Original Research Article

ASSESSING THE SOURCE OF THALLIUM CONTAMINATION IN GROUND AND SURFACE WATERS IN THE LOCALITY OF YAMTENGA (BURKINA-FASO): CORRELATION WITH SOME HEAVY METAL IONS

ABSTRACT

Thallium (Tl) is a non essential element for human being and is considered as a highly toxic trace element at a concentration above 2µg/L. To assess the source of thallium contamination in ground and surface waters in the locality of Yamtenga village (11°43'35.1'' N and 00°11'50.8'' W, Burkina Faso), chemical analyses of thallium concentrations in the soils of Yamtenga village along with geological descriptions (geological map and hydrographic watershed map of the studied area) were undertaken. We found thallium concentrations in this area ranging from 1.61 mg / kg to 404.75 mg / kg. A zoned mineralization in thallium, due to the geological structure of the locality, was established in the soils, suggesting that the source of thallium contamination in ground and surface waters in the locality of Yamtenga village is of natural origin. The concentration of some heavy metals (Pb, Zn, Cd, Cu and Mn) were also evaluated in the soils of Yamtenga village and their concentration relationships with thallium were analyzed by the Pearson correlation coefficient based on matrix correlation. Moderate (0.554), low (0.408) and significant (0.999) correlations coefficients were obtained between thallium and lead, zinc, manganese respectively. Significant correlation coefficients (0.788 and 0.791) were also noted between thallium and copper, cadmium respectively. Thallium concentrations in ground and surface waters in this locality are mainly related to the interactions between water and source rocks, thallium being released following some alteration processes with other heavy metals elements especially manganese.

***Key words**: thallium, mineralization, heavy metals, correlation*

1. INTRODUCTION

Thallium is a relatively toxic element with higher toxicity than Cd, Pb, Zn, and other trace metals for mammals **[1, 2]**, and is recognized among the 13 priority metallic pollutants in the world **[3]**. Thallium is considered a cumulative poison that can cause adverse health effects and degenerative changes in many organs **[4]**. The presence of thallium in the environment is a serious problem because long-term ingestion of small doses of thallium can lead to a range of health problems, cardiovascular disease and acute intoxication **[2, 5]**. The main threat to humans is occupational exposure, environmental contamination and accumulation in food, mainly in vegetables grown on contaminated soil **[4]**. The negative impact of pollution of Tl on health was reported in a rural area in Lanmuchang in southwestern China where symptoms related to thallotoxicosis (weakness, muscle and joint pain, impaired vision and loss of hair) were recorded for 189 cases of Tl poisoning in the 1960s and 1970s **[6]**. In addition, an accidental Tl (0.18-1.03 Tl µg/L) pollution from wastewater from a lead/zinc smelter discharge to a drinking water source in the Pearl River in southern China was reported in 2010 **[7]**. The maximum allowable Tl concentration in drinking water in China is 0.1 µg/L **[8]**, which is significantly lower than the one in US drinking water (2 µg/L) **[9]**.

Thallium exists under two oxidation states, Tl(I) and Tl(III), both of which are considered highly toxic to living organisms **[10, 11, 12]**. Because of its high toxicity to most living organisms, thallium (Tl) is included in the United States Environmental Protection Agency's (USEPA) list of priority toxic pollutants **[13, 14]**.

The sources of thallium in the environment are divided between natural sources and anthropogenic sources. The concentrations of naturally occurring thallium in soils are very dependent on the source rock on which the soil is growing. The work of Voegelin et *al*. **[15]**

reported very high concentrations of thallium in the order of a thousand ppm in soils of a Swiss region resulting from the pedogenesis of hydrothermal clusters rich in thallium, arsenic and iron. Other studies reported thallium concentrations in the order of 10 ppm in soils developing on sulphide-rich mineralization **[16, 17]**. Anthropogenic sources of thallium are related to mining activities, either by the release of atmospheric thallium by smelters **[18, 19, 20, 21]**, or by developing on mining waste **[22, 23]**, with concentrations which might exceed 200 ppm. The permissible content in uncontaminated soils is 1 $\mathrm{mg.kg^{-1}}$ **[16, 24]**.

Groundwater from captive and shallow aquifers are water resources that are exploited by humans for a variety of uses. However, the chemical composition of these waters depends on the geological nature of the soil from which they stem and also on the reactive substances they might have encountered during the flow **[25]**. In the surrounding villages of Ouagadougou, the water consumed generally comes from wells, backwaters and boreholes that are not sanitized. This water is loaded with microorganisms and solid particles, dissolved mineral salts, heavy metals and colloidal matter.

Following the complaints of the population of Yamtenga, village around Ouagadougou, relating to the color of the water (brown rust at certain times of the day), its smell and the solid deposits often observed on the containers used to collect water, Mahamane et *al*. **[26]** conducted investigations focused on the evaluation of the physico-chemical characteristics of the borehole and well water of this locality. In addition, the levels of metallic trace elements responsible for the alteration of the organoleptic characteristics of drinking water were determined. The paper by Mahamane et *al*. **[26]** was the first investigation in Burkina Faso identifying thallium in borehole and well water at levels exceeding the recommended drinking water standard of 2 µg/L **[16, 27, 28]**. The detection of thallium, a non-essential element for humans and highly toxic for the biosphere, was much unexpected and needed to be looked into in more detail. The validity of these findings also needed to be confirmed and any sources to be explained.

In this context, the present work constitutes the follow of our previous article **[26]**. It focuses on the identification of the thallium contamination sources in ground and surface waters in the locality of Yamtenga (11°43'35.1'' N and 00°11'50.8'' W, Burkina Faso). The main objectives of this study were to: (1) determine the concentration and spatial distribution of thallium in soils; (2) identify the sources of thallium contamination in that locality and (3) establish a correlation between thallium and other heavy metals that are present in the ground waters.

