Distribution of Fluoride in the Phosphorite Mining Area of Hahotoe–Kpogame (Togo)

Gnon Tanouayi,1,2 Kissao Gnandi,1,2 Kamilou Ouro-Sama,2 Adoté Agbéko Aduayi-Akue,2 Housséni Ahoudi,2 Yawovi Nyametso,2 Hodabalo Dheoulaba Solitoke2

1 The Geochemical Laboratory (Geology Department); Faculty of Science, University of Lomé, Togo
2 Management, Treatment and Promotion of Wastes Laboratory; Faculty of Science, University of Lomé, Togo

Corresponding Author:
Gnon Tanouayi
tanouayit@yahoo.fr

Background. Phosphorites in the mining area of Hahotoë-Kpogamé contain high levels of fluoride that can cause illness among people living close to the mining and processing sites. Objectives. To assess the distribution of fluoride in the different areas around the phosphorite mining areas in Togo. Methods. Analyses were performed by molecular absorption spectrometer (HACH DR3800) according to the procedure manual at the geochemical laboratory of the University of Lomé. The sodium 2- (parasulfophenylazo) - 1,8-dihydroxy - 3,6-naphthalenedisulfonate (SPADNS) method was used to determine fluoride contents and the PhosVer® 3 with acid persulfate digestion method was used to measure phosphorus pentoxide (P₂O₅). GraphPad Prism version 3.0 software was used for the data processing.

Results. The surface water of the mining sites had a fluoride content ranging from 0.38 to 3.52 mg/l (average = 1.33 mg/l; n = 10, n is the number of samples). Groundwater in this area had a fluoride content between 0.15 mg/l and 1.39 mg/l (average = 0.58 mg/l, n = 15). In the groundwater in the villages around the phosphorite processing plant, the fluoride content ranged between 0.15 and 0.63 mg/l (average = 0.41 mg/l; n = 22). The fluoride content in the water of the phosphorite mining area was higher than in Gbodjomé (reference area). Meanwhile, assessment of the effluents discharged into the ocean had a fluoride content ranging from 12 to 20 mg/l. In dusts, the P₂O₅ and fluoride contents were 36.02% and 1.85%, respectively. Vegetables from the local market garden produce showed levels of fluoride up to 2.06%. The average contents of P₂O₅ and fluoride in one of the phosphorite profiles were 32.38% and 3.00%, respectively. A significant correlation was observed between P₂O₅ and fluoride.

Conclusions. The correlation between P₂O₅ and fluoride in phosphorites shows that phosphorite mining is the main source of fluoride pollution in this area.

Competing Interests. The authors declare no competing financial interests.

Keywords. fluoride, dental fluorosis, ground and surface water, phosphorites, Hahotoë-Kpogamé, Togo

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enriched with numerous trace metals such as cadmium, chromium, copper, nickel, vanadium, zinc, lead, uranium, thorium, molybdenum, silver, fluorine, yttrium and major elements such as fluoride, aluminum, iron etc. The main phosphorite mineral in Togo’s phosphorite is a carbonate fluorapatite, also called francolite, which allows numerous ionic substitutions. The processing of the phosphorite ore to commercial grade is done mechanically by wet sieving using sieves and hydrocyclones. Seawater is pumped in a factory at Kpémé close to the beach situated 25 km from the mining sites. Three types of mine wastes are produced during this processing: fine-grained clayey-muddy tailings, coarse-grained waste and phosphorite dust rejected by the factory chimney. The muddy tailings are dumped directly into the coastal waters of Togo without any pre-treatment, and the coarser waste is disposed of on soils and areas around the factory. Mining activities in the area are a source of metal contamination of soils, air, water and biota.

Dental fluorosis, which is endemic in the local population, especially among children in the Hahotoé-Kpogamé and Kpémé mining areas, calls for more attention and study. Until now, no specific study has been conducted to examine the distribution of fluoride in the different environmental compartments of the mining area, as well as in the phosphorites and wastes, and to identify the source of pollution and provide solutions for the exposed population. Therefore, the present study is aimed at assessing the distribution of fluoride in this phosphorite mining environment.

Methods

Study Area

The industrial activities related to phosphorite mining are mainly located at two sites; the phosphorite mining area at Hahotoé and Kpogamé, and the processing plant at Kpémé.

Both are located in the southeastern region of Togo (Figure 1). This is the area most affected by the industrial activity of ore mining and processing. This delimitation of the study area takes into account wind transport of dust particles and emitted gases and transport of mine tailings by marine currents.

Sampling

Water

Groundwater was taken directly from boreholes and wells (Figure 2) in the mining area of Hahotoé and Kpogamé, and also from boreholes and wells in the processing area in the surrounding villages of Kpémé, Aglomé II, Sewatsri-Copé and Goumou-Copé. In those villages, people use water from boreholes and wells for drinking. Surface water samples were also taken from abandoned mining quarry ponds and from the muddy tailings at the outfall after decantation (Figure 3).
Groundwater samples were also taken at Gbodjomé, the reference area very far away from phosphorite mining activities. For the analysis, water samples were then filtrated using Whatman filter paper and kept at room temperature before running the analysis.

