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Assessment and Health Risks of Glyphosate Residues and Traces Metals Elements in Groundwater Arround Abidjan Region, Côte d'Ivoire

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Hydraulic networks from groundwater are the resources most exploited by the population for their daily needs. These water tables are constantly under pressure from pollution caused by human activities. In the tropical zone, more particularly in Ivory Coast, very few studies have been carried out on glyphosate, aminomethylphosphonic acid (AMPA), glufosinate and metallic trace elements (ETM) in groundwater. This study aims to determine the level of vulnerability of groundwater by these compounds. The study covered the waters of thirteen boreholes with an average depth of

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69.26 meters near the Abidjan region (5°25'0" N / 4°1'60" W) and the analyzes were carried out using the chromatographic method with detection by spectrophotometry. The results revealed the presence of glyphosate 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 higher than the water potability threshold value (0.1 µg/L) defined by the WHO. As for ETM, they are present in these boreholes at high 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 conducted throughout the national territory.

Keywords: ETM; glyphosate; chromatographic method with detection by spectrophotometry; mathematical model; groundwater pollution; health risks.

1. INTRODUCTION

its IUPAC N-Glyphosate or name phosphonomethylglycine is an organophosphate herbicide with the chemical formula C₃H₈NO₅P [1]. It is a synthetic molecule which was produced for the first time in 1970, inspired by glycine, a natural molecule (Fig. 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]. Its degradation in the environment would yield metabolites such as aminomethylphosphonic acid (AMPA) and glufosinate. 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. Trace metal impurities have been found in glyphosate-based herbicide products [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 Abidjan region, 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 glyphosate, on acid aminomethylphosphonic (AMPA) and glufosinate for their persistence and toxicity and trace metal elements (ETM) for their nonbiodegradable 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) (Fig. 1) as well as glufosinate (Fig. 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 ETM 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. 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 $(1.18 \mu g/L)$ in well water and Pb $(4.08 \mu g/L)$, Cd $(0.08 \mu g/L)$ and As $(1.76 \mu g/L)$ 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 Abidian 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 groundwater in the Abidjan region and to assess the health risks linked to the consumption of this water by the population.

2. MATERIALS AND METHODS

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 subequatorial, 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.

Measurement of physicochemicalparameters: Measurements of temperature, pH and electrical conductivity were carried out on site in three tests on each sample taken using electrochemical probes (a WTW multi 3430 brand multiparameter, a METTLER TOLEDO brand pH meter).

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-CI ((9-

fluorenvlmethyl)-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 gradient column. The chromatographic 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.

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).

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).



Fig. 1. Chemical structures of glyphosate, AMPA and glufosinate

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
МС	X=380 287E; Y=598 163N	128,15
DK	X=388 575E; Y=595 409N	45,1

Table 1. UTM coordinates and depth of boreholes

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Locality	UTM coordinates	Drillingdepth (m)
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

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:

 $DJE = (Ce \times Qe \times Te)/Pc(I)$

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: QD = DJE/VTR (II)

With **VTR**: Toxicological reference value (μ g/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).

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:

Vcr= (Ca-Mc)/E

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

3. RESULTS

Measurements of physico-chemical parameters sampled: of water The measurements taken on the water from the parameters: boreholes concerned three temperatures, pH and conductivities. The average values of the measurements carried out on the site are presented in Table 3.

The average values vary from 27.3 ± 1.1 to $31.8\pm1^{\circ}C$ for temperatures, from 4.23 ± 0.01 to 6.56 ± 0.1 for pH and from 39.9 ± 1 .5 to 385 ± 1.3 µS/Cm for conductivities.

The results detected during the analysis of these parameters in the water samples show that the highest average temperature and pH are obtained in the water from the Vridi borehole at respective values of $31.8\pm1^{\circ}$ C and 6.56 ± 0.1 . Concerning the average conductivity, the highest value ($385\pm1.3 \mu$ S/Cm) was obtained in the water from the Koumassi industrial area borehole.

Table 2.	VTR	used	in	this	study	[13,	14]
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	Composé organique	Metal trace elements							
	Glyphosate	As	Cd	Со	Cr	Cu	Ni	Pb	Zn
VTR (µg/kg. j)	300	0,3	0,2	500	3	10	20	3,5	300

Concentrations of glyphosate and its derivatives in groundwater: The concentrations measured in glufosinate, glyphosate and AMPA in the water samples taken from the boreholes are shown in Table 4.

