Université Libre de Bruxelles

Institute for Environmental Management and Land-use Planning

Faculty of Sciences

Master in Environmental Science and Management

Fluorides and trace metals in the riparian zone of the phosphate treatment plant of Kpémé (South Togo):

Detection in well waters and health risks

Master Thesis presented by

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List of abbreviations

Al: aluminium

As: arsenic

Ba: barium

Ca: calcium

Cd: cadmium

Co: cobalt

Cr: chromium

Cu: copper

EDI: Estimated Daily Intake

EF: Enrichment Factor

ERI: Ecological Risk Index

F^-: Fluorides

Fe: iron

Hg: mercury

ICP-MS: Inductively Coupled Plasma Mass Spectrometry

Mn: manganese

Ni: nickel

NPCT: National Phosphate Company of Togo

$oPO4^{3-}$: Orthophosphates

OSF: Oral Slope Factor

Pb: lead

RfD: Oral Reference Dose

Se: selenium

Sr: strontium

SWE: Société Wallonne des Eaux

TDS: total dissolved solids

TEFI: Toxic Equivalent Factor

THQ: Target Hazard Quotient

TR: Target Cancer Risk

U: uranium

WHO: World Health Organization

Zn: zinc

Abstract

The activity of the phosphate treatment plant of Kpémé (South Togo) is known to release fluorides (F^-) and trace metals in the environment. Here, we aimed to study the eventual sanitary problems caused by this industrial exploitation, particularly through the vector of well water used as drinking water. First, the measure of Total Dissolved Solids (TDS), orthophosphates ($oPO4^{3-}$) and total Calcium indicated the presence of phosphate ore residues in well waters of zones A, B and C. Next, F^- was quantified by ionic chromatography and lead, uranium, arsenic, aluminium, copper, nickel, barium and manganese were quantified by Inductively Coupled Plasma Mass Spectrometry in well waters. In all the zones of interest, these elements presented a concentration below their respective guide values. However, the calculation of the Target cancer Risk (TR) suggests that there is a cancerogenic risk associated with arsenic, mainly in zones B and C. Moreover, there is a possible effect of a mix of elements on health in zones A and C. Furthermore, our results strongly suggest that the presence of these elements in well waters is a direct consequence of the activity of the plant. Next, a sociological survey and a health centre survey aimed to evaluate the prevalence of diseases potentially caused by F^- and trace metals. Dental and skeletal fluorosis present a higher prevalence in zones A, B and C than in the reference zone, correlating with F^- level in well waters. Digestive troubles happen in the populations of zones A and C, correlating with the concentration of the F^- and trace elements (taken as a whole) in well waters. In addition, zone C seems to be the zone the most impacted by the pollution. In conclusion, our results suggest that, in the riparian zone of the phosphate treatment plant, the consumption of well water as drinking water might be one of the causes of those health problems. However, dust would be a vector of contamination by F^- and trace elements even more important than well water. This is highlighted by the respiration and eye-related troubles mostly found in zones A, B and C, which correlates with the importance of dust deposition caused by the phosphate treatment plant. This study allowed to better understand the sanitary problems linked with the phosphate treatment plant of Kpémé.

I. INTRODUCTION

A. Description of host institutions

A.1. ULB-*Coopération*, Brussels, Belgium

ULB-*Coopération* is the NGO of *Université Libre de Bruxelles*. It was founded in 2014 by the fusion between CEMUBAC, SLCD and SEDIF. ULB-*Coopération* is an actor of development and North-South cooperation. Its projects aim to contribute to a positive change, and to the construction of a society just, solidary and responsible for all. On that purpose they act on health, territory and resources, entrepreneurship and education. The main zones of action of ULB-*Coopération* are Belgium, Burkina Faso, Democratic Republic of Congo and Senegal. The NGO is part of Uni4Coop, a project founded in 2016, that assemble 4 Belgian university NGOs: Eclosio, FUCID and Louvain *Coopération* together with ULB-*Coopération*. The director of ULB-*Coopération* is Alain Wodon. Thierry de Coster is project manager and was one of the supervisors of the present master thesis [1].

