

# Study of Cyanide Contamination of Market Garden and Agricultural Products Grown Around the Samira Gold Mine (Niger)

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**Abstract:** The term cyanide refers to all the compounds producing the  $\text{—C}\equiv\text{N}$  group. It comes from both anthropogenic and natural origins. Its presence in the environment is largely related to gold mining. Cyanide is very scary because of its toxicity causing very deadly environmental consequences. The objective of this work is to study the fate of cyanide and assess its contamination on the environment in the vicinity of a potential source of pollution such as a gold mine. In this study, soils and foods samples from the Samira gold mine and its surroundings in southwestern Niger were collected, analysed and compared with equivalent control samples grown in areas free of any industrial cyanide source. Total cyanide contents in the soils of the Samira site and its surroundings are 2 to 104 times higher than the Canadian standard ( $0.90 \mu\text{g g}^{-1} \text{CN}^-$ ) for agricultural soils, while the control soils are almost free of cyanide. These results show a migration of cyanide from the mine tailings to the surrounding area and these soils are unsuitable for any crop. The produced foods on these polluted soils have total cyanide contents 2 to 5 times higher than their controls. These contaminated matrices reveal negative impacts of the Samira mine's gold activities on its immediate environment. Ingestion of these foods would lead to serious health consequences for local populations.

**Keywords:** Gold Residues, Cyanide Fate, Contaminated Food, Risks Assessment, Samira Gold Mine

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## 1. Introduction

Cyanide, characterised by the  $\text{—C}\equiv\text{N}$  group, is one of the most lethal chemicals in nature [1-6]. Cyanide in the form of metal salts is widely used in the gold industry because of its excellent efficiency for the extraction of gold [7-10]. It also occurs naturally in more than 2,000 plant species as cyanogenic glycosides [11-16]. The toxicity of cyanide depends on the chemical form in which it occurs [15]. However, all these forms are likely to produce free cyanide ( $\text{HCN}$  or  $\text{CN}^-$ ), which is the most toxic form of cyanide.

Of an annual worldwide production of 880,000 t of sodium cyanide, 81% is used in the leaching process of gold mining. This use represents 30 to 50% of cyanide release into the atmosphere as  $\text{HCN}$  [17]. The storage of cyanide residues from gold ores after cyanidation and the discharge of large

quantities of cyanide-rich industrial effluents into rivers and groundwater have caused several deadly health and environmental consequences [18, 19]. These consequences have been very severe, particularly for aquatic species, and have generated great interest in the fate and environmental consequences of cyanide compounds.

Most often, the assessment of environmental impacts due to gold activities is based on the monitoring of water resources [20, 21]. In groundwater, due to the different mechanisms of cyanide transformation [22-24], the found concentrations are generally less important than the residues before the transformations [18, 21]. This assessment is incomplete, and it is therefore essential to take into account other environmental matrices.

There is a dependence between the environmental matrices, which leads to the passage of cyanide from one medium to

another. Therefore, the assessment of the environmental impacts of mining activities should integrate other environmental matrices such as soils and plants. The potential risks of adverse effects on human health and the environment are strongly related to the behaviour of cyanide in soil [19, 25]. To improve this assessment, some studies have evaluated cyanide contamination in soil [26-28] and in plants whose most studied food is cassava (*Manihot esculenta*), due to its high potential for cyanide poisoning in the diet [13, 29-31]. Studies, which have been devoted to assessing the environmental impacts of cyanide, simultaneously combining soil and plants, are few in number and when coupled, the study was limited to the laboratory with synthetic samples [16, 32, 33].

In Niger, industrial gold mining has been carried out exclusively at the Samira gold mine in the southwest of the country for fifteen years. In this plant, cyanide sludge residues are stored in retention ponds. No studies have been conducted to assess the impacts of the gold activities of this mine on the soils and foods grown there. In view of the high cyanide content of Samira mine effluents [34], particular attention must be paid to these effluents, which can represent a major potential way of contamination of environmental matrices.

The objective of this study is to simultaneously quantify the presence of cyanide in the soils and foods in the neighborhood of the goldmines like the Samira gold mine in order to assess the impact of auriferous activities on the environment through the distribution of cyanide from

residues to market garden products, cereals and fruits in this area. From this presence of cyanide in food, is then evaluated the potential health consequences related to the ingestion of these foods.