Phosphorite Waste
Phosphorite waste (coarse waste and fine muddy tailings) samples (10) were collected from the processing plant and kept in clean plastic bags. Raw phosphorite materials were sampled from the phosphorite layer mined at Hahotoé-Kpogamé in three profiles (vertical samples). The distances between the samples in the profiles were irregular. Dusts from the plant were collected from deposits on house roofs and on tree foliage (Figure 5).
Soil

Soil samples were collected in four villages around the processing plant at Kpémé, Aglomé II, Sewatsri-Copé and Goumou-Copé. We assumed that only the first centimeters of soil would be affected by pollution and therefore the quality of the superficial layer of soil (0-25 cm) may represent a potential risk to humans. A total of 20 composite soil samples were taken according to the French standard (AFNOR X 31-100). At each site, squares measuring 20 m x 20 m were delimited and served as the sample area. These squares were spatially equidistant over the entire area of each village. Therefore, there were 5 squares per village with one composite sample per square. A composite sample consists of several random samples in a square. Gbodjomé soils were also collected and used for the study reference. Soil samples were conserved in plastic bags (polyvinyl chloride) designed for this use. In the laboratory, soil samples were dried in an electric oven at a temperature below 40°C, sieved through a 2-mm sieve and milled (reference method NF X 31-101) in order to obtain a powder with a particle size smaller than 250 μm to improve the efficiency of acid attack during mineralization.

Vegetables

Vegetables growing around the treatment plant were sampled and packed in plastic bags at Goumou-Copé. These samples consisted of leaves (3 or 4 leaves per sample) without petioles, fruits and whole bulbs for fruit and bulb plants, and tubers for tuber vegetables. For each species, the samples were taken at five random points in the 20 m x 20 m squares as described for soils. The samples were washed with deionized water and then rinsed to remove dust and to avoid possible contamination. Food samples were dried in an electric oven at 40-50°C (NF ISO 11464) for 4-5 days, then crushed and stored in a dry place prior to analysis.

Analytical Methods

Soils, raw phosphorites, phosphorite waste and garden products were mineralized to obtain liquid samples for analysis. The method used in the present analysis was mineralization by acid attack (mixture of hydrochloric acid and nitric acid) according to the standard NF ISO 11466 (aqua regia method). It was performed in a closed, hot environment (150°C). The dosage of fluoride and phosphorus pentoxide (P₂O₅) was performed with a molecular absorption spectrometer.

Table 1 — Phosphorus Pentoxide and Fluoride Content in Crude Phosphorite and Commercial Phosphorite

| Abbreviations: MKP, Commercial phosphorite from Kpogamé; MD, Commercial phosphorite from Dagbati |
|---------------------------------------------------------------|
| Profile 1  | P₂O₅ (%) | Fluoride (%) | Profile 2  | P₂O₅ (%) | Fluoride (%) | Profile 3  | P₂O₅ (%) | Fluoride (%) |
|-----------|---------|-------------|-----------|---------|-------------|-----------|---------|-------------|
| P1.1      | 13.75   | 0.48        | P2.1      | 32.13   | 2.18        | P3.1      | 37.51   | 3.92        |
| P1.2      | 17.49   | 1.40        | P2.2      | 8.07    | 0.95        | P3.2      | 11.21   | 0.90        |
| P1.3      | 13.45   | 1.20        | P2.3      | 29.14   | 2.26        | P3.3      | 44.83   | 5.05        |
| P1.4      | 29.14   | 2.56        | P2.4      | 6.73    | 0.16        | P3.4      | 24.06   | 2.54        |
| P1.5      | 37.21   | 0.14        | P2.5      | 20.62   | 2.60        | P3.5      | 30.64   | 3.46        |
| P1.6      | 40.05   | 2.96        | P2.6      | 38.41   | 3.60        | P3.6      | 47.08   | 3.75        |
| P1.7      | 34.22   | 1.87        | P2.7      | 40.50   | 2.35        | P3.7      | 34.37   | 3.36        |
| P1.8      | 43.94   | 2.40        | P2.8      | 42.89   | 2.50        | P3.8      | 44.68   | 4.35        |
| P1.9      | 10.61   | 0.68        | P2.9      | 28.39   | 2.30        | P3.9      | 18.83   | 0.50        |
| P1.10     | 28.39   | 2.52        | P2.10     | 41.40   | 2.10        | P3.10     | 30.64   | 2.15        |
| Max       | 43.94   | 2.96        | Max       | 42.89   | 3.60        | Max       | 47.08   | 5.05        |
| Min       | 10.61   | 0.14        | Min       | 6.73    | 0.16        | Min       | 11.21   | 0.50        |
| Average   | 26.83   | 1.62        | Average   | 28.83   | 2.10        | Average   | 32.38   | 3.00        |
| MKP       | 37.51   | 3.50        |           |         |             |           |         |             |
| MD        | 39.15   | 3.40        |           |         |             |           |         |             |
DR3800 according to the procedure manual HACH DR3800. The sodium 2-(parasulfophenylazo) - 1,8 - dihydroxy - 3,6 - naphthalenedisulfonate (SPADNS) method was used (Method 8029).28