A.2. Laboratory of Ecology of Aquatic Systems, *Université Libre de Bruxelles*, Belgium

The Laboratory of Ecology of Aquatic Systems is a multidisciplinary research group of the *Université Libre de Bruxelles* interested in the modelling of the structure and functioning of aquatic systems such as rivers, lakes, estuaries and coastal waters, as well as their response to natural and anthropogenic changes. More precisely, their main research themes are coastal eutrophication, marine biogeochemical cycles and climatic gases, bacterial ecology of surface waters, microbiological quality of aquatic ecosystems, microbiological aspect of drinking water production and distribution [2]. Dr. Nathalie Gypens is one of the principal investigators and was the supervisor of the present master thesis.

A.3. Laboratory of *Gestion Traitement Valorisation des Déchets* (GTVD), *Université de Lomé*, Togo

The laboratory GTVD aims to perform research in the field of waste management. One of their main topic is to evaluate the pollution released by the phosphate exploitation in the south of Togo [3]. The principal investigator of the laboratory GTVD is Dr. Kissao Gnandi, who kindly welcomed me in his laboratory for the duration of my fieldwork.

B. Togo

B.1. Generalities

Togo is one of the smallest West African countries with an area of 56 785 km^2. It presents a width of 56 km on the coast along the Gulf of Guinea. Its neighbouring countries are Ghana, Burkina Faso and Benin (Figure 1). Lomé is the capital city of Togo. Togo is a subtropical country separated in six geographical regions from the semiarid north to the humid tropical south. Togo is an independent republic since 1960. The current president is Faure Gnassingbé. The Togolese population currently counts approximated 7.6 million inhabitants. According to the World Bank, the GDP per capita was 617.18 USD in 2017. The country is divided into five economic regions, the southern one being the maritime region. Even if exportation of goods (coffee, …) and tourism contribute to the economy, mining transformation activities have one of the biggest contributions to the national economy. These industries are mainly (90%) found in the maritime region because of its strategical position with an opening on the sea. The mining industries of Togo are mainly centred around the extraction of phosphate [4]–[8].

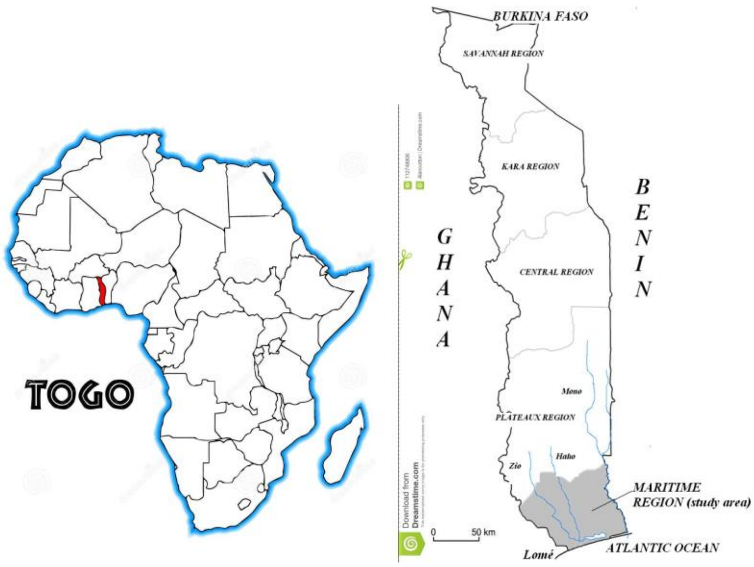

Figure 1. Geography of Togo. (A) Localisation of Togo within Africa (in red). (B) Maritime region of Togo (in grey) [8] comprising phosphate mining and transformation activities.

B.2. Phosphate of Togo

Phosphate is exploited for the production of agricultural fertilizer and phosphoric acid [9]. Phosphates were first mined in Togo in the early 1950s by the *Compagnie Togolaise des Mines du Benin* (CTMB). In 1962, the National Phosphate Company of Togo (NPCT) took the lead. Nowadays, Togo produces about 3.5 million tons of industrial phosphate per year. It is the first producer of phosphate worldwide [6], [10].

Phosphate rock or phosphorite describes natural mineral assemblages containing a high concentration of phosphate minerals. Phosphorites are extracted in Hahotoé and Kpogamé from the layer C1, between the continental terminal layer and the attapulgite layer. Then crude phosphate ore is transported until the treatment plant of Kpémé, near the sea, where it is washed (Figure 2) in order to separate the usable phosphate from its waste [11].

