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Human health risks from the consumption of *Cantareus aspersus* and *Solanum lycopersicum* L. containing residues of glyphosate and trace metals

Béa Gouanda Thibaut[1,2,*], Ouffoué Koffi Sébastien[1, 2], Yapo Ossey Bernard[2,3], Ouattara Lassiné[1]

[1]*Laboratory of Constitution and Reaction of Matter (LCRM), Félix HOUPHOUËT-BOIGNY University, Abidjan, BP 582 Abidjan 22, Ivory Coast*
[2]*Ivorian Antipollution Center (CIAPOL), Abidjan, 04 BP 451 Abidjan 04, Ivory Coast*
[3]*Laboratory of Environmental Sciences, NANGUI Abrogoua University, Ivory Coast*

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***Abstract*:**

To combat predatory species and weeds, the use of glyphosate-based herbicides is necessary. However, the chemical composition and biocidal properties of these substances negatively impact environmental quality and food safety. This study focuses on glyphosate and its metabolites as well as trace metal elements for their persistence and influence on living organisms. The general objective of this study is to determine the residues of glyphosate and its metabolites and trace metal elements present in soils, *Solanum lycopersicum* L. and *Cantareus aspersus*. The analysis is carried out in the samples using chromatographic and spectrometric methods. Aminomethylphosphonic acid is detected in the commercial sample of glyphosate ($14 \times 10^2 \pm 10$ mg/L). Glyphosate is present at concentrations of 0.92 ± 0.01 mg/kg DW (fruits) and 0.18 ± 0.01 mg/kg DW (cephalopods), higher than the standards. For trace metal elements, the highest concentrations are: 40.0 ± 0.3 mg/kg DW (Cr), 140 ± 2 mg/kg DW (Zn) and 0.9 ± 0.2 mg/kg DW (Cd) in soils; 7.10 ± 0.01 mg/kg DW (As) and 56 ± 3 mg/kg DW (Cu) in snails; 8.7 ± 0.5 mg/kg DW (Cr), 6.9 ± 0.6 mg/kg DW (Ni) and 85 ± 2 mg/kg DW (Zn) in tomato fruits. The health risk associated with the consumption of these foods by the population is alarming. This study deserves to be extended to all foods consumed.

***Keywords*:** *Cantareus aspersus*; Glyphosate and metabolites; Health risks; *Solanum lycopersicum* L.; Trace metal elements.

*Corresponding author:
Email address: *gouandathibautbea@yahoo.fr* (G.*T. Béa*)
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1 Introduction

Faced with population growth and to ensure food security, the use of chemical inputs has become the most widely used method in the world [1]. In order to make agriculture intensive and cover large agricultural areas, farmers are increasingly turning to herbicide products for rapid weed control of agricultural plots. These active substances protect soils and plants from the invasion of predatory species. To carry out no-till crops, destroy weeds and manage weeds, the use of glyphosate-based herbicides has proven effective [2]. It is currently the most widely used herbicide by farmers and gardeners due to its ability to spread throughout the plant after application. Today, glyphosate (N-phosphonomethylglycine) is the subject of scientific debates regarding its dangerousness and persistence. For decades, scientists have not yet agreed on a clear decision. This is what has sparked an international debate on whether or not to ban it. In Côte d'Ivoire (West Africa country), glyphosate is the most widely used herbicide. Studies conducted on all crops in the national territory have shown that 53% of the herbicides used contain glyphosate (Ministry of Agriculture).

In 2017, the global production of tomato fruits was 170.8 million tons. To date, tomato fruits occupy a very important place in the global human diet [3]. As for *Cantareus aspersus*, studies have observed that the consumption of the Ivorian population was estimated at around 7.9 million kilograms of snails per year [4]. This study focused on glyphosate and its metabolites as well as trace metal elements (ETM) for their persistence and toxicity to living organisms. According to the data available in the literature, there is a lot of information on the toxicity of these molecules [5-7]. Also, scientific works revealed the presence of glyphosate residues, its metabolites and ETM in all compartments of the environment [4, 5, 8]. However, little research has been done on the study of glyphosate, aminomethylphosphonic acid, glufosinate and trace metal elements in tropical Africa. For Côte d'Ivoire, N'Guessan et *al.* [4] quantified glyphosate in cephalopods and in the viscera of Achatina snails at concentrations of 1.03 and 1.01 mg/kg, respectively. Lead (0.64 mg/kg), copper (0.45 mg/kg) and zinc (1.165 mg/kg) were quantified in shells, while cadmium was quantified in shells and cephalopods at values of 1.03 and 0.13 mg/kg, respectively [4]. Gokou et *al.* [8] showed the presence of glyphosate in the active ingredients of fish muscle ranging from 0.14 to 0.36 mg/kg. Concerning tomato fruits, studies conducted in Daloa (Côte d'Ivoire) revealed concentrations of 0.59 mg/kg (As), 0.007 mg/kg (Cd), 3.02 mg/kg (Ni) and 191.70 mg/kg (Zn) [9].

This study aims on the one hand to search for glyphosate, glufosinate, aminomethylphosphonic acid and trace metal elements in soils, tomato fruits and snail cephalopods collected from two agricultural soils. And on the other hand, to characterize the health risk for humans linked to the consumption of these foods.

2 Materials and methods

2.1 Material

2.1.1 Vegetal and animal material

The analyses were carried out on two matrices ground into fine powders. These are:

- Dried tomato fruit powders composed of fruits obtained on the site treated (To) and not treated with herbicide (TI);
- Dried snail cephalopod powders (*Cantareus aspersus*) composed of snails found on the market (E0), reproduced on the site treated with herbicide (ET) and not treated (EN).

2.1.2 Technical equipment

The technical equipment is composed of:

- High performance liquid chromatography coupled with a tandem mass spectro-photometer (LC-MS/MS) Agilent system. The liquid chromatography column used is an X-Bridge C18 -2.5 µm (50 x 2.1 mm) – WATERS column. The mobile phase is composed of acetonitrile - EMQ 0.1% triethylamine at pH = 9.5 (50:50);
- Inductively coupled plasma mass chromatography (ICP). The determination of trace metal elements in our samples was carried out using a microwave digester (CEM: Mars 5 HP- 500 Plus).