According to the results, the determined glyphosate concentrations vary between 0.12 $\pm 0.02 \mu g/L$ (Vridi site drilling) and 1.9 $\pm 1 \mu g/L$ (Abobo Sagbé drilling). On the other hand, we observed an absence of AMPA and glufosinate in all the samples analyzed.

Concentrations of trace metal elements in groundwater: The average concentrations of trace metal elements in borehole water are reported in Table 5. The raw results show different concentrations from one area to another.

results show cadmium and cobalt The concentrations below the limit of quantification in all samples analyzed. Concerning arsenic, it is only detected in water sampled at FILTISAC with an average value of 39±1.5 µg/L. For Lead, it was detected in seven boreholes at average concentrations varying between 12±1 µg/L and 130±3.3 µg/L. The highest average value (130±3.3 µg/L) was detected in water sampled at FILTISAC. Concerning chromium, it was obtained in the waters sampled in Vridi. Abobo Coco service and FILTISAC at respective concentrations of 20±0.7 µg/L, 5.8±0.9 µg/L and 11±1.5 µg/L. Regarding copper, it was only detected in the water from the FILTISAC borehole at an average concentration of 80±3 µg/L. Nickel is obtained in the waters of four boreholes at average concentrations ranging µq/L between 11±0.7 and 73±1 μg/L.

Table 3. Physico-chemical parameters of water samples

Parameter	n= 3		Locality									
		VR	DK	AC	ER	CR	AP					
T (°C)	3	31,8 <u>+</u> 1	27,3±1,1	27,5±1,1	29,7±0,4	27,6±0,2	27,7 <u>+</u> 0,2					
рН	3	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)	3	367±10	294 ±2	319 ±1,2	87,5± 1	58,1±1	92,2± 2					
	V . Dala	D. AC . ADO										

VR : VRIDI LDC ; DK : Dokui 2; AC : ABOBO COCO SERVICE ; ER : ERYMAKOUGUIE ; CR : 4. CROIX ; AP : ALEPE 1 ; n= number of measurements

Table 3. (Continue)

parameter	n= 3		Locality									
		AR	KM	MC	FI	AK	MB	AS				
T (°C)	3	29,7 <u>±</u> 0,9	29,6±0,9	28,4 <u>+</u> 0,5	28,6±1,5	27,3±1,1	28,1±1,4	27,7±1,2				
рН	3	5,39 <u>+</u> 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)	3	39,9±1,5	385± 1,3	49,3±2,2	259±1,5	66,8±1,3	86,3±1, 8	168,9 <u>+</u> 2,3				
AR : ANYAMA	AR : ANYAMA REFERENCE ; KM : KOUMASSI 1 ; MC : MACA CITE ADO ; FI : FILTISSAC ; AK : AKOUEDO ; MB :											
M'BADON ; A	M'BADON ; AS : ABOBO SAGBE ; Cond : Conductivité ; T : Température ; pH : Potentiel Hydrogène, n= number of											
			r	neasurements	:							

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

Chemical	_	Locality										
compound	n= 3	VR	DK	AC	ER	CR	AP	AR				
Glyphosate	3	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	3	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05				
Glufosinate	3	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05				
VR : VRIDI LDC ;	VR : VRIDI LDC : DK : Dokui 2 : AC : ABOBO COCO SERVICE : ER : ERYMAKOUGUIE : CR : 4. CROIX : AP : ALEPE 1 : AR											

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

Table 4. (Continue)

Chemical compound		Locality										
-	n= 3	KM	MC	FI	AK	MB	AS					
Glyphosate	3	0,38±0,03	0,39±0,02	0,42±0,04	0,43±0,02	1,1±0,07	1,9±1					
AMPA	3	<0,05	<0,05	<0,05	<0,05	<0,05	<0,05					
Glufosinate	3	<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, n= number of measurements The highest value was obtained in the samples taken from the FILTISAC borehole. Sulfur was quantified in all samples at concentrations ranging from $57\pm2 \ \mu g/L$ to $21000\pm120 \ \mu g/L$. The maximum concentration is obtained at Koumassi with an average value of $21000\pm120 \ \mu g/L$. Zinc was detected in all samples at concentrations varying between $24\pm0.5 \ \mu g/L$ and $200\pm1.7 \ \mu g/L$. The highest concentration ($200\pm1.7 \ \mu g/L$) was obtained in FILTISAC water.