B.2.a. Crude phosphate ore composition

Crude phosphorite ore of Hahotoe-Kpogamé is composed of 60% of phosphated matter and 40% of non-phosphated matter (waste of clay exogange). The phosphated matter is a fluoroapatite highly enriched with phosphate. It also contains calcium, cadmium and fluor (4%):

$$Ca_{9,923}\,Cd_{0,004}\,Mn_{0,013}\,[(PO4)_{5,886}\,(CO3)_{0,114}]F_2$$

The non-phosphated matter contains trace metals such as Al, Cd, Pb, Cu, Ni, Cr, Zn (Table 1) [10], [12], [13].

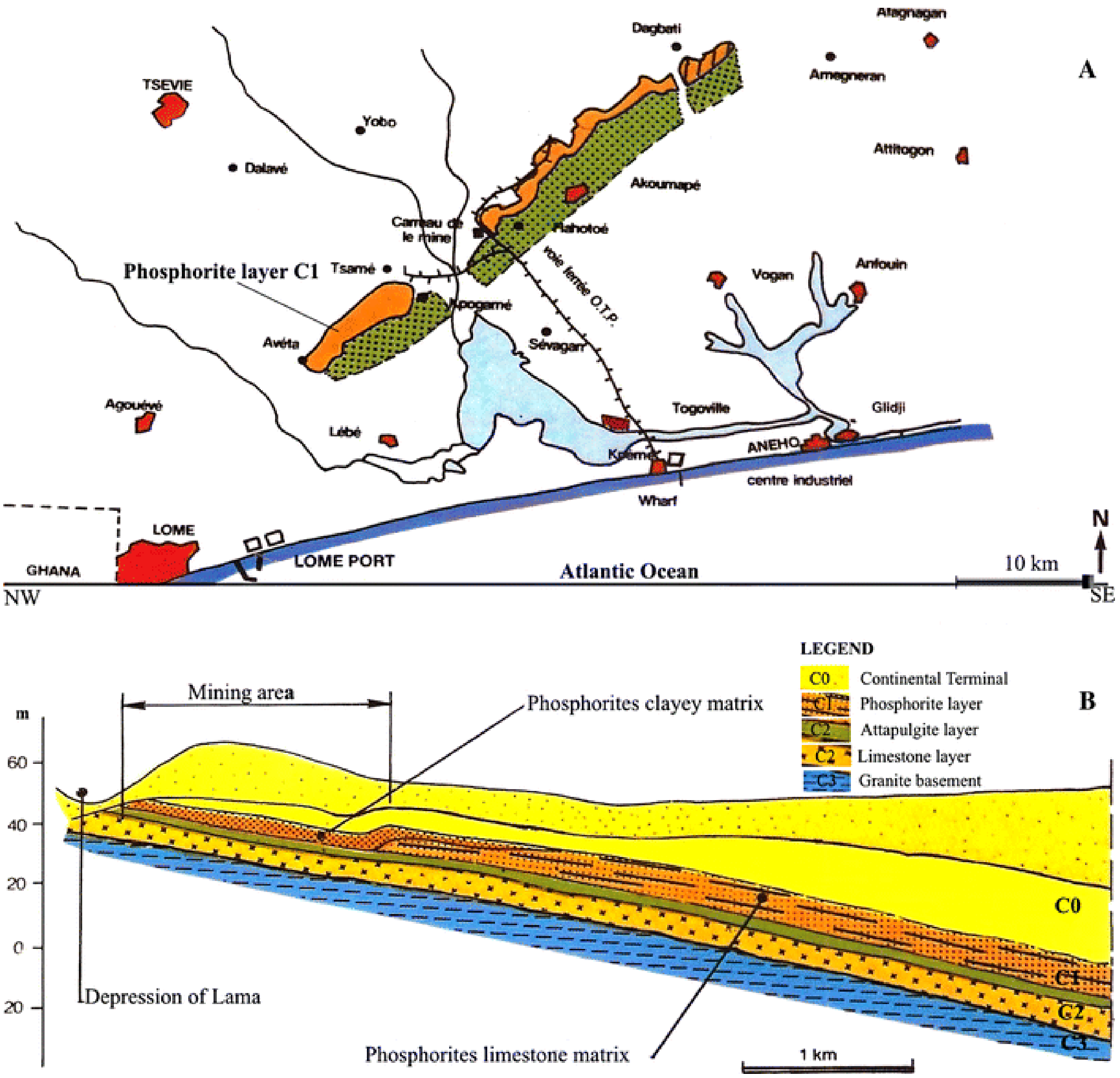

Figure 2. The phosphorite layer (C1) in Hahotoé-Kpogamé and the treatment plant in Kpémé. Crude phosphorite is extracted in Hahotoé and Kpogamé, and transported to Kpémé where is it washed in order to separate useful phosphate from its waste [11].

Eléments Majeurs (%)	Minimum	Maximum	Moyenne	Eléments Traces (mg/kg)	Minimum	Maximum	Moyenne
TiO_2	0,05	0,42	0,17	Cd	2	109	44
Fe_2O_3	0,56	16,04	3,62	Cr	126	707	356
Al_2O_3	0,90	30,86	5,21	Cu	55	511	158
MnO	0,002	0,085	0,02	Ni	38	363	109
MgO	0,09	0,57	0,25	Sr	207	18004	1429
CaO	6,89	48,32	33,86	V	92	339	173
Na_2O	0,19	0,52	0,30	Zn	116	1869	465
K_2O	0,04	0,25	0,10	Zr	19	93	46
P_2O_5	4,96	40,89	29,55	Pb	13	160	67

Table 1. Composition of the crude phosphate ore in South Togo [13].

B.2.b. Phosphate treatment

The crude phosphate ore of south Togo presents a phosphoric anhydride (P_2O_5) concentration of 29.55%. However, the commercial product should reach 38.3%. Moreover, the non-phosphated matter contains sterile and harmful elements. Therefore, the crude ore has to be treated to be transformed into the commercial ore. The treatment takes place in the treatment plant in Kpémé and consists in separating the phosphated matter from its exogange in order to increase phosphate concentration and improve its quality [13], [14]. The treatment consists in mechanical washing steps and is divided into a wet phase and a dry phase:

Wet sieving:

Crude ore is mixed with sea water in big rotating cylinders. 2 steps of sieving allow the elimination of big particles (diameter superior to 3 mm) and then small particles (diameter inferior to 45 µm). The product is then centrifuged in order to eliminate sea water.