2.2 Methods

2.2.1 Treatment of the study soil and cultivation of food crops

A 750 m² agricultural plot (Figure 1) selected within the Nangui Abrogoua University of Abidjan (Côte d'Ivoire) (5°25'0" N / 4°1'60" W) was cleared on February 2, 2021. It was subdivided into two blocks 8 m apart. Part of this block underwent herbicide treatment (''Tasman 360 SL''). The treatment was carried out in a backpack sprayer by diluting the herbicide (addition of 1 mL of herbicide in 75 mL of water). One week after spraying, the tomato plants were grown.

2.2.2 Exposure protocol

The exposure protocol used is that described by Pauget [10] by replacing the microcosms with nets in order to take into account the entire plot. The caged snails were purchased on the market. Before exposure, a few snails were used to analyze the concentrations of the com-pounds sought. The snails caged in the nets were exposed to the soil, humus and vegetation of each plot under natural climatic conditions in the period from July 24, 2021 to August 21, 2021 (28 days). Seven snails were exposed on each plot surrounded by nets.

2.2.3 Sampling

2.2.3.1 Sampling and treatment of soils and tomato fruits

Untreated (SN) and herbicide-treated (SF) soils were collected at a depth of 0-10 cm (Figure 2). The soil samples were dried in an oven (40 °C) for 72 hours. After drying, the soil samples (SN, SF) were crushed using a porcelain pestle and mortar, then sieved using a 45 µm porosity sieve (Plastic-Nylon Sieve Din 4195) and stored in bottles. For the tomato fruit samples, they were made (Figure 2) and then transported to the laboratory by packaging them in polyethylene bags. Once in the laboratory, the fruits were washed with distilled water to remove the largest soil particles. The samples were then dried in an oven at a temperature of 40 °C. After drying, the samples were ground using a Retsch-type electric grinder. The powders obtained are stored in bottles supplied by the Wessling company.

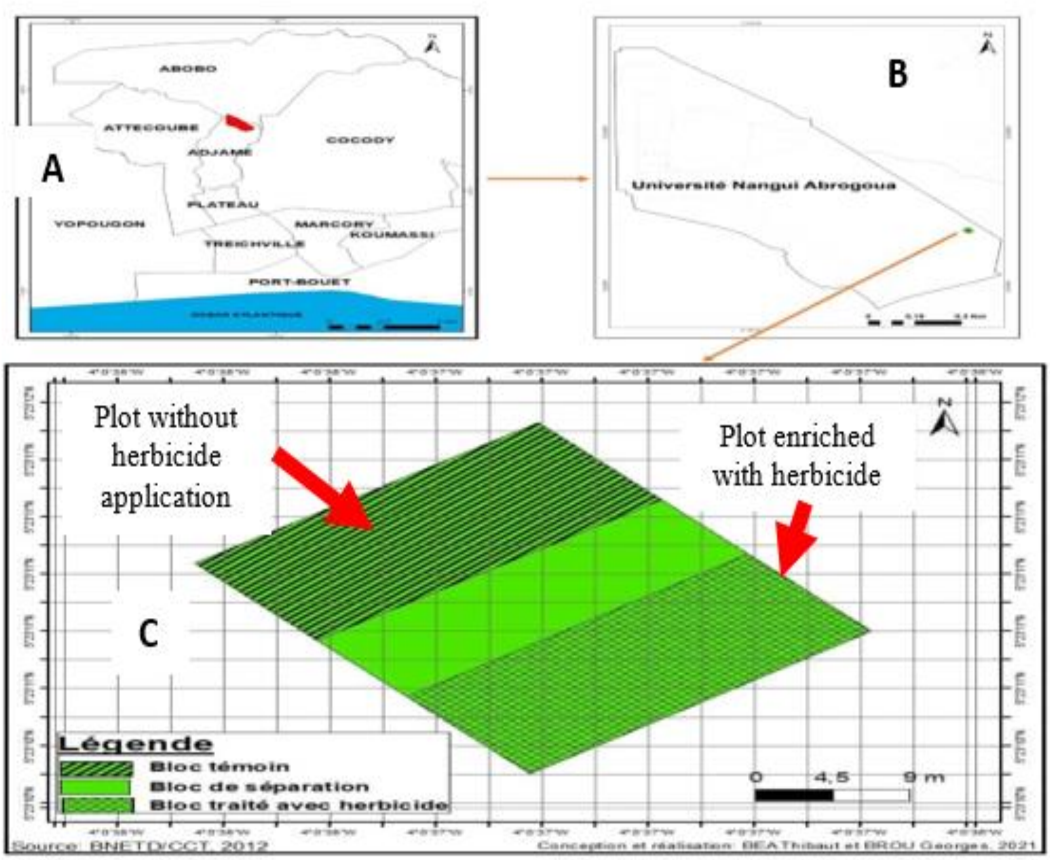

Fig. 1. Location of the cultivation area: **A** (Map of Abidjan), **B** (Map of Nangui Abrogoua University) and **C** (Map of the plot used).

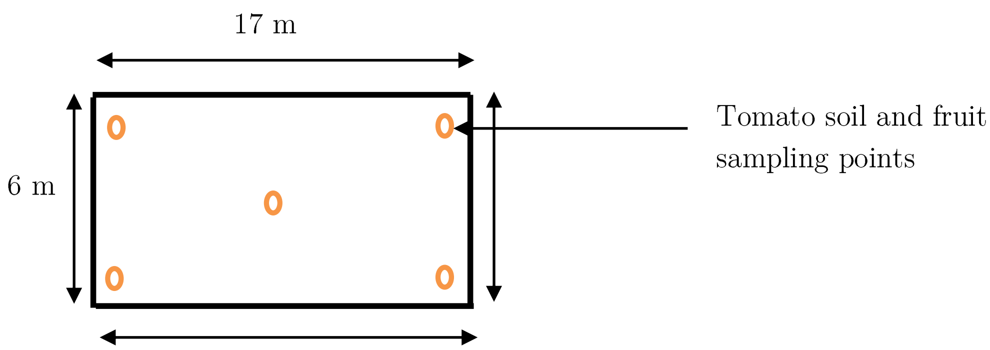

Fig. 2. Sampling points.