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.

Estimated level of exposure of the population: The estimate of the level of

exposure to glyphosate, sulfur and ETM linked to the consumption of water from boreholes near the Abidjan region 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 (Tables 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 μ g/kg/j (in infants weighing 5 kg), 0.19 μ g/kg/j (in children weighing 10 kg) and 0.063 μ g/kg/j (in adults weighing 60 kg). The maximum DJE are observed in the locality of Abobo Sagbé (AS).

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

Table 5. Average concentration	s (µg/L) of ETM in groundwater
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Chemical compound	n= 3				Locality			
		VR	DK	AC	ER	CR	AP	AR
As	3	<15	<15	<15	<15	<15	<15	<15
Pb	3	<10	<10	31±1,3	12±1	<10	<10	12±0,5
Cd	3	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5
Cr	3	20±0,7	<5	5,8±0,9	<5	<5	<5	<5
Со	3	<5	<5	<5	<5	<5	<5	<5
Cu	3	<10	<10	<10	<10	<10	<10	<10
Ni	3	<10	<10	<10	11±0,7	<10	<10	<10
S	3	1700±10	1400±6,7	1700±11	230±8,8	140±0,7	1500±50	260±1,5
Zn	3	24±0,5	61±2	150±5	120±3	50±1	70±2,02	74±3
	kui 2 · AC	· ABOBO CO		· ED · EDVA	INKOUGUIE	· CD · A CD	OIX · AB · AL	

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

Table 5. (Continue)

Chemical	n= 3			Locality	1		
compound		KM	MC	FI	AK	MB	AS
As	3	<15	<15	39±1,5	<15	<15	<15
Pb	3	37±2	13±1	130±3,3	<10	16±1,3	<10
Cd	3	<0,5	<0,5	<0,5	<0,5	<0,5	<0,5
Cr	3	<5	<5	11±1,5	<5	<5	<5
Co	3	<5	<5	<5	<5	<5	<5
Cu	3	<10	<10	80±3	<10	<10	<10
Ni	3	11±1,7	18±1,7	73±1	<10	<10	<10
S	3	21000±120	9800±66,7	1700±33,7	1800±20	900±82,3	57±2
Zn	3	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, n= number of measurements Concerning zinc, the highest DJE are obtained at the population level of the FILTISAC area with values of 30.08 μ g/kg/j (5 kg infants), 20 μ g/kg/j (children weighing 10 kg) and 6.67 μ g/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 μ g/kg/j (infants weighing 5 kg), 13 μ g/kg/j (children weighing 10 kg) and 4.3333 μ g/kg/j (adults weighing 60 kg).

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

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

The only DJE values obtained for copper and arsenic come from the locality of FILTISAC with respective values of 12.032 μ g/kg/j (infants weighing 5 kg), 8 μ g/kg/j (children weighing 10 kg) and 2.67 μ g/kg/j (adults weighing 60 kg) for copper and 5.9 μ g/kg/j (infants weighing 5 kg), 3.9 μ g/kg/j (children weighing 10 kg) and 1 .3 μ g/kg/j (adults) for arsenic.

Characterization of health risk: Danger quotients (QD) for glyphosate and ETM with concentrations above the limit of quantification and known VTR were calculated. The danger quotients corresponding to the different daily exposure doses determined in infants weighing 5 kg, children weighing 10 kg and adults weighing 60 kg are recorded in Tables 9-11.

For glyphosate, the minimum danger quotients (QD) are recorded in the locality of Vridi and the maximums in the locality of Abobo Sagbé. 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, the QD minimums are obtained in the locality of Vridi and the maximums in the locality of FILTISAC. In infants, they vary from 0.012 to 1.55. In children weighing 10 kg, they vary between 0.008 and 0.067. In adults weighing 60 kg, they vary between 0.003 and 0.022.

Concerning lead, the QD minimums are obtained in the localities of Erymakouguie and Anyama and the maximums in the locality of FILTISAC. In infants, they vary from 0.5156 to 5.5862. 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. 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.

Concerning nickel, the minimums are observed in the localities of Erymakouguie and the industrial area of Koumassi, on the other hand the maximums come from the locality of FILTISAC. The QD obtained in 5 kg infants from these localities are between 0.0827 and 0.5490. In children weighing 10 kg, they vary from 0.055 to 0.365. In adults, they vary from 0.0183 to 0.1217.