Dry treatment:

The product is rinsed with fresh water in order to eliminate sodium chloride from sea water. This fraction is dried in the oven at 800°C. Traces of metallic oxides contained in the enriched ore are eliminated by magnetic separation. The final product is highly concentrated in P_2O_5. This is one of the best concentrates commercialized in the world.

Unfortunately, the treatment process releases the contaminants contained in the ore into the environment [13].

C. Safe drinking water availability

Water is essential to life on earth. Therefore, the human population depends on the availability of drinking water. There are 1.3×10^9 Km^3 of water on earth. Among these, 97% is salty water and only 3 % is fresh water. In the fresh water part, 2.5% is locked up in glaciers or lay too far under the earth's surface and only 0.5% is available for human consumption [15], [16].

C.1. In the world

UNICEF and the World Health Organization (WHO) estimated that in 2015, 29% (2.1 billion) of the world population didn't have access to a safely managed drinking water service (located on premises, available when needed and free from contamination). This rate reached 76% in the sub-Saharan populations [17], [18].

C.2. In Togo

Togo is characterized by an almost total absence of infrastructure and legislation on wastewater treatment. In Togo, 52% of the population had no access to safely managed water distribution system in 2016. This rate reached 57,67% in rural places. For these populations the available source of water is either surface or well waters that might be contaminated.

C.3. Underground water pollution

Wells are supplied with water from shallow aquifers, they are therefore a source of underground water. The introduction of a contaminant in underground water leads to underground water pollution which alters its quality and makes it dangerous for the environment and the human population. The main sources of pollution come from human activities such as industrial waste release. The introduction of a contaminant in the underground can be characterized by a slow and durable propagation (groundwater table is contaminated for several years) [13], [20].