2.2.3.2 Sampling and treatment of snails

On each plot, six snails were sampled. The samples taken were placed in polyethylene bags and then transported to the laboratory the same day. Once at the laboratory, the snails were fasted for two days (48 hours) in order to eliminate unabsorbed food and feces from their digestive tract. After two days of fasting, the cephalopods of each sample were separated from the other parts and then washed with distilled water. The cephalopod samples were then dried in an oven at a temperature of 40 °C. After drying, the samples were ground into fine powder using a Retsch type electric grinder and stored in the same types of bottles. A total of 3 samples of soil, 3 samples of snails and 2 samples of tomato were collected.

2.2.4 Analysis of glyphosate, glufosinate and amino-methylphosphonic acid by LC/MS/MS

The method used in our study is that described by the Central Air Quality Monitoring Laboratory and used by Béa et *al.* [5]. The analysis of glyphosate, Amino-methylphosphonyl Acid (AMPA) and glufosinate was carried out after derivatization with FMOC-Cl ((9 fluorenyl-methyl)-chloroformate). LC/MS/MS on a WATERS, UPLC® Acquity and TQD Acquity coupling with an X-Bridge C18 - 2.5 µm (50 x 2.1 mm) –WATERS column was used. The extraction was carried out on quartz filters with a diameter of 150 mm. The standard glyphosate solutions used are obtained by dissolving pure glyphosate crystals in acid form in water. The chromatographic gradient conditions allowing the identification and quantification of glyphosate, glufosinate and AMPA are taken from the NF ISO 16308 standard.

2.2.5 Analysis of trace metal elements by ICP-MS

Aqua regia mineralization for the determination of trace metal elements (ETM) in solid samples was used [5]. From a homogenate of the plant organ sample, 100 mg fractions were taken and attacked with 6 mL of HNO_3 (65%) and 2 mL of hydrogen peroxide (20%). For soil samples, a volume of 3 mL of HF was added. After this attack, the mineralized material was collected in a 50 mL flask and made up to the mark with pure water and then analyzed by ICP-MS.

2.2.6 Assessment of health risks related to the consumption of tomatoes and snails

The calculations were made based on the recommendation of the Ivorian daily ration of 33.3 mg of animal protein per day per person. The FAO and WHO recommendation of 400 mg of fruits and vegetables per day per person was taken into account [11].

The daily dose of exposure to chemical contaminants through the consumption of foodstuffs is calculated according to the following equation:

$$QD = \frac{DJE}{VTR} \qquad (1)$$

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

The VTR used in this study are listed in table 1.

Table 1
VTR used in this study.

	Glyphosate	As	Cd	Co	Cr	Cu	Ni	Zn
VTR (µg/(kg.day))	300	0.3	0.2	500	3	10	20	300

For QD < 1, the occurrence of a toxic effect is unlikely (or very unlikely). In other words, the risk associated with the presence of the toxic chemical element is acceptable. For QD > 1, the occurrence of a toxic effect is probable (or very probable). That is, the risk associated with the presence of the toxic chemical element is unacceptable.
The toxicological reference values used in this study are listed in table 1 [4, 12].

2.2.7 Statistical analysis

One-way analysis of variance (ANOVA) was used to compare the concentrations of chemical elements using Graph Pad Prism version 5. Turkey's test, a multiple comparison test of means, was performed to determine the level of difference between different samples [13]. Significance is accepted at $p < 0.05$.

3 Results and discussion

3.1 Concentrations of glyphosate and its derivatives in commercial herbicide, soils, tomato fruits and snail cephalopods

Table 2 presents the results obtained after the analysis of herbicide, soil, tomato fruit and snail cephalopod samples.
The measured concentrations for glyphosate and its metabolite Aminomethyl-phosphonyl Acid (AMPA) in the commercial glyphosate sample are of the order of ($5.8\times10^5 \pm 104$) mg/L and ($14\times10^2 \pm 10$) mg/L, respectively. The measured concentration for glufosinate is below the detection limit (LD) of the device used. The results of soil samples show average concentrations below the detection limit of the device. For snails, the results show the presence of glyphosate in the samples of snails before exposure (E0) and snails collected from the herbicide-treated site (ET) at respective mean concentrations of 0.18 ± 0.01 mg/kg DW and 0.16 ± 0.01 mg/kg DW. On the other hand, AMPA and glufosinate have concentrations below the detection limit of the device in all the samples analyzed. For tomato fruits, AMPA and glufosinate have concentrations below the detection limit of the device in all the samples analyzed, while the maximum concentration of glyphosate is 0.92 ± 0.01 mg/kg DW (tomato fruits collected from the treated soil).

Table 2
Glyphosate, AMPA and Glufosinate concentrations in cephalopods and fruits.

Samples	n	Concentrations (mg/kg DW for solid samples and mg/L for liquid samples)			
		Glyphosate	AMPA	Glufosinate	LMR
H	3	$5.8\times10^5 \pm 10^4$	$14\times10^2 \pm 10$	< LD	nd
So	3	<LD	< LD	< LD	nd
SN	3	< LD	< LD	< LD	nd
SF	3	< LD	< LD	< LD	nd
E0	3	0.18±0.01	< LD	< LD	0.05
EN	3	<LD	< LD	< LD	0.05
ET	3	0.16±0.01	< LD	< LD	0.05
To	3	0.92±0.01	< LD	< LD	0.1
TI	3	0.39±0.02	< LD	< LD	0.1

E0: Snails before experiment; EN: Snails raised on untreated soil; ET: Snails raised on soil treated with herbicide; H: Commercial liquid herbicide; To: Tomato fruits from treated site; TI: Tomato fruits from untreated site; So: Initial soil before chemical treatment; SN: Post-harvest soil without chemical treatment; SF: Post-harvest soil treated with herbicide; LD: Detection Limit; LMR: Maximum Residue Limit; n: number of measurements; nd: not defined.

The presence of AMPA in the herbicide used at high levels would result from the degradation of the glyphosate contained in the herbicide over time [14]. The herbicide formulation used is highly contaminated with AMPA. In this study, glyphosate, AMPA and glufosinate were not detected in the soils. This could be explained either by the high detection limit of the device or by the degradation of these organic compounds in the soil. Furthermore, studies have shown the absence of these organic compounds in agricultural soils. Most laboratory studies have shown the immediate degradation of glyphosate after soil treatment [15].