2. MATERIALS AND METHODS

2.1. Study area and geological description

Yamtenga is a small village located in the South East of the city of Ouagadougou. The geographical location of the village of Yamtenga is 11°43'35.1''North latitude and 00°11'50.8'' West longitude. The area is characterized by a long dry season from October to May and a rainy season from June to September. The studied area is relatively wooded with many gardens and cultural spaces where the inhabitants practice the off-season crops. These practices are made possible by a water dam and the numerous wells and boreholes in the village. The relief in the region is relatively flat. The altitudes vary between 270 and 340 meters. The boreholes with thallium contaminated waters **[26]** are located on altitudes between 295 and 320 meters. Yamtenga is in a granitic landscape (**Figure 1**). However, the geological description of formations traversed by drilling indicates the presence of pegmatites hosted in the granite. Thallium occurs in igneous minerals and rocks by substitution for potassium. Its geochemical behaviour closely resembles rubidium so that it is concentrated in residual magmas to occur in notable amounts in pegmatitic potassium minerals **[29,30]**. On a structural plan, thallium contaminated drilling waters constitute a major break in the field.

It is noted that Yamtenga area almost lacks outcrops due to well-marked lateritic alteration. In fact, the geological formations of the leaf of Ouagadougou, as elsewhere in Burkina Faso, have undergone a strong lateritic alteration, which explains the rarity or poor quality of rock outcrops over large areas **[31]**. Watersheds are spatially explicit landscape units containing a range of interacting physical, ecological and social attributes related by water flows **[32]**. Watersheds contribute to the enrichment of surface waters at a single location, such as a point on a stream or river, or a single wetland, lake or other body of water **[33]**. Thus, the hydrology of a watershed is not only affected by rainfall and surface water, but also by ground waters which play a major role. To get an idea of the activities carried out in the study area over the past years, and to estimate the anthropogenic contribution, we used the Landsat (Land Surface Observation Program) images.

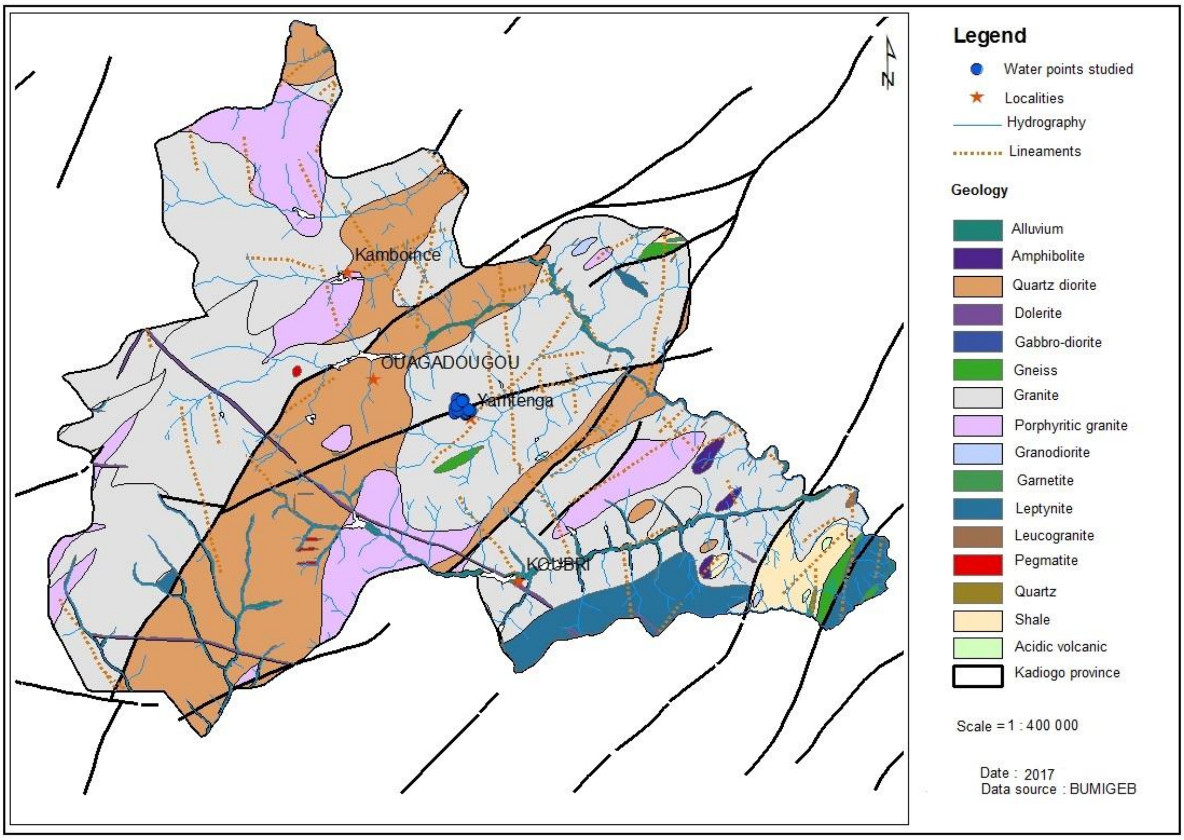

FIG. 1 Geological map of the central region (including the studied area)

2.2 Quality assurance of the chemical analyzes

Quality control measures, including reagent blanks and duplicate samples, were carried out to validate the quality of the chemical analyzes and to examine the accuracy of the data.

Reproducibility was verified by performing three replicates of digestion on 50% of soil samples randomly selected. The analysis of heavy metals was carried out using an ICP-AES. The calibration solutions of the apparatus were prepared from a standard multi-element solution containing elements Tl, Cu, Pb, Mn, Zn and Cd. In addition, the glassware, the pestle and the agate mortar used were washed with soap, then with tap water, rinsed with distilled water and then immersed in a solution of nitric acid 14 M at 5% (vol/vol) for a duration of 24 h. They were then rinsed with ultrapure water and oven-dried at 80° C for five hours. The chemicals used in this study namely nitric acid (HNO_3, VWR) and hydrogen peroxide (H_2O_2, VWR) are of analytical grade. All solutions were prepared with ultrapure water of 18.2 MΩ.cm resistivity.

2.3 Sampling

A total of 92 soil samples were collected at depths ranging from 30 cm to 140 cm. The sampling sites were chosen to represent the entire study area. In the field, the actual positioning of the sampling points was done using GPS map 64s receivers with the WGS 84 datum and UTM coordinates. The collected soil samples (approximately 1.0 kg each) were dried in the open air at room temperature, ground with an agate mortar, homogenized and sieved through a sieve of 80 microns. Passersby were retained for digestion.