C.3.a. Case of the phosphate treatment plant of Kpémé

Phosphate treatment leads to the enrichment of the residual waste with F^- and trace metals. Waste can take different from: solid waste, mud and dust. These 3 types of waste can potentially bring contaminants in the different compartments of the environment, including well waters, and might cause serious environmental and sanitary problems in the region [21]. Figure 4 summarizes the 3 pathways of pollution.

Solid wastes used to be used to repair the streets of the neighbouring villages. Since 2012, this practice progressively decreased, because it was showed to induce pollution, and stopped completely. However, solid wastes are still stored on the ground just beside the treatment plant. Rainwater infiltration through these polluted soils may lead to the contamination of the sand aquifer supplying all the wells with water in our study zone [22].

Mud: about 2.5 million of tons of mud tailings are dumped annually directly into the sea without any pre-treatment. It causes the phenomenon of yellow tide as well as a depletion of the halieutic resources (Figure 3). Marine current flows along the coast to the east and may transport mud. Marine water intrusion might bring the pollutants into the coastal sand aquifer.

Figure 3. Mud tailings discharge into the sea.

Dust is released from the chimneys of the plant and is transported by the wind on a maximal distance of 3 km. As wind changes its direction during the day, all the villages surrounding the plant suffer from dust deposition. However, the winds mainly blows from South-West to North-East [13], [23].

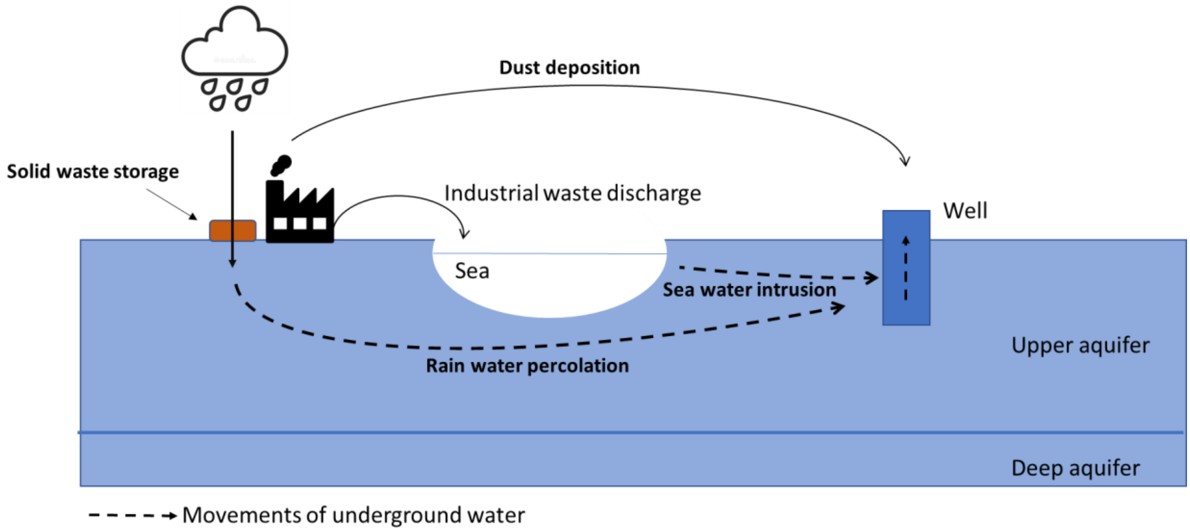

Figure 4. Sources of pollution coming from the plant of Kpémé to well waters. Part of the hydrogeological cycle including the sources of well water pollution [24].

C.4. Chemical elements causing sanitary problems via drinking water

Exposition to chemicals via drinking water is limited compared to other sources (food, air, …). However, there are exceptions. Among these, the main chemicals responsible for sanitary effects at great scale because of their high concentration in drinking water are fluorides (F^-) and trace metals such as arsenic (As), lead (Pb), selenium (Se) and uranium (U) [20].

C.4.a. Fluorides

Fluorine is a yellow green halogenated gas naturally present in the earth crust. Phosphorites of Togo are enriched with fluorine. It is generally in the nature in the form of F^- linked with organic or inorganic matter. Fluorine is the atom the most electronegative and reactive of all elements in the periodic table because of its ability to produce compounds for which the number of oxidation is very high, due to the low dissociation energy and to the solidity of the bonds it has with its compounds. This reactivity makes it one of the elements the most preoccupant for human health.