The concentrations obtained for AMPA and glufosinate in dried cephalopods of snails are below the detection limit of the device. The concentration of glyphosate obtained for snails raised on untreated soil is below the detection limit of the device. On the other hand, glyphosate is detected in samples of snails before exposure and of snails taken from herbicide-treated soil at average concentrations above the maximum residue limit (LMR) (0.05 mg/kg) of glyphosate defined for snails by Commission Regulation (EU) No 293/2013 of 20 March 2013 [16]. The presence of the glyphosate content above the LMR in snails raised on treated soil can be explained by the fact that they consumed during the 28 days of glyphosate not degraded in plant tissues after application of the herbicide. The presence of the glyphosate content above the LMR in snails before breeding on soils can be linked to the fact that they come from a locality where glyphosate-based herbicides are widely used. Our results are consistent with those of some researchers. Indeed, N'Guessan *et al.* [4] quantified glyphosate in cephalopods (1.03 ± 0.1 mg/kg), viscera (1.01 ± 0.37 mg/kg) and shells (0.07 ± 0.03 mg/kg) of the snail *Achatina achatina*, from the locality of Soubré (south-west of Côte d'Ivoire), a locality with a high rate of use of glyphosate-based herbicides for weed control in fields. Elsewhere, work has quantified glyphosate in *Helix aspersa* snails at concentrations of 6 mg/kg and 30 mg/kg for snails continuously fed with glyphosate-contaminated food [17].

The analysis of AMPA and glufosinate in tomato fruits shows concentrations below the detection limit of the device. On the other hand, glyphosate is present at average concentrations above the maximum residue limit (0.1 mg/kg) of glyphosate defined for vegetable-fruit plants by Commission Regulation (EU) No 293/2013 of 20 March 2013 [18]. The fact that glyphosate is detected in samples taken from the plot not treated with herbicide clearly shows that glyphosate contamination occurs more by atmospheric deposition rather than by root sampling. Elsewhere, in the European and American areas, glyphosate is detected at significant concentrations in cereals, dry lentils, beans, peas and soybeans [19].

3.2 Trace metal element concentrations in commercial glyphosate sample, soils, tomato fruits and snail cephalopods

The results of analyses of the total concentrations of trace metal elements obtained are given in table 3.

For soil, statistical analyses for Zn showed the most significant concentration ($p < 0.001$) in soil samples before treatment and cultivation (S0). Comparing the results of Zn concentrations obtained at the SN and SF samples, the most significant concentration ($p < 0.001$) is recorded in the SN sample. As for the concentrations obtained in Cr, no significant difference between the samples was found.

For snails, comparing the concentrations between them, it appears that the Cr concentrations recorded in the E0 and ET samples are more significant ($p < 0.001$) compared to that recorded in EN. On the other hand, no significant difference is observed between E0 and ET. Similarly, regarding the Cu results, the contents obtained at the level of E0 and ET are more significant ($p < 0.001$) compared to that of EN. On the other hand, no significant difference is recorded between E0 and ET. For the Zn concentrations, the values are significant ($p < 0.05$) at the level of EN and ET compared to that of E0 but no significant difference is observed between EN and ET.

For the tomato fruits analyzed, the concentrations obtained show higher values in Cr, Ni and Zn for the samples taken from the herbicide-treated soil.

The results obtained in this study show cases of metallic contamination. To better understand the metallic pollution of our different matrices, the values obtained were compared with those of the guide values defined by renowned organizations and those observed in certain countries.

Concerning the herbicide, it contains ETM (As, Cr, Cu, Ni, Zn, Cd, Co) in significant quantities not declared by the manufacturer. Elsewhere in the world, similar results have been found in glyphosate-based herbicides [20]. These authors found significant amounts of toxic trace metal residues such as As, Pb, Co, Cr and Ni in the herbicide products studied [20].

Table 3
ETM concentrations in the analyzed samples.

		Concentrations (mg/kg DW for solid samples and mg/L for liquid samples)						
Samples	n	As	Cr	Cu	Ni	Zn	Cd	Co
H	3	0.42±0.01	1.1±0.03	0.04±0.003	0.2±0.003	0.4±0.01	0.002±0.0002	0.01±0.002
SF	3	<LD	39±1	< LD	< LD	10±0.33	< LD	< LD
So	3	< LD	40±0.33	18±0.5	9.6±0.53	140±2	0.87±0.2	< LD
SN	3	< LD	40±0.21	< LD	< LD	18±0.2	< LD	< LD
ET	3	<LD	3.8±0.02	51±3	< LD	64±1	< LD	< LD
E0	3	7.1±0.01	3.3±0.1	56±3	< LD	61±0.2	< LD	< LD
EN	3	5.9±0.01	2.8±0.1	26±0.02	< LD	65±1.2	< LD	< LD
TI	3	< LD	3.1±0.03	10±0.3	3.5±0.3	53±0.93	< LD	< LD
To	3	< LD	8.7±0.5	7.5±0.5	6.9±0.6	85±2	< LD	< LD

E0: Snails before experiment; EN: Snails raised on untreated soil; ET: Snails raised on soil treated with herbicide; H: Commercial liquid herbicide; To: Tomato fruits from treated site, TI: Tomato fruits from untreated site; So: Initial soil before chemical treatment; SN: Post-harvest soil without chemical treatment, SF: Post-harvest soil treated with herbicide; LD: Detection Limit; LMR: Maximum Residue Limit; n: number of measurements; nd: not defined.

As for soils, the results show the presence of non-negligible concentrations of some of these trace metal elements. Although they are present in the herbicide at considerable concentrations, As, Cu, Cd, Ni and Co have concentrations below the detection limit of the device in all soil samples after harvest. This can be explained by the influence of pH [21]. Studies have shown the effect of pH on the content of ETM in soil [21]. As for Cu, the results obtained in this study are contrary to those of Geoffrey [21]. For Cr, we observe practically the same contents in soils above the defined normal value (30 mg/kg DW). Comparing the concentrations obtained in S0 soil with those in SN and SF soils, it appears that the concentration of Zn has considerably decreased ten months after the experiment in SN and SF soils. Bolan et *al.* [22] found similar results. Also, the absence of significant quantities of these ETM in the soil after herbicide application is linked to the influence of glyphosate and its metabolite (AMPA) on the concentration of these ETM in soils. Indeed, Bemelmans et *al.* [23] observed a decrease in the available concentrations for certain metals in the presence of AMPA and an increase in the latter in the presence of glyphosate. In this study, the first hypothesis was recorded. The studies of Barrett and McBride [24] showed that the presence of glyphosate in the soil has an influence on the mobility of ETM from the soil to the hydrosystem. The decrease in the concentrations of these ETM in soils in the presence of glyphosate and AMPA can impact their mobility in soils.