The SPADNS method for fluoride determination involves the reaction of fluoride with a red zirconium dye solution. PhosVer® 3 with the acid persulfate digestion method was used for P₂O₅.29

**Quality Control and Precision Analysis**

The validity of the analytical methods was verified by internal control. A procedural blank was prepared simultaneously using the same acids (nitric acid) and hydrogen chloride, for the samples in the same experimental conditions and measured for each sample series. This allows for the identification of sample contamination and elimination of errors. The standard solution for the measured elements (fluoride and P₂O₅) was prepared and incorporated into the normal series of interval analyses to check the internal precision of the method. In addition, in order to verify the repeatability of the results, multiple trials on one sample (duplicates) were randomly incorporated into the analytical batch through a blind analytical procedure (without the knowledge of the analyst).

**Statistical Analyses**

Microsoft Excel 2013 and GraphPad Prism version 3.00 software were used for data processing. The quantitative results are expressed as averages. Student’s t-test was used to compare the results of water and soil samples from the study area with the samples from Gbodjomé (reference area). The significance level was set at 5%. In
addition, Pearson's correlation test was used to establish the connection degree between fluoride and $P_2O_5$.

**Results**

**Phosphorus Pentoxide and Fluoride Content in Phosphorites**
The $P_2O_5$ and fluoride content of the crude and commercial phosphorite processing waste can be found in Table 1. The total average $P_2O_5$ and fluoride content in the three profiles were 29.35% and 2.24%, respectively. Profile 1 and 2 presented high concentrations of clays, calcites and oxide of iron and manganese, which explains the low content of $P_2O_5$ in both profiles. There was also a very significant correlation between the $P_2O_5$ concentration and fluoride in Profile 3 ($r = 0.90; P <0.0003$), followed by Profile 2 ($r = 0.76; p <0.0094$) and Profile 1 ($r = 0.54; P <0.10$). This shows that fluoride is incorporated into the apatite structure.

Table 1 indicates that the commercial phosphorite has been processed (enriched) from crude phosphorite, as the $P_2O_5$ content in commercial phosphorite (37.51%) is higher than in crude phosphorite (29.35% total average for the three profiles).

**Phosphorus Pentoxide and Fluoride Content in Phosphorite Processing Waste**
The $P_2O_5$ and fluoride content of the various types of processing waste is summarized in Table 2. In dusts, the $P_2O_5$ content was 36.02% and 1.85% for fluoride. For iron oxide, the contents were 19.05% for $P_2O_5$ and 1.43% for fluoride. Fluoride and $P_2O_5$ levels were the highest in dust, followed by coarse mud, iron oxide, fine wet mud, and fine dry mud. It was also noted that there was a significant correlation between $P_2O_5$ and fluoride in the waste ($r = 0.58; p <0.0455$).

**Fluoride Content in Surface Water and Groundwater at the Mining area of Hahotoé-Kpogamé**
The results of the analyses of surface and ground water in the mining site of Hahotoé Kpogamé are shown in Table 3 and compared to the reference area (Gbodjomé).

It appears from these results that the average fluoride content in surface groundwater was below the WHO guideline (1.5 mg/l), although 30% of the surface water was above this value.$^{3,10}$

**Fluoride Content in Water, Soil and Vegetables Around the Phosphorite Processing Plant**
The results of the analyses of ground water in villages around the phosphorite processing plant are shown in Table 4 and compared to the reference area (Gbodjomé). In all cases, the fluoride content in the water in these villages was below the WHO drinking water guideline of 1.5 mg/l.$^{3,10}$ The high fluoride content in the waters of Goumou-Copé may be due to a slightly basic pH. This pH level was the most basic of all of the water samples. A basic pH with moderate conductivity favors the dissolution of fluoride in water. Goumou-Copé is also next to the outfall of phosphorite tailings. Fluoride and conductivity in these waters is highly variable and this may be due to the intrusion of seawater into groundwater and the influence of surface water by rainfall.

The fluoride content in mining effluents is shown in Table 5. Overall fluoride contents in water and effluents showed a negative correlation with pH ($r = -0.04; P <7760; n = 51$) and a positive correlation with electrical conductivity ($r = 0.97, P <0.0001, n = 51$).

The results of the analyses of fluoride in soils of villages around the phosphorite processing plant compared to those of Gbodjomé (reference area) are reported in Table 6. There was a higher concentration of fluoride in the soil of Aglomé II, followed by soils in Kpémé, Goumou-Copé and Séwatsri-Copé. This can be explained by wind direction, which causes dust distribution from the
processing site towards these villages, often in a northeast direction. As for village distribution, the village of Aglomé II is located northeast of the plant, Goumou-Copé is located east of the plant, Séwatsri-Copé is located north of the plant, and Kpémé is located to the northwest. The phosphorite treatment plant is located 3 km from Goumou-Copé, 1 km from Aglomé II, 2 km from Séwatsri-Copé and 1.6 km from Kpémé.