The QD obtained for chromium have minimums observed in the locality of Anyama Reference, on the other hand the maximums were found in the Vridi area. They vary from 0.2908 to 1.0027 in infants weighing 5 kg, from 0.1933 to 0.6667 in children weighing 10 kg and from 0.0644 to 0.2222 in adults weighing 60 kg.

he QD for copper were found only in the locality of FILTISAC with respective values of 1.2032 in infants weighing 5 kg, 0.8 in children weighing 10 kg and 0.27 in adults weighing 60 kg.

Regarding arsenic, QD of 19.6 (well above 1) were detected in infants weighing 5 kg, 13 (well above 1) in children weighing 10 kg and 4.33 also above the normal danger quotient for adults weighing 60 kg.

Considering these results, it appears that all the QD in infants weighing 5 kg and children weighing 10 kg are all higher than those of adults weighing 60 kg. Some of these QD are less than 1, while others are greater than 1.

4. DISCUSSION

Distribution of physico-chemical parameters: Temperature, pH and conductivity in borehole water: The physicochemical parameters of the samples were carried out on site. The minimum mean temperature value found in our study is close to that found by Yao et al. [15] in the Soubré area, a tropical watershed in the southwest of lvory Costa. It is also substantially

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

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

Chemical compound	nical 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			
Glyphosate S Zn Pb Ni Cr Cu As	0,012 170 2,4 2	0,021 140 6,1	0,022 170 15 3,1 0,58	0,027 23 12 1,2 1,1	0,028 14 5	0,031 150 7	0,032 26 7,4 1,2	0,038 2100 8,7 3,7 1,1	0,039 980 7,8 1,3 1,8	0,042 170 20 13 7,3 1,1 8 3,9	0,043 180 9,2	0,11 90 7,5 1,6	0,1 5,7 8,4

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

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

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 equal to those found by Kouadio [6] and by Yapo et al. [15] in well water in Korhogo. On the other hand, the maximum value obtained in our study is much higher than those of peers. Our values are higher than 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 [6,15].

The groundwater from the thirteen boreholes has average pH values similar to those of the waters of the sedimentary basin of Ivory Coast. The average pH values obtained in this study are lower than 7 and much lower than those of commercial mineral waters from the AWA company in Côte d'Ivoire (pH=8) [15]. All water from these boreholes is acidic. Other studies carried out in certain cities in Ivory Costa have detected similar values [6,16]. These pHs are within the Chemical Potability Standards (6.5-8.5) established by the WHO [14]. However, Kouadio [6] showed in his studies that acidic water would be aggressive and would release metals in the pipes. The acidity of the water taken from our various boreholes would be linked to the presence of CO₂ resulting from the biodegradation of glyphosate deposited in groundwater by infiltration. Indeed, Angelica et al. [17] showed that glyphosate undergoes biodegradation to CO2. Ahoussi et al. [16] showed during their study on the groundwater of Abidjan and the water of the city of Man that the CO_2 presence of resulting from the biodegradation of certain organic compounds deposited at the bottom of the soil would promote the acidity of these waters.

Regarding conductivities, all the values obtained in our study are lower than the admissible (2000 μ S/Cm) and acceptable (400 μ S/Cm) standards of the WHO [14]. Our results are close to those obtained in Korhogo well water by Yapo et al. [15] and those of Kouadio [6]. The average conductivity values found in our study show that the waters of the forages studied are poorly mineralized due to the presence of glyphosate in large quantities in these waters.

Contamination of groundwater by glyphosate and its derivatives: The analyzes carried out showed the presence of glyphosate at high concentrations and undetermined concentrations for glufosinate and AMPA.

The concentrations obtained in our study were compared to the World Health Organization

(WHO) drinking water standard values of 0.1 μ g/L per substance [14].