2.4. Determination of thallium concentrations in soils

The goal was to achieve the most complete thallium extraction which is possible, simple and fast to be used on many samples. We made a wet solution with nitric acid HNO_3 ($14\ mol.L^{-1}$) and hydrogen peroxide H_2O_2 (30% by volume). Hydrogen peroxide supplements the action of nitric acid in the oxidation of organic matter and turns into water during heating, so does not complicate the matrix. Five grams of sample were dissolved in 25 ml of nitric acid at 14 $mol.L^{-1}$ at room temperature for 5 h with constant stirring. Then 50 ml of hydrogen peroxide (30% vol/vol) were added. After stirring for 12 h, the mixture was gradually heated to gentle boiling for 2 h. After cooling, the samples were filtered into a 250 ml flask, the volume of which was supplemented with ultrapure water, then stored at 4 ° C and analyzed at ICP-AES. The concentrations of heavy metals in soil samples were calculated according to the following formula **[32]**:

$$\mathbf{Concentration(\ mg/kg)} = \frac{\mathbf{Concentration\ (mg/L)\times V}}{\mathbf{M}}$$

Where V and M are respectively the final volume of solution after digestion and the initial mass of the measured sample.

2.5 Statistical analysis

Principal Component Analysis is performed using XLSTAT software version 2018.1. The goal was to establish a relationship between thallium and Cu, Zn, Mn, Pb and Cd from the analysis of Pearson coefficients. The study of the correlation between thallium and the metals analyzed gave information on the degree of possible association between them.

3. RESULTS AND DISCUSSION

3.1. Methodological approach for the delimitation of the study area

Drilling whose waters are contaminated with thallium belong to a small hydrologic basin with an estimated area of 16 km^2. The basin is drained by a river on which is built a hydraulic dam. Two main arms contribute to the put in water of the dam located more or less in the heart of the basin (**Figure 2**).

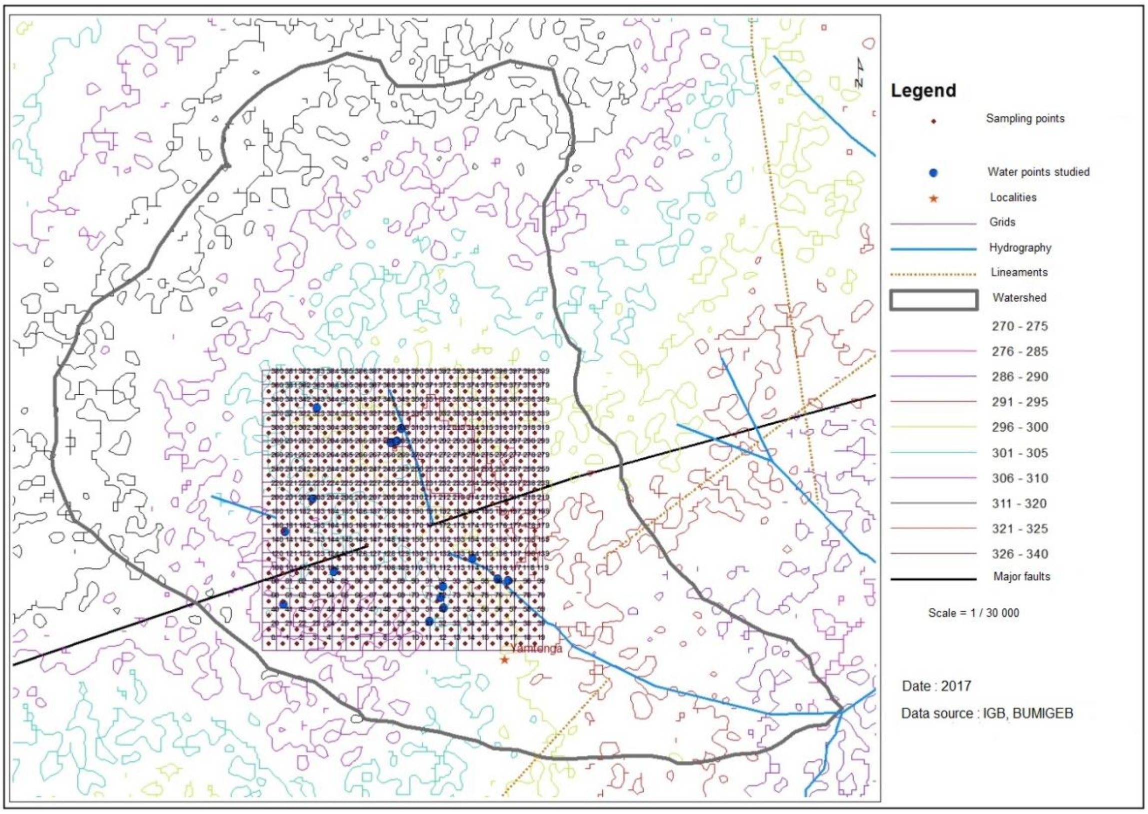

FIG. 2 Hydrographic Watershed Map of the Study Area

The study of the evolution of the environment of the study area from Landsat images indicates that from 1995 to 2015, the watershed considered had a rapid occupation of the soil. In 1995, residential areas were noticeable only outside the basin. The northwestern part of the basin was marked by farms (**Figure 3**). In 2000, the proliferation of habitats is observed within the basin (**Figure 4**). And in 2015, the sampling area also becomes a site of high concentration of habitat (**Figure 5**). However, the areas bordering the dam remain a breeding ground for vegetable crops. Thus, thallium surface and groundwater contamination could have an anthropogenic source related to agricultural practices, transport and deposits of contaminated or thallium-bearing objects and/or a natural source related to soil geology.