Because it had the highest fluoride content of the tested soils of the study villages, fluoride in market produce in Goumou-Copé was analyzed in order to estimate the accumulation in foodstuffs consumed by the local population. Figure 7 shows the fluoride content of different local produce. Daucus carota had a higher fluoride concentration (2.06%) compared to Allium cepa leaves (0.16%). It appears from these results that the reserve organs of these plants (tubers, bulbs) accumulate more fluoride than leafy vegetables.

Discussion

Most sedimentary phosphorite deposits contain a variety of carbonate-fluoroapatite, grouped under the collective name of francolite.31 By establishing a series of systematic relationships between francolites, some authors have used X-ray diffraction, chemical analysis and statistical methods to show that calcium, sodium, magnesium, phosphorus, carbon dioxide and fluorine contents can adequately describe most francolites.17-19 The incorporation of carbon dioxide in the structure of francolite is accompanied by increased and excess content of fluoride.32-34 Substitution of the phosphate by the carbonate is coupled with that of fluoride, which explains the high fluoride content in francolite.35 This is consistent with the results of our analysis, which showed (Table 1) an average content of fluoride and P<sub>2</sub>O<sub>5</sub> in one of the study profiles of 3.00% and 32.38%, respectively, suggesting that mining activities are the primary source of the fluoride contamination in other environmental compartments.

Coarse wastes have a higher fluoride content than fine mud (1.78% vs 1.23%), because the coarse wastes consist of apatite and coprolites (fossilized fish dung) accompanied by teeth, vertebrae and other pieces of fossilized animals, while fine mud is mostly rich in clay. Meanwhile, dusts have almost the same P<sub>2</sub>O<sub>5</sub> and fluoride content as phosphorites, because they mainly consist of fine apatite particles released into the

| Groundwater     | pH    | Electrical Conductivity (μS/cm) | Fluoride (mg/l) |
|-----------------|-------|-------------------------------|-----------------|
| **Kpémé n=7**   |       |                               |                 |
| Min             | 5.98  | 427.00                        | 0.17            |
| Max             | 6.77  | 1766.00                       | 0.63            |
| Average         | 6.39  | 893.71                        | 0.38±0.06       |
| P value         | —     | —                             | 0.0019 **       |
| **Aglomé II n=5** |     |                               |                 |
| Min             | 6.85  | 428.00                        | 0.15            |
| Max             | 7.21  | 1286.00                       | 0.60            |
| Average         | 7.02  | 735.80                        | 0.37±0.10       |
| P value         | —     | —                             | 0.0112 *        |
| **Séwatsri-copé n=5** | |                               |                 |
| Min             | 6.35  | 515.00                        | 0.34            |
| Max             | 7.07  | 2520.00                       | 0.63            |
| Average         | 6.76  | 1057.00                       | 0.43±0.05       |
| P value         | —     | —                             | 0.0001 ***      |
| **Goumou-Copé n=5** |     |                               |                 |
| Min             | 6.92  | 480.00                        | 0.39            |
| Max             | 7.37  | 967.00                        | 0.58            |
| Average         | 7.19  | 682.20                        | 0.48±0.03       |
| P value         | —     | —                             | P<0.0001 ***    |
| **Gbodjomé (Reference area) n=5** | |                               |                 |
| Min             | 6.63  | 139.30                        | Not detected    |
| Max             | 6.95  | 505.00                        | 0.10            |
| Average         | 6.79  | 344.46                        | 0.04±0.02       |

Table 4 — Fluoride Content in Groundwater in Villages Around the Phosphorite Processing Plant
air when large particles of ore are crushed, as well as during the drying of enriched ore. A study by Gnandi in 2003 showed almost the same $P_2O_5$ content in raw phosphate (average=28.37%).\textsuperscript{36} The internal chemical analysis of plants showed similar results ($P_2O_5 = 35.70\%$ and fluoride=3.92\%) for commercial phosphate.\textsuperscript{37} It should also be noted that the phosphorite treatment method is not appropriate since the $P_2O_5$ content in waste ranges up to 16.81\% (fine mud) and 25.48\% (coarse waste). This method is not economically profitable and strongly contributes to environmental pollution.

The surface water in Hahotoé-Kpogamé (mining area) had an average fluoride content of 1.33 mg/l. This high content is due to leaching layers in the phosphorite quarry, dust emission and dropping of ore material during transport. The average content of fluoride in groundwater from extraction and treatment sites is higher than in the reference area (or background) at Gbodjomé, situated far away from the mining zone. In principle, the fluoride content in groundwater does not pose direct health problems from consumption, since most levels were below the WHO guidelines (1.5 mg/l).\textsuperscript{39,30} However, if one takes into account the very high water consumption in this region due to its semi-arid climate, these concentrations will result in a daily intake of fluoride of 1.74-3.48 mg/day (for 3-6 liters of water consumed.