Comparing the Cr and Cu concentrations obtained in the cephalopods of snails collected from the herbicide-treated soil, it follows that they are higher than those obtained in the samples collected from the soil not treated with herbicide. This can be explained by the fact that they consumed the dead fraction of the organic matter which trapped more of these two elements [25]. Studies conducted in Benin by Mahoudjro et *al.* [26] detected cadmium and lead in the species *Archachatina marginata* (boiled) at maximum mean concentrations of 0.046 mg/kg and 0.096 mg/kg, respectively, and in the species *Limicolaria spp* (boiled) at maximum mean concentrations of 0.422 mg/kg and 1.024 mg/kg, respectively. In fried snails, the mean concentrations detected were between 0.003 and 0.067 mg/kg (Cd) for *Archachatina marginata* and between 0 and 0.769 mg/kg (Cd) then between 0 and 0.275 mg/kg (Pb) for *Limicolaria spp.* In Côte d'Ivoire, N'Guessan et *al.* [4] quantified copper (0.45 mg/kg) and zinc (1.165 mg/kg) in the shell, cadmium (0.13 mg/kg) in cephalopods and cadmium (0.14 mg/kg) in the viscera of the snail *Achatina achatina*. Our values are much higher than those found by these researchers. This contradiction in the results may be linked to the study areas and the analysis methods used.

The Cr concentrations obtained for fruits collected from untreated and treated soil are above the defined normal value (1.5 mg/kg) [12]. The chromium concentration obtained in fruits collected from sprayed soil is well above that obtained for fruits harvested from the plot not treated with herbicide. This suggests a root uptake of Cr provided by the herbicide glyphosate after treatment. The Cu concentrations obtained in tomato fruits from untreated and treated soil are within the standards (10 mg/kg) [12]. However, the highest value is obtained in samples collected from the plot treated with herbicide. The Ni concentrations obtained in samples collected from both soils are well above the defined standard (1.5 mg/kg) [12]. The highest value is obtained in samples from the plot treated with herbicide. This suggests a Ni contribution by the herbicide. Regarding zinc, it was detected in all samples taken. The concentration in fruits taken from treated soil is much higher than that obtained from untreated soil. This can be explained by the fact that there was a root uptake of Zn from the herbicide by the tomato plants. The Zn concentrations obtained are well above the normal concentration (50 mg/kg) [12].

Observing our results, it appears that the use of glyphosate-based herbicide contributes to the supply and facilitation of the transfer of certain ETM from the soil to the plants and the biological organism studied.

3.3 Health risks associated with the consumption of tomato fruits and snail cephalopods in adults, children and infants

The study of health risks in this study focuses on chronic exposures because vegetables and cephalopods are consumed recurrently orally.

3.3.1 Estimation of the level of exposure of consumers of tomato fruits and cephalopods

The tables 4, 5 and 6 present the daily exposure dose (DJE) to glyphosate and ETM due to the ingestion of vegetables and cephalopods in three categories of individuals.

Table 4

Daily exposure doses (µg/(kg.day)) for a 60 kg adult consuming vegetables and snails.

Chemical compound	Samples				
	TI	To	E0	EN	ET
Glyphosate	2.6	6.13	0.10		0.09
Zn	353.33	566.67	33.86	36.08	35.52
Cr	20.67	58	1.83	1.55	2.11
Cu	66.67	50	31.08	14.43	28.31
Ni	23.33	46	---	---	---
As	---	---	3.94	3.27	---

E0: Snails before experiment; EN: Snails raised on untreated soil; ET: Snails raised on soil treated with herbicide; To: Tomato fruits from treated site, TI: Tomato fruits from untreated site.

Table 5

Daily exposure doses (µg/(kg.day)) for a 10 kg child consuming vegetables and snails.

Chemical compound	Samples				
	TI	To	E0	EN	ET
Glyphosate	15.6	36.8	0.60		0.53
Zn	2120	3400	203.13	216.45	213.12
Cr	124	348	10.99	9.32	12.65
Cu	400	300	186.48	86.58	169.83
Ni	140	276	---	---	---
As	---	---	23.64	19.65	---

E0: Snails before experiment; EN: Snails raised on untreated soil; ET: Snails raised on soil treated with herbicide; To: Tomato fruits from treated site, TI: Tomato fruits from untreated site.

Table 6

Daily exposure doses (µg/(kg.day)) for a 5 kg baby consuming vegetables and snails.

Chemical compound	Samples				
	TI	To	E0	EN	ET
Glyphosate	31.2	73.6	1.20		1.07
Zn	4240	6800	406	432.9	426.24
Cr	248	696	21.98	18.65	25.31
Cu	800	600	372.96	173.16	339.66
Ni	280	552	---	---	---
As	---	---	47.29	39.29	---

E0: Snails before experiment; EN: Snails raised on untreated soil; ET: Snails raised on soil treated with herbicide; To: Tomato fruits from treated site, TI: Tomato fruits from untreated site.

By observing the results, it appears that the DJE found for infants weighing 5 kg and children weighing 10 kg are significantly higher than those found for adults weighing

60 kg. The DJE obtained for glyphosate in the three categories of individuals are lower than its Toxicological Reference Value. This suggests that the consumption of tomato fruits and snail cephalopods containing this toxic substance does not expose populations. However, the three categories of individuals are more exposed to the trace metal elements contained in these foods (DJE > VTR) [27].

3.3.2 Characterization of the health risk for adults, children and infants consuming tomatoes fruits and cephalopods

The tables 7, 8 and 9 present the danger quotients (QD) calculated for adults, children and infants.

Table 7

Danger quotients for a 60 kg adult consuming tomatoes and snails.