Acute toxicity of F^- results mainly in digestive troubles and fatigue. Even if F^- are necessary for dental health, a chronical exposure to a high concentration of F^- leads to its fixation on calcium-rich tissues of the organism, teeth and bones. It provokes dental and skeletal fluorosis, respectively. Dental fluorosis is characterised by the degradation of teeth enamel. Teeth become opaque and develop marbled yellow-brown stains and hypoplasia. It happens since childhood. Adults that have been exposed during many years to F^- may develop skeletal fluorosis. Symptoms are fractures, structural changes, skeletal pain, articulation pain and atrophy of feet leading to walking difficulties [20], [25], [26].

C.4.b. Trace metals

Trace metals (Pb, Se, U, Al, Cu, As, Cr, Ni, Ba, Sr, Mn, Zn, Co, …) are natural metals or metalloid found in low concentration in the environment (soil, plant, tissue, water, sediment,). They are naturally present in the earth crust and can be released in the environment via natural (infiltration,…) or anthropogenic process (industries,…) [27].

Trace metals are micropollutants. It means that they may display toxic effects even at low concentration. Indeed, trace metals can't be degraded by biological or chemical processes and are therefore persistent in the environment. Moreover, marine organisms can accumulate high amounts of trace metals in their tissues (Bioaccumulation). This accumulation can be transferred to the food chain (Biomagnification) and exceed acceptable thresholds for human consumption. Therefore, they may represent a serious risk for human health. Cadmium (Cd), and lead (Pb) are non-essential metals and are therefore toxic even at low concentrations. In contrast, essential metals such as copper (Cu), zinc (Zn), manganese (Mn) and iron (Fe) are beneficial at low concentrations and become toxic at higher concentrations [28], [29].

Trace metals are toxic if they are bioavailable (if they cross the cellular membrane of organisms). Bioavailability and therefore toxicity are function of chemical speciation. Total trace metal (M) is separated in the dissolved phase and the particulate phase (Figure 5):

$$M_{T\text{otal}} = M_{D\text{issolved}} + M_{P\text{articulate}}$$

Dissolved trace metals can be labile (free ion or complexed with dissolved inorganic constituents) or non-labile (bound to organic matter). Only the labile form of the dissolved phase might be bioavailable and therefore toxic. In contrast, particulate trace metals are bound to particles. By sedimentation, they may go down the water column. They are therefore not bioavailable. Adsorption and precipitation allow the dissolved trace metals to become particulate. Surface adsorption consists in the accretion of atoms or molecules of solutes on the surface of an adsorbent. Adsorption can be due to either physical, chemical or hydrogen bounds.

The distribution of trace metals between the dissolved and the particulate phase in water depends on the physicochemical properties of water. Firstly, pH influences adsorption of elements on organic matter. Increasing acidity will generally increase elements dissolution and therefore their toxicity. In addition, salinity (the concentration of dissolved salt in a given volume of water) increases trace element solubility. Finally, Total dissolved solids (TDS) comprises inorganic salts (mainly calcium, magnesium, potassium, sodium, bicarbonates chlorides and sulphates) and small quantities of organic matter dissolved in water. In simple terms, TDS refers to anything present in the water that is not pure water and is not a suspended solid. TDS can act as adsorbents and therefore increase trace elements adsorption [13], [20], [27].

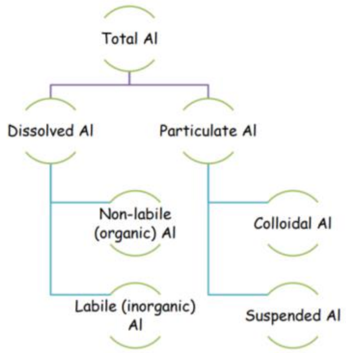

Figure 5. Aluminium distribution between the dissolved and particulate phases. The labile form of the dissolved phase might be bioavailable and therefore toxic.