## 2. Materials and Methods

### 2.1. Description of the Study Area

The Samira gold site is located in southwestern Niger (13°25'N, 01°13'E), 140 km from the capital Niamey. Mineral mining of this site began around 2005. This mining site is located in a Sahelian climate zone where annual precipitation varies from 600 to 1200 mm. In this part, the average temperature is 29°C and the highest temperature goes up to more than 42°C while the cooler temperature goes down to 17°C. This zone is characterised by a highly fractured base that is highly sensitive to infiltration, thus promoting the transfer of toxic contaminants to deep aquifers and sediments. The interconnection of some aquifers would extend contamination to the rest of the area.

In this work, the main focus of the investigations was on the tailings pond area, a facility installed on the ground without any prior protective layer and open pit (Figure 1). Thus, soils and foods from the Samira gold site and its surrounding villages were sampled. Equivalent control samples were also sampled in the rest of the country (control area), an area free of any industrial activity that could generate cyanide.

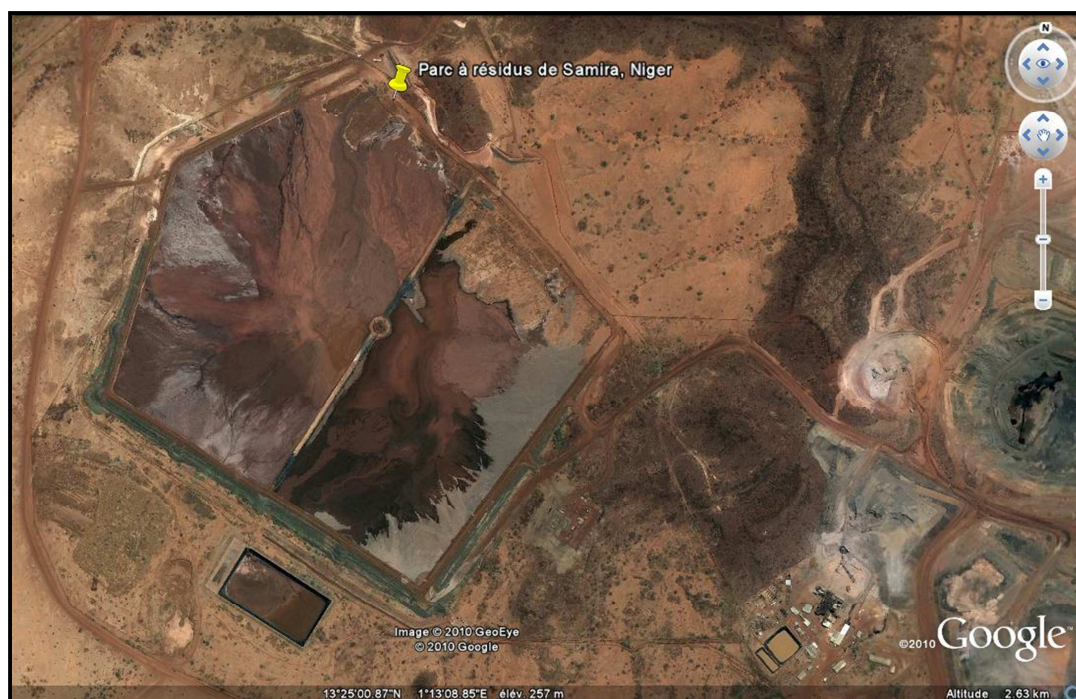


Figure 1. Aerial view of the tailings pond (Samira).

### 2.2. Studied Samples

Seventeen (17) types of local market garden products,

cereals and fruits were used in this study (Figure 2). These foods are commonly produced and widely consumed by the inhabitants of this area. It was about:

market garden products: cabbage (*Brassica oleracea*), cassava (*Manihot esculenta*), eggplant (*Solanum melongena*),

1. moringa (*Moringa oleifera*), pepper (*Capsicum*), salad (*Lactuca sativa*), sorrel (*Rumex acetosa*), three-tailed coretia (*Corchorus tridens*), tomato (*Solanum lycopersicum*);
2. cereals: beans (*Phaseolus vulgaris*), maize (*Zea mays*), millet (*Pennisetum glaucum*), peanut (*Arachis hypogaea*), sorghum (*Shorgum bicolor*);
3. fruits: jujube (*Ziziphus jujuba*), lemon (*Citrus × silt*), mango (*Mangifera indica*).