| Effluent sample | pH   | Electrical Conductivity (µS/cm) | Fluoride (mg/l) |
|----------------|------|---------------------------------|-----------------|
| E1             | 6.55 | 44.50                           |                 |
| E2             | 6.47 | 44.70                           | 19.00           |
| E3             | 6.40 | 43.60                           | 12.00           |
| E4             | 6.45 | 44.60                           | 19.00           |
| Min            | 6.40 | 43.60                           | 12.00           |
| Max            | 6.55 | 44.70                           | 20.00           |
| Average        | 6.47 | 44.35                           | 17.50           |

Table 5 — Fluoride Content in Muddy Effluents

| Soil samples | Kpémé | Aglomé II | Séwatsri-Copé | Goumou-Copé | Ghodjomé (Reference area) |
|--------------|-------|-----------|---------------|-------------|---------------------------|
| S1           | 0.05  | 1.49      | 0.21          | 0.25        | 0.00733                   |
| S2           | 0.84  | 1.54      | 0.05          | 0.25        | 0.00265                   |
| S3           | 0.35  | 0.85      | 0.59          | 0.55        | 0.00630                   |
| S4           | 0.17  | 0.75      | 0.30          | 0.30        | 0.00763                   |
| S5           | 1.15  | 0.98      | 0.45          | 0.63        | 0.00538                   |
| Min          | 0.05  | 0.75      | 0.05          | 0.25        | 0.00265                   |
| Max          | 1.15  | 1.54      | 0.59          | 0.63        | 0.00763                   |
| Average      | 0.51±0.21 | 1.12±0.16 | 0.32±0.09    | 0.40±0.08   | 0.00586±0.00090           |
| F            | 87.10 | 191.28    | 54.65         | 68.32       | —                         |
| P value      | 0.0415*| 0.0001*** | 0.0100**      | 0.0013**    | —                         |

Table 6 — Fluoride Content in Soil of Villages Around the Phosphorite Processing Plant
Abbreviations: $F$, (enrichment factor) Fluoride content in target soils/Fluoride content in soils of Gbodjomé (reference)
daily), and this is not negligible. The inhabitants consume water from wells without filtration. The water contains phosphorite particles caused by dust deposit in the wells. The study by Gnandi in 2007 showed that once those particles enter the body through consumption, they can release fluoride in the stomach after digestion due to the presence of gastric acid. The study also found that up to 6.05 mg/l fluoride was found in well water particles that were separated by filtration and acid digestion.

The negative correlation found between fluoride content and pH \( r = -0.04; P < 0.050 \), and positive correlation with conductivity \( r = 0.97; P < 0.0001 \) in the water was confirmed by Saxena in 2001. Experimental results indicated that alkaline pH (7.6 to 8.6), high concentration of bicarbonate (ranging from 350 to 450 mg/l), and moderate specific conductivity (ranging from 750-1750 µS/cm) favor fluoride dissolution.

Like any solid particle, dust grains, even if sent by wind several kilometers away, end up falling naturally onto open surfaces such as soil, water (sea, lakes, rivers, wells etc.) and vegetation. These deposits cause water pollution. Phosphorite dust falling in the villages surrounding the plant and on soils is contaminated by fluoride with a content ranging from 0.05% to 1.54%, as the results have shown. Produce grown on these soils also accumulate fluoride.

Fluoride is not considered to be an essential element in mammals, but may be considered as a beneficial element, forming fluorapatite in teeth and bones. The example of fluoride is revealing of this prophylactic role. Indeed, while the ingestion of a small amount (≤ 2.5 mg/day) can prevent or reduce tooth decay and strengthen bones, excessive ingestion of this element (> 7.75 mg/day) usually induces the development of conditions such as dental or skeletal fluorosis. In phosphate-rich regions of Morocco, high levels of fluoride in water, soil and plants were found, and dental and bone abnormalities have also been reported. Haikel et al. (1986) demonstrated that dental fluorosis encountered in the Khouribga region of Morocco was mainly due to inhalation of phosphorite dust, not only fluoride content in drinking water and incidental accumulation of fluoride due to consumption of agricultural products.

### Conclusion

We examined the distribution of fluoride in different environmental compartments of a phosphorite mining area in Togo. The high content of fluoride in raw phosphorite shows that in these phosphorites, the main apatite mineral is francolite. Waste from phosphorite processing also contains high levels of fluoride.
The level of fluoride enrichment in groundwater was not negligible. The soils around the treatment plant were also found to be contaminated by fluoride. Produce from these soils accumulates fluoride. Consumption of water, agricultural products and dust cause dental fluorosis observed in the target populations. The significant correlation between P₂O₅ and fluoride in phosphorites indicate that mining is the main source of fluoride pollution in this area.

References

1. Fluoride in drinking-water: background document for development of WHO guidelines for drinking-water quality [Internet]. Geneva, Switzerland: World Health Organization; 2004 [cited 2016 May 10]. 17 p. Available from: http://www.who.int/water_sanitation_health/dwq/chemicals/fluoride.pdf

2. Mazet P. Les eaux souterraines riches en fluor dans le monde [The underground waters rich in fluorine worldwide] [Internet]. Montpellier, France: Maison des Sciences de l’Eau [House of Water Sciences]; 2002 Jun [cited 2015 Mar 31]. 45 p. Available from: http://horizon.documentation.ird.fr/exl-doc/pleins_textes/divers4/010031017.pdf French.