Samples from thirteen boreholes in the autonomous district of Abidian showed concentrations well above the WHO threshold value for drinking water. In particular, the M'Badon and Abobo Sagbé boreholes showed concentrations ten times higher than the threshold value defined by the WHO. The fact that the last two organic compounds 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. 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 compound considered toxic in borehole waters would be linked to repeated and non-compliant use of weedkillers by farmers in these localities, the presence of industries, landfills and auto packs. Furthermore, Cissokho et al. [18] noted the abusive and unhealthy use of herbicides in African countries. As for Soro et al. [8], they observed the intensive use of glyphosate by market gardeners in the town of Korhogo. 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 our study are lower than those found in groundwater in Argentina by Lutri et al. [19] (1.3 to 2 µg/L). Okada et al. [20] found concentrations similar to those found in this study (0.1 to 8.5 μ g/L) in the groundwater of the Argentine Pampean Plain. On the other hand, our values are higher than those found (0.17-0.5 μ g/L) in Niger by Zabeirou et al. [21]. The concentrations obtained in the M'badon and Abobo Sagbé boreholes are much higher than those detected in Ivorian borehole waters (0.67 µg/L) by Soro et al. [8]. Studies have observed that groundwater pollution in market gardening sites would be intensified by the leaching of crop soils through runoff and infiltration [21]. On the other hand, studies carried out in Canada have shown that after application, it is impossible for glyphosate and AMPA to migrate into groundwater supplies.

In view of these results, it should be noted that the waters in the boreholes located near packs, plantations. automobile industries. landfills and market gardens in the autonomous district of Abidjan are exposed to diffuse pollution places. coming from these The high concentrations observed in these waters above the drinking standard show the impact of the repeated use of glyphosate-based herbicides. 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 also household waste. This is the case of the Akouédo landfill. This could create health risks for populations using this water for their daily needs. The presence of alvohosate in all the water samples taken from the boreholes allows us to validate the hypothesis of the solubility and stability of glyphosate in water.

Contamination of groundwater by ETM: The results of this study show the presence of metallic elements analvzed trace at higher concentrations 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. By comparing our results to those found by our peers in water from wells and boreholes in Ivory Coast, it appears that our results differ from those of Djadé et al. [10] for Cd and Ahoussi et al. [16] for Co. For zinc, all concentrations detected in borehole water are within WHO standards (500µg/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 (10µg/ L). It is also present in the Abobo Coco Service and Koumassi industrial area boreholes at concentrations three times higher than the value recommended by the WHO (10 μ g/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

ug/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). Concerning nickel, it is present at concentrations consistent with that established by the WHO (70 μ g/L) in the waters of Erymakouguie (Agboville), MACA Cité ADO and the Koumassi industrial zone. The presence of these metallic trace elements in significant quantities in aroundwater 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, the work of Ahoussi et al. [16] showed that anthropogenic activities could have effects on metal pollution of groundwater in the city of Abidjan. As for Rasheed et al. [22] and Zhang et al. [23], they showed the impact of discharges from anthropogenic activities and soil erosion on the presence of certain metallic trace elements in well water. The concentrations of As observed in our study are much higher than those obtained in the groundwater of San-Pedro and Abidian by Kouadio [6] and also those found in the waters of wells and boreholes in the mining area of Zouan-Hounien by Djadé et al. [10]. A study conducted by Ahoussi et al. [16] on the water tables of the city of Abidjan made it possible to detect high concentrations of Cr and Co higher than those found in this study and concentrations of Zn and Pb lower than those of our study.

Principal component analysis (ACP) of chemical compounds in water and drilling parameters: The ACP was carried out on 13 samples of water from the boreholes. 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 variables (p= 0.05000) used to carry out our ACP.

The principal component analysis of these variables reveals that the first two axes (Factor 1 and Factor 2) were extracted with a total contribution of 61.37%.

Compared to Factor 1 (axis 1) which represents 33.29% of the total variability of glyphosate contamination and physicochemical parameters

of water, the group formed by arsenic (-0.875604), the lead (-0.926540) and zinc (-0.742363) are released. 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 such as agriculture and industries but also from soil erosion.

Compared to Factor 2 (axis 2) representing 28.08% of the total variability of glyphosate contamination and physicochemical parameters of water, the group formed by the variables that are depth (-0.842222) and the 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) representing 14.33% of the total variability of glyphosate contamination and physicochemical parameters

of water, the group formed by the Sulfur variable (-0.904595) stands out. Sulfur is an element naturally present in soils. Studies have shown that sulfur in the environment appears in the form of sulfur compounds whose presence in the waters of the aquifer comes from the dissolution of gypsum and the oxidation of pyrite.