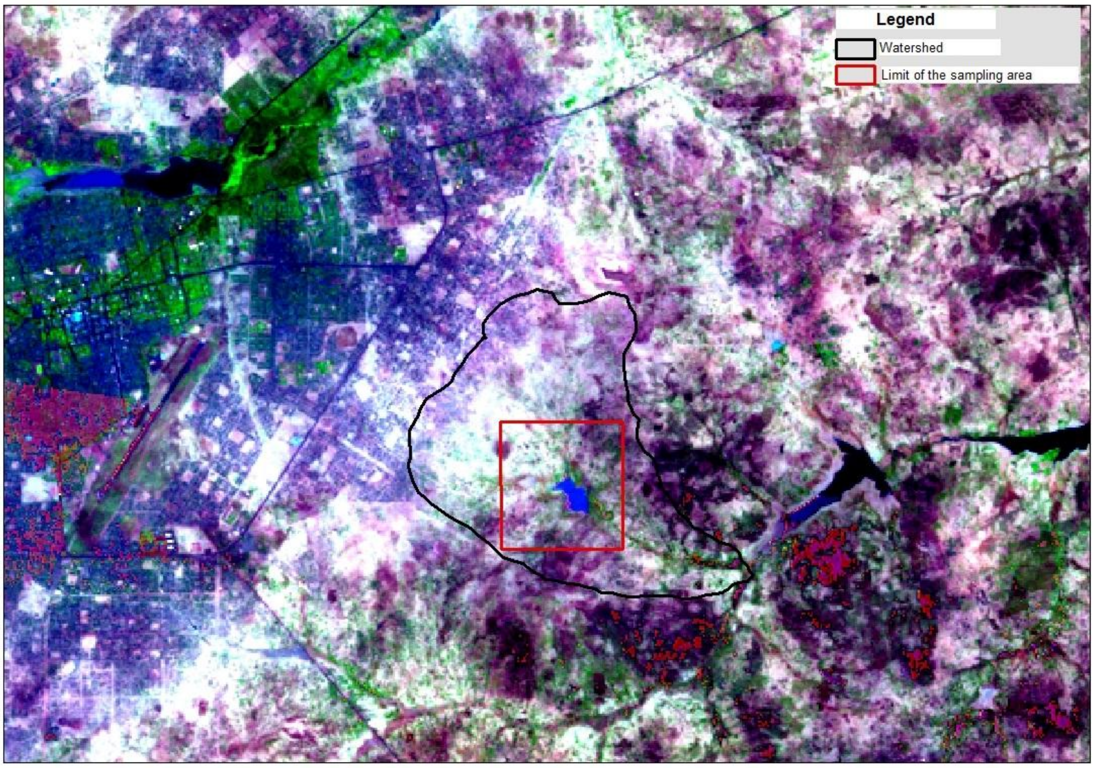

FIG. 3 Landsat image in 1995

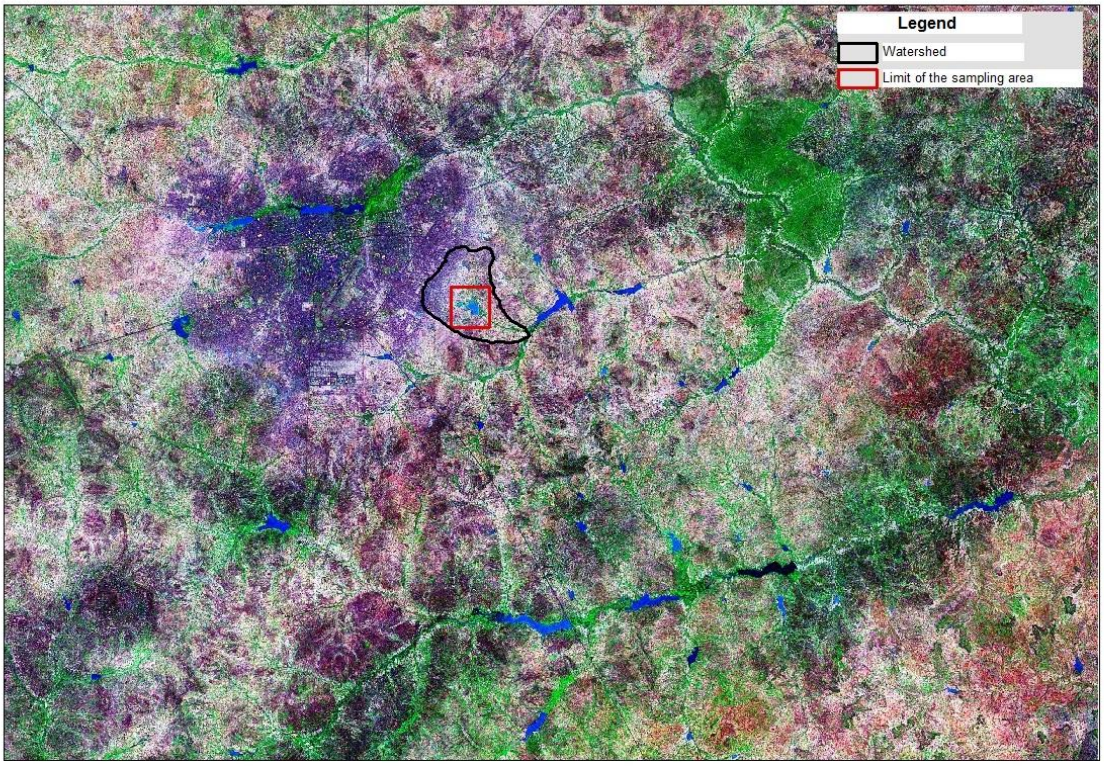

FIG. 4 Landsat image in 2000

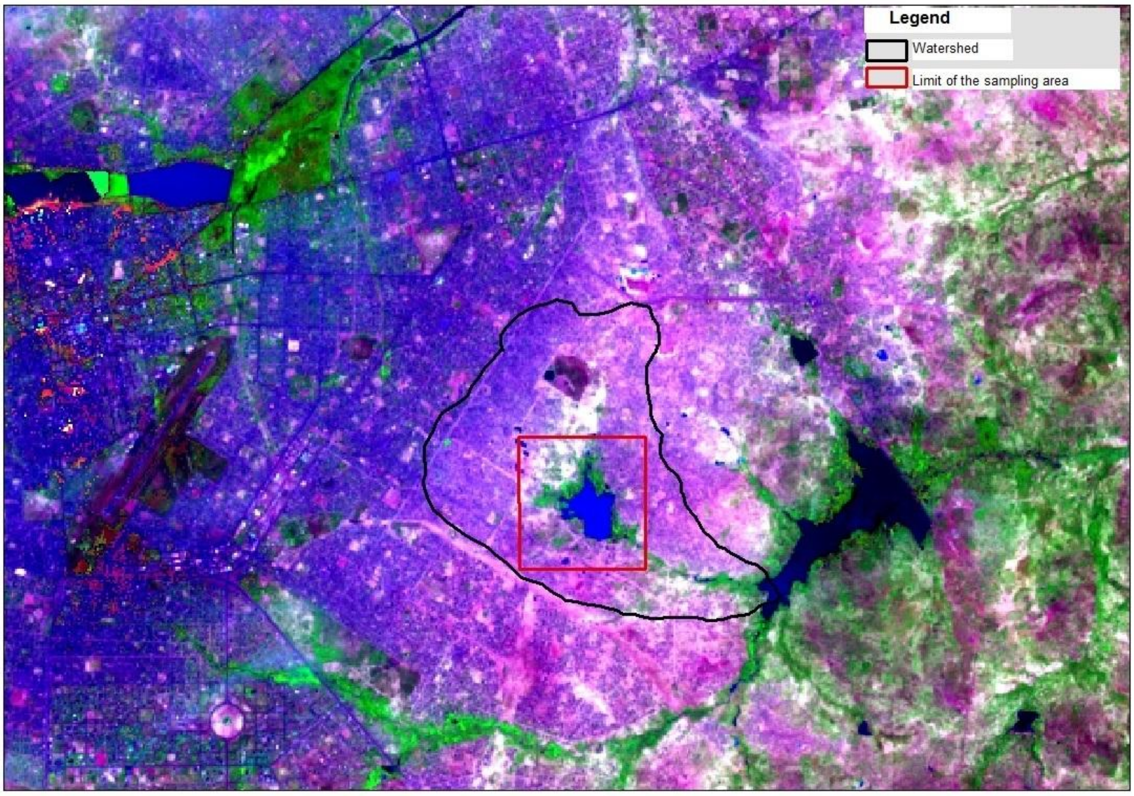

FIG. 5 Landsat image in 2015

Taking into account the structure and the geology of the ground, a grid of 100 x 100 meters covering all the water points to be studied was selected in a North-West direction for the soils sampling. We first selected Platform 1 (**Figure 6**) for our study. It mainly consisted of geochemical soil sampling with a spacing of 100 m between the profiles and a sampling rate every 100 m. A theoretical grid (profiles with sampling points) was then provided (**Figure 7**). At first we swept the superficial horizon by sampling at about 50 cm depth. The first samples were analyzed and from the obtained results, two abnormal points out of forty-two (42) were identified. We carried out a mesh tightening around these two (02) geochemical anomalies whose geographical coordinates in UTM are summarized in **Table 1**. These two points correspond to zones of thallium mineralization.