3. Arnesen AK, Abrahamsen G, Sandvik G, Krogstad T. Aluminium-smelters and fluoride pollution of soil and soil solution in Norway, Sci Total Environ [Internet]. 1995 Feb 24 [cited 2016 May 9];163(1-3):39–53. Available from: http://www.sciencedirect.com/science/article/pii/004896979504479K Subscription required to view.

4. Ashley RP, Burley MJ. Controls on the occurrence of fluoride in groundwater in the Rift Valley of Ethiopia. In: Nash H, McCall GJ, editors. Groundwater quality. New York: Chapman and Hall; 1995. p. 45–54.

5. Camargo JA. Fluoride toxicity to aquatic organisms: a review. Chemosphere [Internet]. 2003 Jan [cited 2016 May 9];50(3):251–64. Available from: https://fluorideresearch.files.wordpress.com/2014/01/fluoride-toxicity-to-aquatic-organisms-a-review-julio-a-camargo.pdf

6. Fornasiero RB. Phytotoxic effects of fluoride. Plant Sci [Internet]. 2001 Oct [cited 2016 May 9];161(5):979–85. Available from: http://www.sciencedirect.com/science/article/pii/S01689452000499X Subscription required to view.

7. Klumpp A, Domingos M, Klumpp G. Assessment of the vegetation risk by fluoride emissions from fertiliser industries at Cubatao, Brazil. Sci Total Environ [Internet]. 1996 Dec 9 [cited 2016 May 9];192(3):219–28. Available from: http://www.sciencedirect.com/science/article/pii/S0048969796052989 Subscription required to view.

8. Klumpp A, Domingos M, Moraes RM, Klumpp G. Effects of complex pollution on tree species of the Atlantic Rain Forest near Cubatao, Brazil. Chemosphere [Internet]. 1998 Feb [cited 2016 May 9];36(4-5):989–94. Available from: http://www.sciencedirect.com/science/article/pii/S0045653597101606 Subscription required to view.

9. Fluor et santé [Fluoride and health]. Geneva, Switzerland: Organisation mondiale de la Santé [World Health Organization]; 1972. French.

10. Pontie M, Rumeau M, Ndiaye M, Diop CM. Sur le probleme de la fluorose au Sénégal: bilan des connaissances et presentation d’une nouvelle methode de defluoruration des eaux de boisson [On the problem of fluorosis in Senegal: state of knowledge and presentation of a new method of defluoridation of drinking water]. Cahiers d’études et de recherches francophones/Sante [Internet]. 1996 [cited 2016 May 9];6(1):27-36. Available from: http://www.jle.com/download/san-26943-sur_le_probleme_de_la_fluorose_au_senegal_bilan_des_connaissances_et_presentation_dune_nouvelle_methode_de_defluoruration_d--VxCatnAQAEEAF-5wBgAAAAL-a.pdf French.

11. Travi Y. Hydrogeologie et hydrochimie des aquifères du Sénégal: hydrogeochemie du fluor dans les eaux souterraines [Hydrogeology and hydrochemistry of the aquifers of Senegal: hydrogengeochemistry fluoride in groundwater] [dissertation], Strasbourg, France: Universite Louis Pasteur, Institut de geologie; 1993. 95 Vol. French.

12. Strategie de croissance accelerée et de promotion de l’emploi: 2013-2017 [Strategy of accelerated growth and employment promotion: 2013-2017] [Internet]. Togo: Maastrichtien - Eocene moyen (Sud du Togo). 2012 Aug [cited 2016 May 9];8(5):2347-55. Available from: http://www.aijol.info/index.php/jbsc/article/view/11549/104275 French.

13. Country profiles of environmental burden of diseases. In: Quantifying environmental health impacts [Internet]. Geneva, Switzerland: World Health Organization; 2009 [cited 2016 May 9]. Available form: http://www.who.int/quantifying_ehimpacts/national/countryprofile/en/

14. Altschuler ZS. The geochemistry of trace elements in marine phosphorites part 1. characteristic abundance and enrichment. In: Bentor YK, editor. Marine phosphorites – geochemistry, occurrence, genesis [Internet]. Special Publication, Vol. 29. Tulsa, Oklahoma: Society of Economic Paleontologists and Mineralogists; 1980 [cited 2016 May 9]. p. 9–30. Available from: http://geoscienceworld.org/content/ marine-phosphorites-geochemistry-occurrence-genesis Subscription required to view.

15. Johnson AK. Le bassin cotier a phosphates du Togo: Maastrichtien - Eocene moyen [doctoral thesis]. Dijon, France: Universite de Dijon [University of Dijon]; 1987. French.

16. Kankele H. Über die Cadmiumverteilung in den Phosphoritlagerstätten von Hahote und Kpogame [dissertation]. Erlangen, Germany: Universitat Erlangen-Nurnberg [University of Erlangen-Nurnberg]; 1990. German.