Intoxication with trace metals can be acute (nausea, …) or chronical. Chronical effects on health comprise allergies, cancers, mutations, hormonal perturbations, impairment of the reproductive system, developmental impairment and post-natal lethality. For example, Pb can be associated with the impairment of the neurological development and the cognitive abilities in children. Arsenicosis (intoxication with arsenic) provokes skin lesions (hyperkeratinisation) on hand palm and foot palm. Moreover, all the effect of trace elements on human health are not known yet [20], [30], [31].

D. Study zone

The study zone of the present work consists in the riparian villages of the phosphate treatment plant of Kpémé.

D.1. Hydrogeology

There are different aquifer levels in the coastal zone of Togo. The upper level consists in the sand aquifer that supplies all the wells of the region with underground water [22].

D.2. Description of the villages

Figure 6 is a map of the study area.

Figure 6. Map of the study zone. Gbodjomé (zone R) with water samples 1 and 2, Kpémé (zone A) with water samples 3 to 6, Goumou-Kopé (zone B) with water samples 7 to 11, Aglomé (zone C) with water samples 12 to 16, west Aného (zone D) with water samples 17 to 20. The phosphate treatment plant is situated on the coast between Kpémé and Goumou-Kopé. Wind blows mainly to the north-east. Sea current flows to the east. Villages are impacted differentially by marine water intrusion, dust deposition and solid waste storage according to their geographical localisation.

Gbodjomé (**zone R**) was used as the negative reference zone because it is not impacted by the pollution coming from the treatment plant. Indeed, it is located 11 km west of the plant. It doesn't receive dust or contaminated sea water intrusion. Moreover, there is no solid waste storage in Gbodjomé.

Kpémé (zone A) is situated beside the treatment plant on the west. Because it is localized next to the plant, it is prone to be impacted by solid wastes. Even if it is not the village the most impacted by dust deposition (wind mainly blows to the north-east), it receives dust in some moment of the day when wind changes its direction. Even if marine water intrusion might happen, the direction of the sea current (to the east) limits contamination of Kpémé via marine water intrusion.

Goumou-Kopé (zone B) is located beside the solid waste storage sites. Moreover, the sea current allows it to be highly impacted by contamination via marine intrusion. Finally, dust deposition is also highly present.

Aglomé (zone C) might be the zone the most impacted by the pollution because of its geographical localisation. It is close to the solid waste storage site. This is the zone that receives the biggest amount of dust from the chimney because it is located north-east of the plant. Finally, its wells are also supplied by the sand aquifer, making Aglomé prone to be polluted via marine water intrusion.

The western districts of Aného (zone D) are located along the coast 10 km east of the treatment plant. It is too far to receive dust from the plant. However, contamination of well waters via marine water intrusion is possible but limited because of the distance. Finally, solid waste storage should not impact this zone [32].

E. State of the art: pollution caused by phosphate treatment at Kpémé

Many studies have shown the presence of F^- and trace elements in different compartments of the environment (water, air, sea fauna, agricultural products, grounds, human) near the phosphate treatment site (Kpémé) and have highlighted a direct link with the activity of the plant [33]. More precisely:

In 2 studies, held in 2006 and in 2016, non-negligible concentrations of F^- were found in soils, vegetables, dust, sea water, fishes, surface waters of the mining site, well waters of the mining site and well waters of the treatment site. In well waters of the treatment site, F^- concentrations were between 0.2 and 6.05 mg/L in 2006 and between 0.15 and 0.63 mg/l in 2016. The authors insisted on the fact that even if concentrations were below the WHO value guide for drinking water (1.5 mg/L), F^- enrichment in groundwater was not negligible and might be problematic because people drink this water during their whole life. Moreover, they pointed out different facts that proved that this F^- contamination was due to the phosphate treatment: 1) the high F^- concentration in the mud discharge; 2) the fact that, in sea water, concentration was higher near the discharge site of the plant and decreased with distance from the discharge site; 3) the correlation between P_2O_5 and F^- contents in dust and vegetables. Finally, numerous cases of dental fluorosis were detected in children of the riparian villages of the plant. This may come from consumption of water, agricultural products and dust [23], [34].