TABLE 1 Geographical coordinates in UTM

Samples	X	Y
SY14	668158	1365258
SY19	668358	1365458

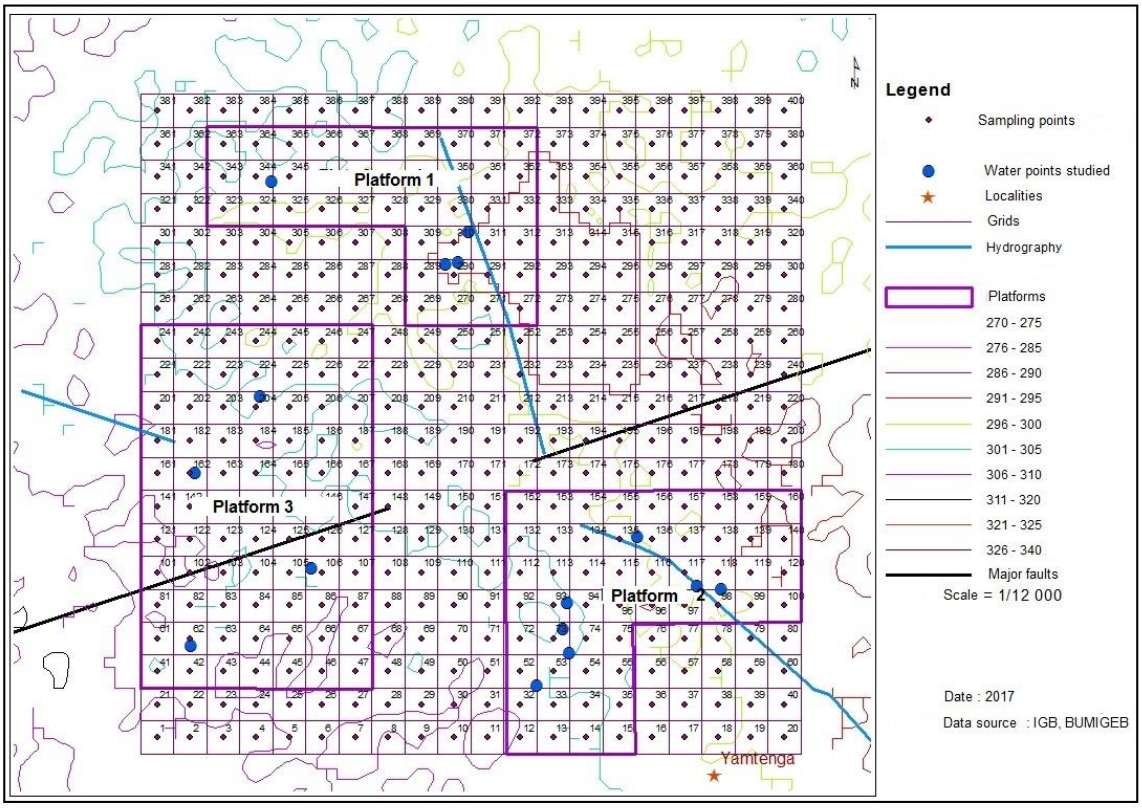

FIG. 6 Map of targeted platforms

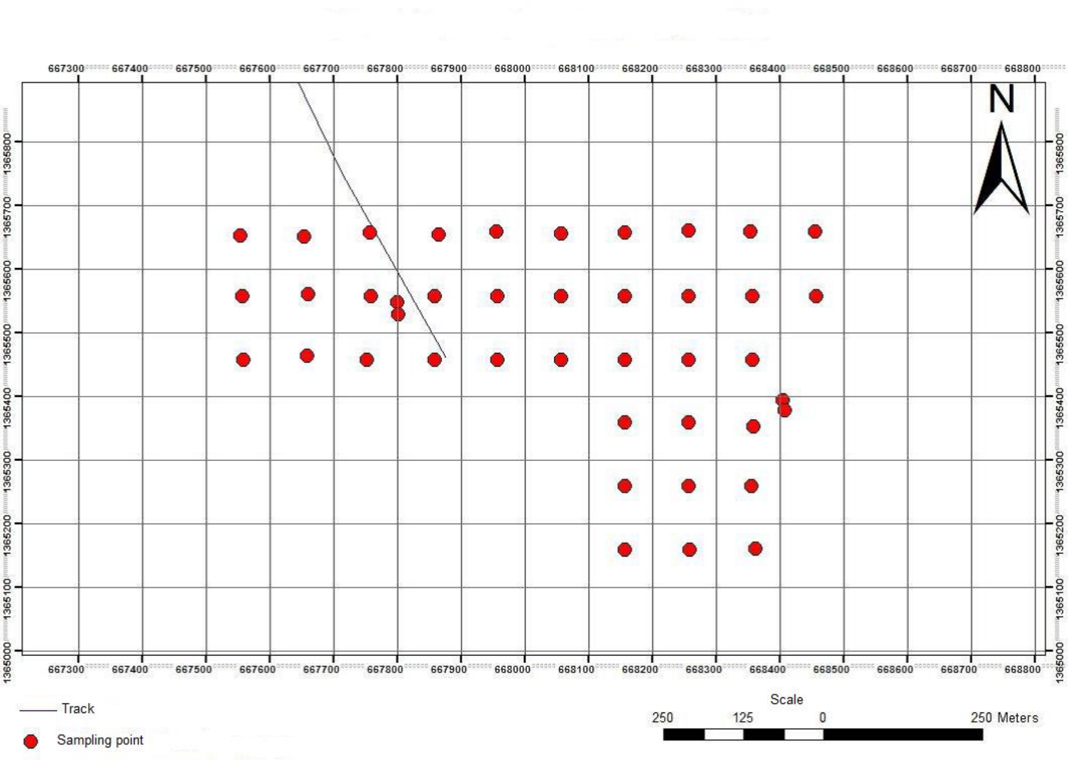

FIG. 7 Map of sampling points

A second sampling step was then performed between these two abnormal points. A new theoretical grid (**Figure 8**) with a sampling mesh of 25 m and step of sampling of 25 m was adopted for the soil sampling. A total of thirty-four (34) soil samples were then taken at approximately 50 cm depth and ten (10) well samples at depths ranging from 30 cm to 1.4 m were recorded. At each well, sampling was done on three separate horizons.