17. McClellan GH, Lehr JR. Crystal chemical investigation of natural apatites. Am Mineralogist. 1969;54(9-10):1374–91.

18. McClellan GH. Mineralogy of carbonate fluorapatites. J Geological Soc [Internet]. 1980 Dec [cited 2016 May 9];137:675-81. Available from: http://jgs.lyellcollection.org/content/137/6/675.abstract Subscription required to view.

19. McClellan GH, Van Kauwenbergh Sj. Mineralogy of sedimentary apatites. Geological Soc Lond Special Publ [Internet]. 1990 [cited 2016 May 9];52:23–31. Available from: http://jgs.lyellcollection.org/content/52/1/23.abstract Subscription required to view.

20. Aduyi-Akue AA, Gnandi K. Evaluation de la pollution par les metaux lourds des sols et de la variete locale du mais Zea mays dans la zone de traitement des phosphates de Kpeme (Sud du Togo). Int J Biol Chem Sci [Internet]. 2014 Oct [cited 2016 May 9];8(5):2347-55. Available from: http://www.ajol.info/index.php/ijbcs/article/view/11549/104275 French.

21. Gnandi K. Cadmium et autres polluants inorganiques dans les sols et sedimentes de la Region cotiere du Togo: une etude geocheimique [dissertation]. Erlangen, Germany: Universite d’Erlangen-Nuremberg [University of Erlangen-Nuremberg]; 1998. 165 p. French.

22. Gnandi K, Tobschall H. Heavy metals
distribution of soils around mining sites of cadmium-rich marine sedimentary phosphorites of Kpogame and Hahote (southern Togo). *Environ Geol* [Internet]. 2002 Jan 1 [cited 2016 May 9];41(5):593-600. Available from: https://www.deeppyeve.com/lp/springer-journals/heavy-metals-distribution-of-soils-around-mining-sites-of-cadmium-rich-q5wk2cxZd

Subscription required to view.

23. Tanouayi G, Gnandi K, Ahoudi H, Urosama K. La contamination métallique des eaux de surface et des eaux souterraines de la zone minière d'exploitation des phosphates de Hahote-Kpogame (Sud-Togo): cas du cadmium, plomb, cuivre et nickel. *Larhyss J* [Internet]. 2015 Mar [cited 2015 May 10];(21):35-50. Available from: http://oasi.net/articles/2015/262-1452112095.pdf French.

24. Gnandi K, Tobschall HJ. Heavy metal release from phosphorite tailings into seawater: a simulated laboratory study. *Sci Total Environ* [Internet]. 1999 Sep 15 [cited 2016 May 10];236(1-3):181-90. Available from: http://www.sciencedirect.com/science/article/pii/S004896979900279X Subscription required to view.

25. Yacoubi, N., Yang, Y., Gao, S., Hu, L., Ladevie, B., Nezou, A. Stabilization of heavy metals from contaminated sediment – engineering properties for valorization. Conference paper at the 2007 London geo-environmental engineering conference; 2007. [cited 2016, May 27]; p. 100. Available from: www.iom3.org/fileproxy/528

26. International Standards Organization, (2006). ISO 11464 Soil quality -- Pretreatment of samples for physico-chemical analysis. [cited 2016, May 27]. Available from: http://www.iso.org.iso/home/store/catalogue_tc/catalogue_detail.htm?csnumber=37718

27. International Standards Organization, (1995). ISO11466 Soil quality -- Extraction of trace elements soluble in aqua regia. [cited 2016 May 24] Available from: http://www.iso.org.iso/home/store/catalogue_tc/catalogue_detail.htm?csnumber=19418

28. Jaradat, A. Q., Dissanyake, D., Holsen, T. M., Fu, J., Nichols, R., and Grimberg, S. J. Green courtyard system to remove fluoride from stormwater: modeling and field measurements. *Environmental Engineering Science*. September 2013, 30(9) [cited 2016 May 27] 573-581. Available from: http://online.liebertpub.com/doi/abs/10.1089/ees.2012.0484

29. Nelson, N. S. An acid-perulfate digestion procedure for determination of phosphorus in sediments. *Communications in Soil Science & Plant Analysis*. 1987. [cited 2016, May 27] 18(4), 359-369. Available from: http://www.tandfonline.com/doi/abs/10.1080/00103628709367826

30. Fluoride in drinking water: background document for development of WHO guidelines for drinking-water quality [Internet]. Geneva, Switzerland: World Health Organization; 2004 [cited 2016 May 10]. 17 p. Available from: http://www.who.int/water_sanitation_health/dwq/chemicals/flouride.pdf

31. McConnell D. A structural investigation of the isomorphism of the apatite group. *J Mineralogical Soc Am* [Internet]. 1938 Jan [cited 2016 May 10];23(1):1-19. Available from: http://www.minsoasm.org/ammin/AM23/AM23_1.pdf

32. McClellan GH, Van Kauwenbergh SJ. Relationship of minerology to sedimentary phosphate rock reactivity. In: Bachik AT, Bidin A, editors. Workshop on phosphate sources for acid soils in the humid tropics of Asia; 1990 Nov 6-7; Kuala Lumpur, Malaysia. Serdang, Selangor: Malaysian Society of Soil Science; 1990. p. 1-17.

