risk of poisoning of the population using these waters. In view of these results, the consumption of this water from drilling in the autonomous district of Abidjan must be done with great moderation because of the very high levels of contaminants and danger quotients. We call on public decision-makers to become aware of the dangers to which populations are exposed in order to preserve, protect and improve public hygiene conditions by offering good quality drinking water to the population to reduce the risk. poisoning and mortality.

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