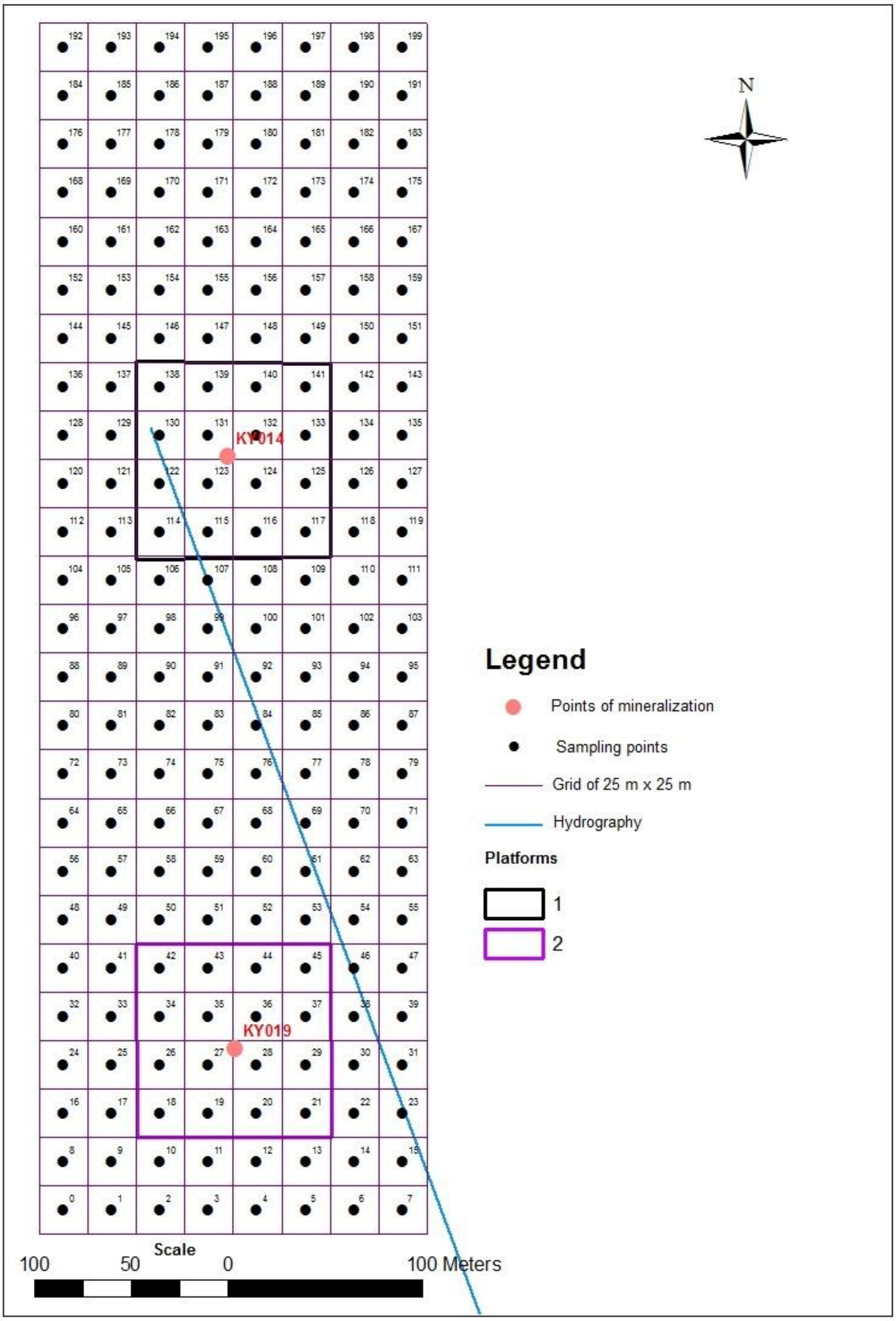

FIG. 8 Theoretical sampling grid

3.2. Concentrations of heavy metals

Thallium concentrations in soil samples are shown in **Tables 2** and **Table 3** indicates the concentrations of thallium and other heavy metals in soil samples.

TABLE 2 Thallium concentrations of the first sampling

Samples	Thallium content (mg/kg)
KY014	339,62
KY019	25,75

Two samples out of a total of forty-two samples show strong thallium mineralization with concentrations of 25.75mg / kg and 339.62mg / kg. This result shows that the watershed is locally mineralized in thallium, especially the upper horizon. At this stage, therefore, we cannot conclude on the source of thallium contamination, hence a second sampling step to address this concern was undertaken. In this second step, we associated thallium, lead, cadmium, copper, zinc and manganese for correlation studies.

TABLE 3 Heavy metals concentrations of the second sampling

Samples	Depth (cm)	Tl (mg/kg)	Mn (mg/kg)	Pb (mg/k)	Cd (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
SKY01	54	1,61	438,63	6,22	0,26	3,14	2,64
SKY020	57	44,48	1582,79	7,5	0,27	3,67	2,22
SKY021	60	19,98	746,02	6,01	0,23	2,69	2,30
SKY026	55	404,75	10231,33	14,26	0,60	5,86	4,36
SKY030	55	17,83	1212,40	12,16	0,46	3,35	2,27
SKY031	55	53,05	1672,30	10,14	0,42	2,93	1,94
P2SKY03	30	163,19	4222,73	25,09	0,40	6,72	2,69
P6SKY09	140	6,03	409,44	7,56	0,21	2,50	5,25
P8SKY012	120	4,82	370,65	5,73	0,19	2,04	1,94

Mineralization at the reference points of the first sampling was confirmed by the second sampling. Mineralization of the second sampling indicates that nine (09) samples out of a total of 50 are mineralized in thallium. Thallium concentrations range from 1.61 mg/kg to 404.75 mg/kg. In addition, those of manganese oscillate between 370.65mg/kg and 10231.33mg/kg. Also, lead concentrations range from 5.73mg/kg to 25.09mg/kg. As for cadmium, concentrations range from 0.19 mg/kg to 0.60 mg/kg. For copper, concentrations range from 2.04 mg/kg to 6.72. Finally zinc concentrations range from 1.94 mg/kg to 5.25 mg/kg.

3.2. Identification of the source of thallium contamination

The results of the first sampling justify the mineralization of the dam and thallium wells. In fact, the dam's water is a mixture with some of the runoff from the watershed identified for this study. In addition, the context and the hydrogeological characteristics of the study area support an interconnection between the surface water (dam), the well water and the intermediate and deep aquifers exploited by the boreholes. The results of the second sampling indicate that the lateral distribution of thallium in the zone is discontinuous overall **(Figure 9)**. However, it is oriented in the South East-North West direction in the soil. This direction is consistent with the direction of the geological structures (major faults) defined by the geological map of the central region **[31].** Thallium mineralization is therefore controlled by geological structures, including pegmatite veins, which are highly represented in the area. Vertical thallium distribution also remains local and variable in soil content. This mineralization related to structures such as pegmatites is a zonal or point mineralization. The variation in soil content can be explained by a change in the concentration of thallium during the mineralization phase. This is due to the weathering process of the mineralized bedrock, which favors mineralization by progressive contamination of the immediate environment. Thus one could start from a kernel strongly mineralized in thallium which justifies a high concentration at certain points or a less mineralized aureole justifying a low concentration in other points.

The mineralization of surface water comes mainly from the leaching of soil horizons contaminated by runoff that transport thallium with it and accumulate it in the zone of low topography corresponding to the water body. Mineralization of well water stems from two sources: (i) contaminated surface water that feeds wells by indirect infiltration; (ii) direct infiltration of waters by privileged routes that leach the mineralized zones into the soil towards the wells. As for the contamination of the drilling water, it is justified by the direct or indirect infiltration of waters which leach the mineralized zones in the waters of the drillings. In addition, there are drains or reservoirs in the rocks beneath the alterites that host the thallium released by the altered profile of the source rock. This thallium is then released into the groundwater. We can therefore conclude that thallium contaminations in ground waters in the village of Yamtenga stem from a natural origin, and that the source is linked to the geology of the environment (endogenous).