To assess the degree of cyanide contamination at the Samira gold mine and its distribution in the environmental matrices, in addition to food samples, soil samples from the mine (crop soils (Sc1, Sc2), extraction pits (Sf1, Sf2, Sf3), tailings pond (Sr1, Sr2)) and fifteen (15) surrounding villages (S1 to S16) over a distance of 75 km were collected at a

depth of 0.3 to 40 m and analysed.

These foods and soils samples were wrapped in black plastic bags, transported directly to the laboratory in coolers and stored in the refrigerator at a temperature around 4°C away from light to prevent possible photodissociation of cyanide metal complexes.



Figure 2. Some sampled foods.

### 2.3. Apparatus

The compact distillation apparatus, KTC Behr Labor-Technik, extracted total cyanide from the samples. The determination of total cyanide was performed by using a double-beam UV-Visible spectrophotometer, Evolution 300. Crison pH meter was used to measure the pH in the soils samples.

### 2.4. Preparation of Soil for Analysis

After drying in the laboratory at room temperature, the samples are crushed and sieved with a 2 mm sieve.

### 2.5. Soil pH Measurement

In a 25 mL vial with a lid, 20 mL of distilled water were added to 20 g of soil sample. This vial was closed and shaken for five (5) minutes. Then, after leaving it to rest for one hour, the aqueous phase was collected for pH measurement [35].

### 2.6. Preparation of Plant Material for Extraction

Cyanide is naturally present in many plants as cyanogenic glycosides [11, 12]. These compounds consist of an alkyl part (CN group) and an ose linked to the central carbon by an ether bond. This CN group decomposes into free cyanide. For each food, the part commonly consumed (fruit, seeds, leaves, flesh, root) was analysed. Each sample was finely divided and dried in the darkness at a temperature of 32 to 40°C in a dry place before being packaged in powder form using a mortar. The powders were then stored in glass vials.

### 2.7. Determination of Total Cyanide

Quantitative determination of total cyanide, sum of natural (cyanogenic glycosides) and anthropogenic (metal salts of cyanide) forms of cyanide, in the examined foods and soils in this study was made. This determination was carried out in two steps. The first step consisted of decomposing all forms of cyanide in the sample and recovering them as total cyanide by distillation. In the second step, the total cyanide was determined by UV-Visible spectrophotometry.

The total cyanide extraction procedure described by [34] was used. 0.5 g of food powder or soil sample was dissolved in 100 mL of NaOH solution (96%, Wagtech International LTD) in a concentration of  $5 \times 10^{-2}$  M. This mixture, completed to 250 mL with distilled water, was then transferred to a distillation flask. 15 mL of 9.2 M  $\text{H}_2\text{SO}_4$  (98.08%, Fisher Scientific) was added and boiled to 182°C and allowed to reflux for 30 minutes.

The distillate containing the total cyanide was thus recovered and the total cyanide was determined according to the UV-Visible spectrophotometric method of [21]. After diluting the distillate to 100 mL with the same NaOH solution, 20 mL were diluted with 20 mL of  $5 \times 10^{-2}$  M NaOH solution in a 50 mL volumetric flask. Then, two drops of phenolphthalein (0.1%) ( $\text{C}_{20}\text{H}_{14}\text{O}_4$ , Merck), 2 mL of glacial acetic acid (20%) ( $\text{CH}_3\text{COOH}$ , 99.5%, Merck) followed by 1 mL of the chloramine-T trihydrate solution ( $10 \text{ mg L}^{-1}$ ) ( $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCINa} \cdot 3\text{H}_2\text{O}$ , 98%, Merck) were added to the volumetric flask. After 2 min of reaction, 5 mL of the colored reagent prepared in a 100 mL volumetric flask from 1.68 g of barbituric acid ( $\text{C}_4\text{H}_4\text{O}_3\text{N}_2$ , 99%, Merck) and 1.28 g of

pyridine-4-carboxylic acid ( $C_6H_5NO_2$ , 98%, Merck) in alkaline medium (0.175 M NaOH) was added to the medium. Finally, the volumetric flask was completed to the mark with distilled water. A colored complex of violet coloration was developed and its maximum absorbance was measured after 50 min against distilled water as a reference to the wavelength of 598 nm.

The total cyanide contents of the different soils and foods were obtained from a calibration curve performed with potassium cyanide (KCN, 96%, Prolabo) as the cyanide source.

## 2.8. Data Analysis

The obtained results were processed with Microcal Origin 6.2 software. These total cyanide contents in foods and soils

were presented as a mean  $\pm$  standard deviation and expressed in  $\mu\text{g g}^{-1} \text{CN}^-$ .