33. Van Kauwenbergh SJ, McClellan GH. Mineralogy of sedimentary apatites and the relationship to phosphate rock reactivity. National workshop on fertilizer efficiency; 1990 Nov 12-3; Cisarua, Indonesia. [place unknown]; [publisher unknown]; [1990?].

34. Van Kauwenbergh SJ. Mineralogy and characterization of phosphate rock. In: Dahanyake K, Van Kauwenbergh SJ, Hellums DT, editors. Direct application of phosphate rock and appropriate technology fertilizers in Asia - what hinders acceptance and growth. Kandy, Sri Lanka: Institute of Fundamental Studies; 1995. p. 29-47.

35. Jarvis I, Burnett WC, Nathan Y, Almibainy F, Attia AK, Castro LN, Flicateaux R, Hilmy ME, Husain K, Outwahna A, Jerjani A, Zanin YN. Phosphorite geochemistry: state-of-the-art environmental concerns. *Ecolage Geol Helvetiae*. 1994;87(3):643-700.

36. Gnandi K, Tobschall HJ. Distribution patterns of rare-earth elements and uranium in tertiary sedimentary phosphorites of Hahote-Kpogame, Togo. *J Afr Earth Sci* [Internet]. 2003 Jul-Aug [cited 2016 May 10];37(1-2):1-10. Available from: http://www.sciencedirect.com/science/article/pii/S0899536203000885 Subscription required to view.

37. Notice de présentation de l’exploitation des phosphates du Togo [Notice of presentation of phosphate mining in Togo] ; 2010. French.

38. Tanouayi G, Tobschall HJ. Distribution patterns of rare-earth elements and uranium in tertiary sedimentary phosphorites of Hahote-Kpogame, Togo, *J Afr Earth Sci* [Internet]. 2003 Jul-Aug [cited 2016 May 10];37(1-2):1-10. Available from: http://www.sciencedirect.com/science/article/pii/S0899536203000885 Subscription required to view.

39. Saxena V, Ahmed S. Dissolution of fluoride in groundwater: a water-rock interaction study. *Environ Geol* [Internet]. 2001 Aug [cited 2016 May 10];40(9):1084-7. Available form: http://link.springer.com/article/10.1007%2Fs002540100290 Subscription required to view.

40. Bonnard R. Impact des incertitudes lies aux coefficients de transfert dans les evaluations de risque sanitaire [Internet]. Dakar, Senegal: Ministere de l’Environnement et du Developpement Durable [Ministry of Environment and Sustainable Development]; 2005 Oct 19 [cited 2016 May 10]. 24 p. Available from: http://www.ineris.fr/centredoc/impact-coef-transf.pdf French.

41. Caille N. Mobilité et phytodisponibilité du mercure dans les depots de sediments de curage [dissertation]. Vandoeuvre-les-Nancy, France: Institut National Polytechnique de Lorraine [National Polytechnic Institute of Lorraine]; 2002. 167 p. French.

42. Arnaud J. Fluor. In: Ambroise M, editor. Apports nutritionnels conseiles pour la population francaise. 3rd rd. Paris, France: Tec et Doc Lavoisier; 2001. 171-2. French

43. Melila M. Bioaccumulation of the cadmium, of plomb and du fluor and consequences biologiques sur l’Homme et Phyraena barracuda (poisson marin) dans la zone de traitement des phosphates au Togo [dissertation]. Lome, Togo: Universite de Lome [University of Lome]; 2013. French.

44. Abdennebi EH, Fandi R, Lammaouer D. Human fluorosis in Morocco: analytical and clinical investigations. *Vet Hum Toxicol*. 1995 Oct;37(5):465-8

45. Kessabi M, Assimi B, Braun JP. The effect of fluoride on animals and plants in the South Safi zone. *Sci Total Environ* [Internet]. 1984 Sep [cited 2016 May 10];38:63-8. Available from: http://www.sciencedirect.com/science/article/pii/0048969784902080 Subscription required to view.

46. Kessabi M, Khouzaimi M, Braun JP, Hamliri A. Serum biochemical effects of fluoride on cattle in the Darmous area. *Vet Hum Toxicol*. 1983 Dec;25(6):403-6.

47. Haikel Y, Voegel JC, Frank RM. Fluoride content of water, dust, soils and cereals in the endemic dental fluorosis area of Khouribga (Morocco). *Arch Oral Biol*. 1986;31(5):279-86.

*Journal de la Recherche Scientifique de l’Universite de Lome* [J Sci Res Univ Lome] [Internet]. 2006 [cited 2016 May 10];8(2). Available from: http://www.aouj.info/index.php/jsrl/article/view/52222 Subscription required to view. French.

49. Serum biochemical effects of fluoride on cattle in the Darmous area. *Vet Hum Toxicol*. 1983 Dec;25(6):403-6.