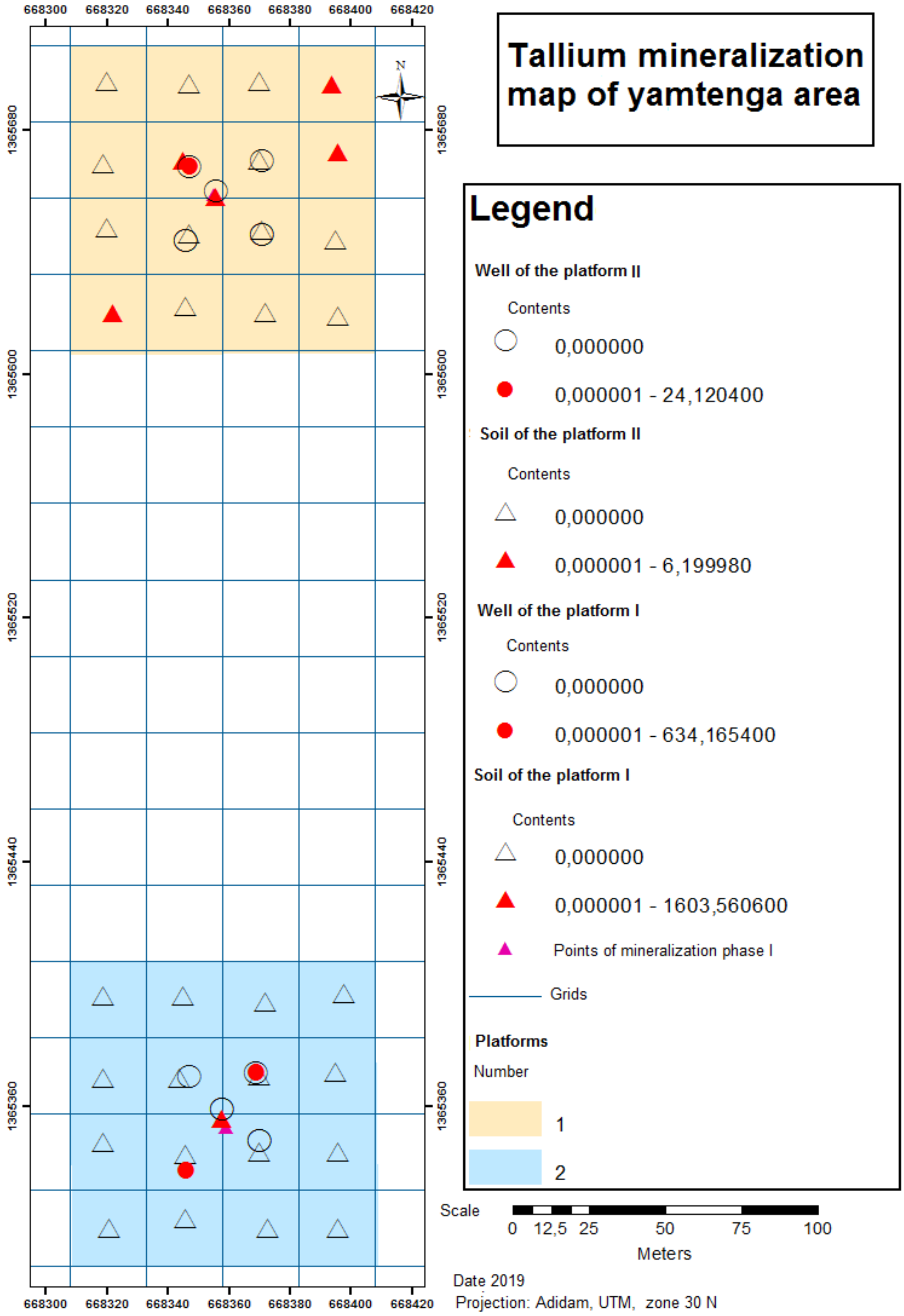

FIG. 9 Spatial distribution of thallium in the soil

3.3. Correlation study between heavy metal concentrations

Correlation analysis is a preliminary descriptive technique for estimating the degree of association between the involved variables. The purpose of correlation analysis is to measure the intensity of the association between two variables. Such an association is likely to lead to an understanding about the cause-and-effect relationship between the variables **[34, 35**].

The Pearson correlation coefficient was used to describe the relationship between the heavy metal concentrations studied in the Yamtenga village soil samples. The correlation matrix between the metals analyzed is shown in Table 4. Most of the parameters have a statistically significant correlation to each other indicating a close association of these parameters with each other. Rakesh et *al*. **[36]** reported that a high correlation coefficient (close to +1 or -1) meant a good relationship between two variables, and around zero meant no relationship between them at a significant level of 0. 05%. There is a strong correlation if the value of the correlation coefficient r is greater than 0.7 ($r > 0.7$). When the values of r are between 0.5 and 0.7, this indicates a moderate correlation between two different parameters. As shown in **Table 4**, the results of the correlation coefficients indicate a strong positive correlation between Tl and Mn ($r = 0.999$), Tl and Cd ($r = 0.791$), Tl and Cu ($r = 0.788$), Cd and Mn ($r = 0.815$), Cu and Mn ($r = 0.788$) and Pb and Cu ($r = 0.895$). This strong positive correlation shows that the elements are closely associated, thus suggesting their common origin. In addition, moderate positive correlations between Tl with Pb ($r = 0.554$), Pb with Mn ($r = 0.554$), Cd with Pb ($r = 0.603$) and Cd with Cu ($r = 0.683$) were recorded. Finally, weak positive correlations were found between Tl and Zn ($r = 0.408$), Zn and Mn ($r = 0.396$), Zn and Pb ($r = 0.091$), Zn and Cd ($r = 0.144$), Zn and Cu ($r = 0.204$). This low correlation indicates that the presence or absence of one of this element affects less the magnitude of the other. The positive correlations of thallium, especially with toxic metals such as lead and cadmium, are alarming due to the fact that these metals are known for their toxic effects on health.

TABLE 4 Matrix of correlation coefficients for heavy metals concentration in Soil Samples

Variables	Tl	Mn	Pb	Cd	Cu	Zn
Tl	**1**					
Mn	0,999	**1**				
Pb	0,554	0,554	**1**			
Cd	0,791	0,815	0,603	**1**		
Cu	0,788	0,788	0,895	0,683	**1**	
Zn	0,408	0,396	0,091	0,144	0,204	**1**

4. CONCLUSIONS

Levels of thallium and other metals were evaluated in the soils of Yamtenga village. The analysis of the obtained results showed a discontinuous contamination by thallium in the Yamtenga area. This source of contamination has a natural origin. In fact, the alteration of the parent rock releases the thallium and the concentration differs according to the amount of thallium found in the altered substrate of the source rock. Correlation studies show that thallium is usually released with other metals such as manganese. Therefore, the impact on agricultural production and human health of these soils is to be assessed.

The perspectives of the present investigations will be the following: 1) to extend the study on drill cuts to various horizons of the soil and; 2) to identify the nature, to describe and characterize the source rocks that are responsible for the release of thallium.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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