## 3. Results and Discussion

### 3.1. Distribution and Contamination of Total Cyanide in the Soils of Samira and Its Surroundings

Soil is an important receptor of contaminants. The determination of total cyanide in soil is an important step in the process of assessing the cyanide contamination of the environment due to gold activities at the Samira mine. The total cyanide contents and pH values of the analysed soils at this mine and its surroundings were recorded in Table 1.

**Table 1.** pH and total cyanide contents ( $\mu\text{g g}^{-1} \text{CN}^-$ ) in the soils of Samira and its surrounding villages.

Location	Samples	pH	Total cyanide contents ( $\mu\text{g g}^{-1} \text{CN}^-$ )
Samira	Sc1	6.70	$2.93 \pm 0.25$
	Sc2	6.50	$3.54 \pm 0.15$
	Sf1	7.50	$2.93 \pm 0.25$
	Sf2	7.30	$2.10 \pm 0.20$
	Sf3	7.00	$1.53 \pm 0.17$
	Sr1	8.00	$5.68 \pm 0.25$
	Sr2	7.80	$93.37 \pm 1.14$
	S1	6.50	$3.08 \pm 0.10$
	S2	6.50	$2.75 \pm 0.05$
	S3	6.30	$2.25 \pm 0.05$
	S4	6.00	$2.55 \pm 0.05$
	S5	6.55	$3.62 \pm 0.13$
	S6	5.75	$2.94 \pm 0.03$
	S7	7.50	$2.23 \pm 0.03$
	S8	6.50	$3.18 \pm 0.08$
	S9	6.40	$1.70 \pm 0.09$
Surrounding Villages	S10	7.20	$3.65 \pm 0.22$
	S11	6.40	$2.42 \pm 0.15$
	S12	6.75	$2.67 \pm 0.15$
	S13	6.00	$2.57 \pm 0.06$
	S14	7.10	$1.67 \pm 0.06$
	S15	6.80	$2.03 \pm 0.06$
	S16	5.80	$1.55 \pm 0.05$

The soils of the Samira mine were almost neutral or slightly alkaline in pH and those of the surrounding villages were relatively acidic. The basic character of these soils would come from the products used in the cyanidation of gold such as lime and soda. Acid pH would result from irrigation on the soils of neighboring villages of the Samira mine.

Total cyanide contents of Samira's soils at the gold site ranged from 1.53 to  $93.37 \mu\text{g g}^{-1} \text{CN}^-$ . The highest concentrations were found in the soils Sr1 and Sr2, very close to cyanide residues. At the place of residence of the mine staff, the soils (Sc2 and Sc1) where market garden is carried out, recorded total cyanide contents of 2.93 and  $3.54 \mu\text{g g}^{-1} \text{CN}^-$ . All of these total cyanide contents found in the soils around the mine exceeded the Canadian cyanide standard for agricultural soils of  $0.90 \mu\text{g g}^{-1} \text{CN}^-$  [25], which is almost 2 to 104 times higher. These significant contents of total cyanide were derived from the diffusion and dispersion of cyanides from the tailings pond to environmental matrices under certain climatic conditions (rain, sun, temperature) and

depending on soil characteristics [15, 25, 36, 37].

In addition to dissociating and dispersing in the immediate environment of the tailings pond, cyanides from the industrial activities of the Samira mine were transported over long distances under the influence of solar radiation to form hydrogen cyanide, a volatile and highly mobile species. Indeed, the total cyanide contents in the soils (S1 to S16) of the surrounding villages the Samira mine ranged from 1.55 to  $3.65 \mu\text{g g}^{-1} \text{CN}^-$ , with an average of  $2.55 \mu\text{g g}^{-1} \text{CN}^-$ . As a result, these soils, on which agriculture and seasonal crops are grown, were characterised by higher cyanide contents than the Canadian standard. The dispersion and accumulation of cyanide in soils far from the tailings pond is also explained by the high affinity of cyanide for metal cations in the soil ( $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ...) by easily forming stable metal complexes in these low acid pH soils [37, 38]. Similarly, the migration of cyanides from the mine to these analysed soils could result from soil runoff and leaching in the area. Soil organic matter content has a strong influence on the soil's



ability to retain and release cyano-metallic complexes, thus posing a likely risk of infiltration and drainage that leads to contamination of food and groundwater [28, 39].