Compared to Factor 4 (axis 4) representing 9.99% of the total variability of glyphosate contamination and physicochemical parameters of water, the group formed by glyphosate (-0.847445) stands out. Indeed, glyphosate is an exogenous compound, that is to say it is a synthetic molecule whose presence in the environmental environment comes from human activities such as agriculture. It stands out from other elements whose presence in the environment is natural. Considering these results, it appears that the presence of glyphosate in borehole water is independent of ETM, sulfur, pH, temperature and conductivity.





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

Variable	Factor-varia	able correlations	s (factor loading	s) based on cor	relations (Stand	lardized ACP) M	arked correlatio	ns are significa	nt at p<0,05000
	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
рН	-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

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

Health risks linked to the consumption of water from drilling: Although daily consumption of borehole water is low in infants and children, risk quotients calculated in relation to daily exposure doses reveal that QD in infants and children are higher than in adults consuming more water. 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 [24].

The level of population exposure to glyphosate due to ingestion of borehole water is very unlikely (QD < 1) in infants weighing 5 kg, children weighing 10 kg and adults weighing 60 kg. However, Glyphosate is an organic compound with proven toxicity. The level of exposure to glyphosate of the entire population near the Abidjan region is very unlikely [25].

However, it has been demonstrated that glyphosate is mutagenic, genotoxic, carcinogenic and has cellular, reproductive, cardiovascular, cerebral, cellular, digestive effects for humans [26] and congenital malformations in children [26].

The level of population exposure to zinc linked to the ingestion of borehole water is unlikely (QD < 1) in infants weighing 5 kg, children weighing 10 kg and adults weighing 60 kg. But probable in infants (QD = 1.55) in the Koumassi industrial area. Indeed, studies have shown that acute zinc poisoning linked to ingestion of water causes gastrointestinal disorders and diarrhea in exposed populations [27].

The level of population exposure to nickel linked to the ingestion of borehole water is unlikely (QD < 1) in infants weighing 5 kg, children weighing 10 kg and adults weighing 60 kg from 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 [28] as well as cases of intestinal disorders such as nausea, abdominal cramps and diarrhea within the population [29].

The literature has observed that depending on the route of penetration into the body, immunological, hematological, hepatic, renal, genotoxic effects on embryonic development and reproduction of nickel would be possible [27]. 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 low and prolonged exposure levels, nausea, vomiting and dizziness have been observed. Studies have shown effects such as pulmonary embolisms, respiratory failures, birth failures, asthma and chronic bronchitis, allergic reactions (skin rashes and heart problems) [30].

The level of population exposure to chromium from ingestion of borehole water is unlikely among infants, children and adults in most study areas. However, it is probable in infants (QD = 1.0027) 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 [31].

The level of exposure of the population to arsenic linked to the consumption of water from boreholes in the FILTISAC zone is probable among adults weighing 60 kg (QD = 4.33). It is very likely in children weighing 10 kg (QD = 13) and in infants weighing 5 kg (QD = 19.6). Indeed, 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 water from boreholes is unlikely in infants, children and adults (QD < 1) in several localities but probable in certain places. In adults (QD = 1.2381) from the locality of FILTISAC, this is probable. In children, it is very probable in the locality of FILTISAC (QD= 3.7143) and probable in the locality of Koumassi (QD= 1.0571). In infants, it is very probable in the localities of FILTISAC (QD= 5.5862), probable in Koumassi (QD= 1.5899) and Abobo Coco Service (QD= 1.3321). Pb would be declared in the literature as a metallic element not essential to metabolism in humans [32]. 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 [33] to be sensitive to the neurobehavioral toxic effect of lead.

The level of population exposure to copper linked to the consumption of borehole water is unlikely among infants, children and adults in the study areas. However, it is probable in infants (QD = 1.2032) in the FILTISAC area. Indeed, the studies carried out by Pizarro et al. [34] on 60 women who received doses varying from 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, Tanouavi et al. [35] showed 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.

Considering the results obtained during this study, it appears that the consumption of water from boreholes near the Abidjan region containing glyphosate and ETM does not present any health risk within the population in certain areas consuming this water given that QD < 1. For reference institutions in toxicological studies. populations the of these localities are theoretically out of danger (QD < 1). On the other hand, the consumption of this water in other localities is very risky (QD > 1) for ETM such as Zn, Pb, Cr, Cu and As. As a result, the health of the population of these localities is affected, that is to say exposed to danger.

5. 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. We would like to extend this study to the aquatic matrices and the country's basic foodstuffs.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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