Chemical compound	Samples				
	TI	To	E0	EN	ET
Glyphosate	0.01	0.02	3.33×10^{-4}		2.96×10^{-4}
Zn	1.18	1.89	0.11	0.12	0.11
Cr	6.89	19.33	0.61	0.51	0.70
Cu	6.67	5	3.12	1.44	2.83
Ni	1.17	2.3	---	---	---
As	---	---	13.14	10.92	---

E0: Snails before experiment; EN: Snails raised on untreated soil; ET: Snails raised on soil treated with herbicide; To: Tomato fruits from treated site; TI: Tomato fruits from untreated site.

Table 8

Danger quotients for a 10 kg child consuming tomatoes and snails.

Chemical compound	Samples				
	TI	To	E0	EN	ET
Glyphosate	0.05	0.12	1.99×10^{-3}		1.78×10^{-3}
Zn	7.07	11.33	0.68	0.72	0.71
Cr	41.33	116	3.66	0.70	4.22
Cu	40	30	18.65	8.66	16.98
Ni	7	13.8	---	---	---
As	---	---	78.81	65.49	---

E0: Snails before experiment; EN: Snails raised on untreated soil; ET: Snails raised on soil treated with herbicide; To: Tomato fruits from treated site; TI: Tomato fruits from untreated site.

Table 9
Danger quotients for a 5 kg baby consuming tomatoes and snails.

Chemical compound	Samples				
	TI	To	E0	EN	ET
Glyphosate	0.10	0.25	3.99×10^{-3}		3.55×10^{-3}
Zn	14.13	22.67	1.35	1.44	1.42
Cr	82.67	232	7.33	6.22	8.44
Cu	80	60	37.30	17.32	33.97
Ni	14	27.6	---	---	---
As	---	---	157.62	130.98	---

E0: Snails before experiment; EN: Snails raised on untreated soil; ET: Snails raised on soil treated with herbicide; To: Tomato fruits from treated site, TI: Tomato fruits from untreated site.

The results of this study reveal that children weighing 10 kg and infants weighing 5 kg consuming these foods are more exposed than adults with high body weight. This is justified by their low body weight and their physiological fragility [28].

Ingestion of contaminated food can cause harmful effects in adults, children and infants. This is evidenced by danger quotients higher than the normal quotient (QD = 1).

- Risk of exposure of the population to glyphosate: The level of exposure of populations linked to the ingestion of tomato fruits and cephalopods of snails containing glyphosate residues is very unlikely (QD < 1) in the three categories of individuals. The risk is therefore accep-table. However, glyphosate is a very toxic organic compound. Regular consumption of these foods containing glyphosate residues can create health problems within the population. According to studies conducted on the toxicity of glyphosate, it has been shown to be a mutagenic, genotoxic, carcinogenic compound that has effects on cells, reproduction, cardiovascular, cerebral and digestive systems of humans [6]. It also causes congenital malformations in children [7].

- Risk of exposure of the population to zinc: The level of exposure of adults consuming tomatoes fruits (QD = 1.18 for TI, QD = 1.89 for To) is probable. The level of exposure of children of 10 kg is very probable by consuming tomatoes fruits (QD = 7.07 for TI, QD = 11.33 for To). On the other hand, it is very probable in infants consuming tomatoes fruits (QD = 14.13 for TI, QD = 22.67 for To). Which suggests that the risk related to the presence of zinc in these foods is unacceptable.

For snails, the level of exposure of populations to zinc relative to the ingestion of snail cephalopods is very unlikely (QD < 1) in infants with a body weight of 5 kg, children of 10 kg and adults of 60 kg. This means that the population is safe from consuming the cephalopods of these snails containing zinc. According to the literature, regular consumption of foods containing zinc causes diseases such as gastrointestinal disorders and diarrhea in the population [29].

- Risk of population exposure to chromium: The occurrence of a toxic effect in adults who eat tomato fruits from the untreated site (TI) with herbicide is probable (QD = 6.89) but very probable (QD = 19.33) in those consuming tomato fruits collected from the treated site (To). The level of exposure of children who eat tomato fruits from the untreated and treated site is very probable (QD = 41.33; QD = 48, respectively). The level of exposure of infants weighing 5 kg due to the ingestion of tomato fruits from the untreated and herbicide-treated site is very probable (QD = 82.67; QD = 232, respectively). This means that the consumption of this food containing chromium which is a very toxic chemical element is very risky.

For snail cephalopods, the level of population exposure to chromium is unlikely in adults (QD = 0.6105 for E0, QD = 0.518 for EN, QD = 0.703 for ET), unlikely (QD = 0.703) in children consuming the snails exposed on the untreated plot but very likely in children (QD = 3.66 for E0, QD = 4.22 for ET) and in infants (QD = 7.33 for E0, QD = 6.22 for EN, QD = 8.44 for ET). This means that the consumption of these snails by children and infants is very risky. The risk is therefore unacceptable. Indeed, epidemiological studies have shown the harmful effects linked to the ingestion of chromium in humans such as bloody diarrhea, vomiting, spasms, methemoglobin malformations and liver and kidney damage [30].

- Risk of exposure of the population to copper: The level of exposure of the population to copper resulting from the consumption of tomato fruits from both plots is probable in adults (QD = 6.67 for TI, QD = 5 for To), but very probable in children (QD = 40 for TI, QD = 30 for To) and infants (QD = 80 for TI, QD = 60 for To).

For snails, the level of exposure of the population to copper due to the consumption of cephalopods of snails exposed on both plots is probable in adults (QD = 3.12 for E0, QD = 1.44 for EN, QD = 2.83 for ET). On the other hand, it is very likely in children (QD= 18.65 for E0, QD= 8.66 for EN, QD= 16.98 for ET) and in infants (QD= 37.30 for E0, QD= 17.32 for EN, QD= 33.97 for ET).

The results prove that the consumption of these foodstuffs is very risky for any category of individual. In fact, epidemiological studies have shown cases of significant increase in the incidence of gastrointestinal disorders such as diarrhea, nausea, abdominal pain and vomiting related to the ingestion of foods polluted by copper sulfate [31].