The control soils, far from gold activities, were suitable for cultivation. Indeed, almost free of cyanide (contents from 0.00 to 0.65  $\mu\text{g g}^{-1} \text{CN}^-$ ), these soils had contents lower than the Canadian standard. Similar results have been observed for agricultural soils free of potential sources of cyanide contamination [40]. This proves that the presence of cyanide in Samira's soils is not natural, but industrial, that means the use of cyanide in gold mining, explain the existence and contamination of cyanide in the soils of Samira and its surrounding villages.

### 3.2. Transfer of Cyanide Contamination from Soils to Samira's Food

Cyanide, naturally present as cyanogenic glycosides, is found in a number of edible plants [11, 12]. The presence of cyanogenic glycosides for these plants serves as protection against herbivores [33]. Some plants also absorb cyanide from the soil [41]. The analysis of cultivated foods is paramount in assessing the degree of contamination of a soil pollutant and its integration into the food chain [42]. Thus, the gold -bearing impacts of the Samira mine were assessed on foods grown on soils that were contaminated with cyanide.

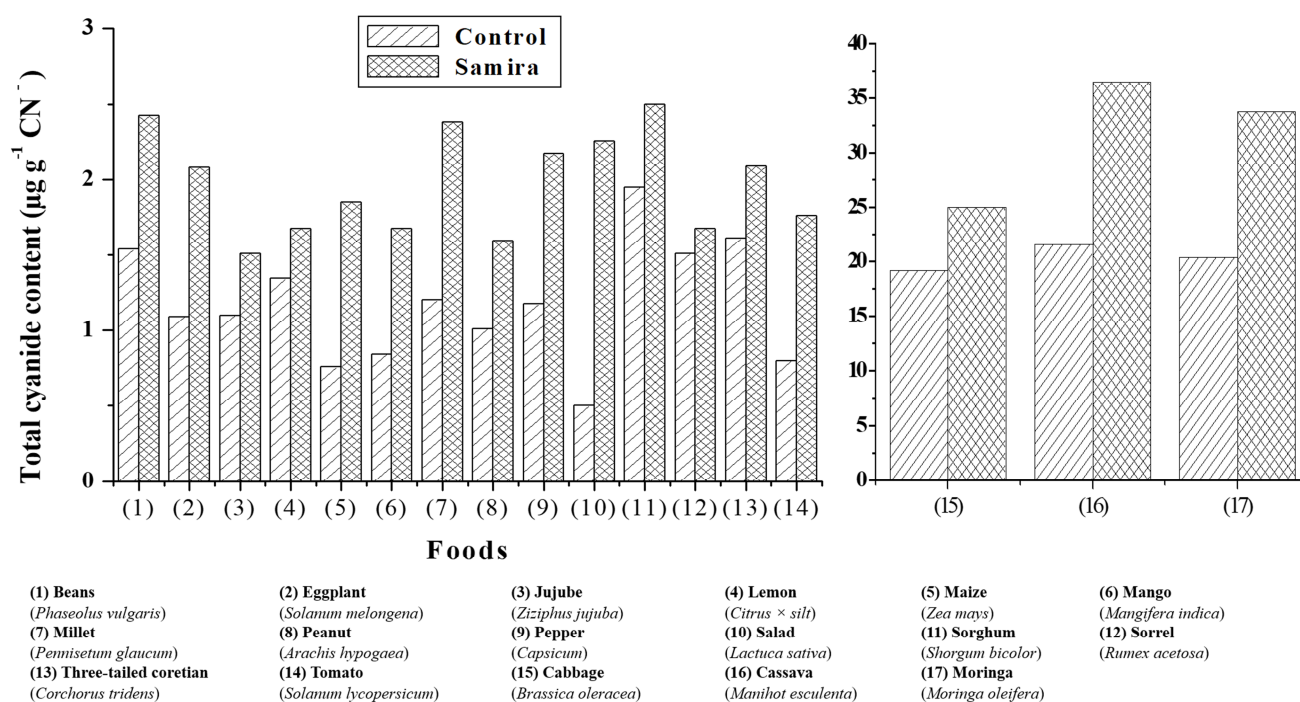


Figure 3. Total cyanide contents ( $\mu\text{g g}^{-1} \text{CN}^-$ ) in control and Samira's foods.