- Risk of exposure of the population to nickel: The level of exposure of the population to nickel relative to the ingestion of tomato fruits from the two plots is probable in adults (QD = 1.17 for TI, QD = 2.3 for To), but very probable in children (QD = 7 for TI, QD = 13.8 for To) and infants (QD = 14 for TI, QD = 27.6 for To). This suggests that the consumption of these tomato fruits is very risky for the population of all ages. Indeed, epidemiological studies report cases of disorders linked to nickel ingestion such as nausea, abdominal cramps, diarrhea, vomiting, dizziness, lightheadedness, pulmonary embolism, respiratory failure, failure at delivery, asthma, chronic bronchitis, allergic reactions (skin rashes and heart problems) and immunological, hematological, hepatic, renal and genotoxic effects on embryonic development [29, 32, 33].

- Risk of exposure of the population to arsenic: The level of exposure of the population to arsenic resulting from the consumption of cephalopods of snails exposed on the two plots is very likely in adults (QD = 13.14 E0, QD = 10.92 for EN), in children (QD = 78.81 for E0, QD = 65.49 for EN) and in infants (QD = 157.62 E0, QD = 130.98 for EN). The results show that children are approximately five times more exposed than adults. Concerning infants, they are approximately twelve times more exposed than adults. The risk linked to the presence of arsenic, a non-essential chemical element and very toxic to humans, is unacceptable. Indeed, epidemiological studies have observed toxic effects linked to the consumption of foods containing arsenic through gastrointestinal manifestations, more or less pronounced liver and kidney disorders, cardiovascular manifestations, hypertension and tachycardia [34, 35].

Based on the results obtained, it appears that the consumption of tomato fruits and snail proteins containing glyphosate does not present any health risk within the population consuming these foods. For reference institutions in toxicological studies, populations consuming these foods containing this toxic chemical substance are theoretically out of danger ($QD < 1$). On the other hand, the consumption of these foods containing ETMs by the population is very risky ($QD > 1$). That is to say, the risk linked to the presence of ETMs in these foods is unacceptable. As a result, the health of the population consuming tomato fruits and snails is affected, that is to say exposed to danger [36, 37].

4 Conclusion

The present work aimed to study the level of contamination of soils, tomatoes and snails by ETM, glyphosate and its metabolites in order to assess the health risks to which the population is exposed by consuming these foods. The study was carried out on eight samples taken from two agricultural soils.

Regarding the commercial sample of glyphosate used, the results show the presence of glyphosate, AMPA and ETM at very high concentrations not declared by the manufacturer. On the other hand, glufosinate was not detected. This could lead the competent authorities to strictly check the products sold on the markets.

At soil level, the results obtained show average concentrations of glyphosate, AMPA and glufosinate below the detection limit of the device. This led to the validation of the hypothesis of the degradation of these organic compounds in the soil studied after ten months. Several ETMs were detected in the samples analyzed at concentrations sometimes higher than the established standards.

In tomato fruits, the results obtained showed cases of contamination. Glyphosate was quantified at values higher than the standard established for vegetables. Cases of metallic contamination were also observed with concentrations higher than the standard. Most cases of contamination were observed in samples from soil treated with herbicide.

Concerning the species *Cantareus aspersus*, the results found show cases of contamination by glyphosate and ETMs. The analysis of glyphosate in the samples revealed its presence in the samples of snails before exposure (E0) and of snails taken from the site treated with herbicide (ET). ETMs were detected in the samples analyzed at significant concentrations. This means that the tomato fruits and the cephalopods studied are highly contaminated.

Regarding the characterization of health risks related to the consumption of these foods, the results obtained show that populations are in danger. The risk of poisoning of the population remains alarming given that glyphosate and ETM are toxic chemical compounds.

We call on public decision-makers to take appropriate measures to protect the population. This study deserves to be carried out on all foods consumed by the population.

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References

[1] R. Calvet, Les pesticides dans le sol : Conséquences agronomiques et environnementales, France Éditions agricoles (2005).

[2] E. Pelzer, M. Bazot, D. Makowski, G. Corre-Hellou, C. Naudin, M. Al Rifaï, E. Baranger, L. Bedoussac, V. Biarnès, P. Boucheny, *Pea–wheat intercrops in low-input conditions combine high economic performances and low environmental impacts*, European Journal of Agronomy 40 (2012) 39-53. doi.org/10.1016/j.eja.2012.01.010

[3] J.R.F. Mazzei, E. Freire, E.G. Serra, J.R. Macedo, A.C. Oliveira, L.H.P. Bastos, M.H.W.M. Cardoso, *Recherche sur le terrain: Une analyse comparative entre les méthodes conventionnelles, biologiques et durables de production de tomates,* Revista Científica Multidisciplinar Núcleo do Conhecimento 2(5) (2021) 125-146.

[4] O. N'Guessan, D. Kouassi, A.C. Yapi, V. Kouamé, *Evaluation of the bioaccumulation of heavy metals and glyphosate in theachatinaachatina snail (linne 1758) collected under cocoa trees in the locality of Soubré (southwest of Ivory Coast)*, African Agronomy 34(1)(2022) 93-100.

[5] G. Béa, K.S. Ouffoué, O.B. Yapo, L. Ouattara, *Assessment and Health Risks of Glyphosate Residues and Traces Metals Elements in Groundwater Arround Abidjan Region, Côte d'Ivoire,* International Research Journal of Pure and Applied Chemistry 24(5) (2023) 122-138. DOI: 10.9734/IRJPAC/2023/v24i5832

[6] C. Peillex, M. Pelletier, *The impact and toxicity of glyphosate and glyphosate-based herbicides on health and immunity,* Journal of Immunotoxicology 17(1) (2020) 163-174. doi: 10.1080/1547691X.2020.1804492

[7] R. Mesnage, J.G. Zaller, *Herbicides: A necessary evil? An integrative overview Herbicides: Chemistry, Efficacy,* Toxicology and Environmental Impacts, Elsevier (2021) 321-333. doi.org/10.1016/B978-0-12-823674-1.00003-1

[8] J.M.D. Gokou, G.K.K. Kouakou, A.C.Y. Dopé, V.K. Kouamé, S.T. Abiba, *Impact of Glyphosate and 2,4-D used in agriculture on the quality of Chrysichthys-nigrodigitatus (Lacépède, 1803) from the Sassandra River in Guessabo (Côte D'Ivoire)*, World Journal of Advanced Research and Reviews 14(01) (2022) 212- 222. doi.org/10.30574/ wjarr.2022.14.1.0298

[9] K.D. Traoré, Assessment of health risks linked to the ingestion of ETM (As, Cd, Cr, Hg, Ni, Pb, Zn) contained in market garden crops in the town of Daloa (Ivory Coast), Master's thesis, Jean LOROUGNON GUEDE University of Daloa (Ivory Coast) (2019).

[10] B. Pauget, Determination of soil factors modulating the bioavailability and accumulation of metals for the snail (*Cantareus aspersus*), Doctoral thesis, University of Franche-Comté (France) (2012).

[11] FAO, CIRAD, Fruits and Vegetables – Opportunities and Challenges for Small Farm Sustainability, Rome (2021).

[12] WHO, Drinking water quality guidelines: 4th edition, incorporating the first additive (2017) 564.

[13] W.J. Westlale, *A one-sided version of the Turkey-Duckworth test,* Technometrics 13(4) (1971) 901-903.

[14] M. Rueppel, B. Brightwell, J. Schaefer, J. Marvel, *Metabolism and degradation of glyphosate in soil and water*, Journal of Agricultural and Food Chemistry 25(3) (1977) 517-528.

[15] A.L. Gimsing, O.K. Borggaard, P. Sestoft, *Modeling the kinetics of the competitive adsorption and desorption of glyphosate and phosphate on goethite and gibbsite and in soils*, Environmental Science and Technology 38(6) (2004) 1718-1722.

[16] Commission Regulation (EU) No 293/2013 of 20 March 2013. https://eur-lex.europa.eu/eli/reg/2013/293/oj/eng (Accessed 11/04/2023).

[17] D. Coline, Effects of vine pesticides on the biological cycle of snails in various exposure contexts, Doctoral thesis, University of Franche-Comté (France) (2011).

[18] INERIS, *Level of pesticide contamination and ecotoxicological risks in two aquatic ecosystems in Niger: Lake Guidimouni and Tabalak pond*, Africa Science 18(2) (2021) 1-13.

[19] T. Bøhn, M. Cuhra, *Compositional differences in soybeans on the market: Glyphosate accumulates in Roundup Ready GM soybeans*, Food Chemistry 153 (2014) 207-215.

[20] N. Defargea, J. Spiroux de Vendômoisb, G.E. Séralini, *Toxicity of formulants and heavy metals in glyphosate-based herbicides and other pesticides*, Toxicology Reports 5 (2018) 156–163.

[21] L. Geoffrey, Leaching of Chromium, Copper and Arsenic (CCA) from contaminated soils on wood treatment sites, Doctoral thesis, National School of Mines of Saint-Etienne and Jean Monnet University (France) (2003).

[22] N. Bolan, A. Kunhikrishnan, R. Thangarajana, J. Kumpiene, J. Park, T. Makino, M.B. Kirkham, K. Scheckel, *Remediation of heavy metal(loid)s contaminated soils–To mobilize or to*

immobilize, Journal of Hazardous Materials 266 (2014) 141-166.

[23] N. Bemelmans, B. Arbalestrie, Y. Agnan, Influence du glyphosate et de l'AMPA sur l'extractibilité des éléments traces dans les sols contaminés et non contaminés. 50ème congrès du Groupe Français de recherche sur les Pesticides, 18-20 mai 2022, Namur, Belgique (2022).

[24] K.A. Barrett, M.B. McBride, *Trace Element Mobilization in Soils by Glyphosate*, Soil Science Society of America Journal 70 (2006) 1882-1888.

[25] R. Esteban, Tolérance et accumulation des métaux lourds par la végétation spontanée des friches métallurgiques : vers de nouvelles méthodes de bio-dépollution, Thèse de Doctorat, Université Jean Monnet - Saint-Etienne (France) (2006).

[26] R.A. Mahoudjro, Y.A.P. Elisabeth, Y.D. Adjouavi, *Contamination of snails collected in the Ouémé valley in Benin by heavy metals and assessment of health risks*, International Journal of Biological and Chemical Science 13(1) (2019) 126-143.

[27] INERIS, Techno- economic data on chemical substances in France: DRC-16-158744-09774A (2015) 58.

[28] P. Tohouri, G. Soro, K. Ahoussi, M.G. Adja, G.E. Ake, J. Biemi, *Pollution by trace metal elements in surface water during high water periods in the Bonoua region (South-eastern Ivory Coast)*, Larhyss Journal 29 (2017) 23-43.

[29] ATSDR (Agency For Toxic Substances and Disease Registry). «Toxicological profile for nickel ». In: "ATSDR, Toxic Substances Portal – Nickel" (2005), Available online: http://www.atsdr.cdc.gov/toxprofiles/tp15.pdf (Accessed 11/20/2022).

[30] M.T. Gueye, *Biomonitoring of soils contaminated with hexavalent chromium: assessment of the risks of groundwater contamination and food insecurity*, Environmental and Water Sciences, Public Health and Territorial Intelligence 6(3) (2022) 855-860.

[31] F. Pizarro, M. Olivares, M. Araya, V. Gidi, R. Uauy, *Gastrointestinal effects associated with soluble and insoluble copper in drinking water*, Environmental Health Perspectives 109(9) (2001) 949-952.

[32] Z. Mingang, V. Angela, D. Guodong, *Nickel allergic contact dermatitis*, Canadian Medical Associal Journal 194(49) (2022) 1705-1706.

[33] WHO (World Health Organization). Drinking-water quality guidelines: Hygiene criteria and supporting documenttation, Geneva 2 (1986) 341.

[34] A. Rasool, A. Farooqi, S. Masood, K. Hussain, *Arsenic in groundwater and its health risk assessment in drinking water of Mailsi, Punjab, Pakistan*, Human and Ecological Risk Assessment 22(1) (2016) 187-202.

[35] E.F. Kouadio, Factors associated with quality and assessment of health risks linked to drinking water in seven localities in Côte d'Ivoire, Doctoral thesis, National Polytechnic Institute FELIX HOUPHOUËT- BOIGNY, Yamoussoukro (Ivory Coast) (2021).

[36] InVS (Health Monitoring Institute). Guide for analyzing the health aspect of

impact studies. Saint-Maurice: Health monitoring institute (2000) 49.

[37] US-EPA (United States Environmental Protection Agency). Risk assessment guidance for superfund, Volume I: Human health evaluation manual (Part A). Washington, D.C. (1989) 248.