Figure 3 shows the total cyanide contents found in food grown on and around the Samira gold mine soils and those grown on control soils in the rest of the country where there is no industrial activity that could generate cyanide. This assessment showed total cyanide assimilation in plants grown on cyanide-contaminated soils. Indeed, these results showed that, with the exception of sorrel, for each type of food, the total cyanide content found at Samira far exceeded that of the control sample. Contents ranged from 0.50 to 21.53  $\mu\text{g g}^{-1} \text{CN}^-$  in the control foods while those of Samira's foods ranged from 1.38 to 36.50  $\mu\text{g g}^{-1} \text{CN}^-$ .

The total cyanide contents of the control foods would only come from cyanogenic compounds. The presence of cyanide in these foods, specifically the control foods, proved that all the studied foods in this study naturally exhibited a capacity to produce hydrogen cyanide (HCN), which means that they contained cyanogenic glycosides. The content of cyanogenic compounds varies with plant organ, age, variety and environmental conditions such as soil, moisture and

temperature [31, 43].

The difference in cyanide contents in the plants grown at Samira and its surroundings compared to controls from the rest of the country was explained by the absorption of cyanide from soils highly polluted with cyanide in the area. In addition, the use of contaminated water from this area [21] for irrigation also allowed the transfer of cyanide to food, leading to their contamination. Reference [16] experimentally demonstrate that free cyanide (HCN or  $\text{CN}^-$ ) does not accumulate in healthy plants and therefore suggest that  $\text{CN}^-$  detected in plants comes from the accumulation of cyanide in plant tissues that is present only in complexed form, presumably in the form of an iron complex.

Among the control foods, those with less and more cyanogenic compounds were salad and cassava respectively. At Samira, cassava was always the most cyanogenic and the least was jujube. It is noted that through the ratio of Samira's contents to controls, salad was the food that absorbed the most cyanide metal complexes. Fruits

absorbed less than cereals, also less than market garden products. Indeed, Samira's contents were 1.3 to 2 times higher than controls in fruits, 1.3 to 2.5 times higher in cereals and 1.2 to 4.6 times higher in market garden products. These data correlate with the total cyanide contents in Samira's soils, which were significantly higher than those found in the control soils.

These market garden products, in direct contact with the ground, were the ones that absorbed the most cyanide metal complexes. This result is in perfect agreement with the published study by [32], in which they show a high absorption of metal cyanides in the root part of a plant compared to other organs of a plant.

Foods such as cabbage, moringa and cassava have naturally cyanide contents exceeding the FAO/WHO Codex Alimentarius standard [44] of  $10 \mu\text{g g}^{-1} \text{CN}^-$  in human food. Moringa, consumed almost daily in Niger, and cabbage are unsuspected foods with high contents of cyanide. These foods were therefore added to the cassava previously known on the list of highly cyanogenic foods. Raw moringa is sold in pharmacies as a dietary supplement for babies and pregnant women in Niger. In order to better secure the consumption of cabbage and moringa, it is important to conduct further investigations.

### 3.3. Impact of the Ingestion of Cyanide-contaminated Food on the Population

These Samira's foods, in which cyanide was accumulated in complexed form, are consumed by the populations of this area. The cyanide of these foods could be traced back to humans and animals by the consumption of these foods. Cyanide compounds undergo hydrolysis to hydrocyanic acid in the stomach, hence its toxicity if ingested. This would expose populations and wildlife to serious health consequences such as leg paralysis in children and women, dwarfism and tropical ataxic neuropathy [45, 46].

The health consequences would be more harmful when these cyanogenic foods are ingested raw, without any treatment that could reduce the amount of cyanide and therefore its toxicity. As a result, animals are more exposed to cyanide poisoning than humans, as cooking some foods significantly reduces potential toxicity [47, 48].

## 4. Conclusion

The results of this study show that cyanide is absorbed by the soil due to gold activities at the Samira mine at contents ranging from 2 to 104 times the Canadian standard. Cyanide contents in market garden products, cereals and fruits grown on the soils of this mine and its surroundings are 2 to 5 times higher than those found in their control equivalents.

This study highlights the causality between cyanide-contaminated soils and total cyanide contents in food grown on these polluted soils. It also provides crucial information on total cyanide contents in food grown in gold areas in particular and in Niger in general.

The impacts of the Samira mine's gold activities are

strongly felt through the highly cyanide-contaminated soils. These environmental impacts are quite revealing with the high contents found in foods grown on these polluted soils. If these foods are ingested, this would have short- and medium-term health consequences for local populations.

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