Cr, Cu, Ni, Pb, Cd, Sr and Zn have been found in the marine coastal sediments [35]–[37]. Cd, Cr, Ni, Pb, As were detected in water, sediments and fishes of the lake Togo [38][39]. Pb, Cr, Cu, Cd, Ni, Zn, Mn, As, Se and Sr were detected in soils of the mining area [40][41]. Bioaccumulation of Cd, Pb, Cu, Fe was observed in sea fishes and crustaceans near Kpémé [10]. Cd, Pb, Zn, Cu, Mn, As, Cr, Se, Ni and Sr were detected in the vegetables grown near the phosphate treatment site [41][33]. In 2015, one study showed Cd, Cu, Pb and Ni in the blood of inhabitants living next to the plant and in employees of the plant [33]. In the main part of these studies, element concentration was shown to be maximal near the phosphate treatment plant and to decrease with the distance from the plant, highlighting that the pollution is a direct consequence of the treatment plant activity.

In 2015, Pb, Ni, Cu and Cd concentrations were evaluated in well waters of the mining area and the treatment area. Wells in Goumou-Kopé presented a high concentration of Pb (259 µg/L) and Ni (83 µg/L). It would be due to the phosphate treatment. The authors also assessed the associated toxicity risk. They highlighted that Pb might display a toxic effect in children and adults [42]. This study was the last quantification of trace metals in well waters of the treatment zone. This highlights the importance to update and broaden these findings.

II. OBJECTIVES AND HYPOTHESES

In the present work, we aimed to study the potential sanitary problems caused by the phosphate treatment plant of Kpémé. Particularly by the vector of well water consumption as drinking water.

Firstly, we aimed to quantify fluorides (F^-), lead (Pb), selenium (Se), uranium (U), aluminium (Al), copper (Cu), arsenic (As), chromium (Cr), nickel (Ni), barium (Ba), strontium (Sr), manganese (Mn), zinc (Zn) and cobalt (Co) in well waters of zones A, B, C and D. F^- concentration was measured by ionic chromatography. Trace metal concentrations were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). More precisely, we aimed to confirm results of the last studies about Cd, Pb, Cu, Ni and F^- concentrations in well waters [23], [42]. In contrast, it was the first time that Se, U, Al, As, Cr, Ba, Sr, Mn, Zn and Co were quantified in well waters of the phosphate treatment zone. Orthophosphates ($oPO4^{3-}$) and total calcium (Ca) were measured in the same samples and used as indicators of the presence of phosphate residues in well waters. It allowed to evaluate whether the contaminants come from the phosphate treatment process or not. We advanced the hypothesis that well waters of zones A, B, C and D are contaminated with F^- and trace metals because they are close to the phosphate treatment plant. Moreover, well waters of zone D might also be contaminated but to a lesser extend because of its localisation further away from the plant.

Secondly, we aimed to study the prevalence of different health problems potentially linked with F^- and trace metals among the populations of zones A, B, C and D. The sociological survey aimed to evaluate health troubles known by the populations. The questionnaire was divided into 3 parts. Part 1 and 2 were preliminary and were interested in the habits of well water use and the perception of water quality, respectively. Part 3 focused on the occurrence of the health troubles. A health centre survey was performed in health centres of zones A, B and D and aimed to 1) confirm the results of the sociological survey with the point of view of a health specialist, 2) bring other information about diseases not known by the population, 3) know the opinion of a health specialist whether these diseases might be due to the phosphate treatment plant activity and/or to well water consumption. Through these 2 types of survey, we wanted to confirm results from 2016 highlighting the occurrence of dental fluorosis in the treatment zone. Moreover, we evaluated the occurrence of skeletal fluorosis, arsenicosis, cerebral troubles in children, general state and acute digestive problems. We also studied the eye and respiration troubles potentially caused by the direct contact with dust. We advanced the hypothesis that populations of zones A, B and C present diseases linked to the intoxication by F^- and trace metals because they are close to the plant. Moreover, population from zone D might also present these diseases but to a lesser extend because of its localisation further away from the plant.

Finally, we aimed to study the existence of a correlation between F^- and trace metal concentrations in well waters and the prevalence of these diseases in the populations. We advanced the hypothesis that this correlation exists.

III. METHODS

A. Exchanges with actors

A.1. Before the fieldwork

The first contact with the laboratory GTVD of University of Lomé was taken by e-mail. The team accepted me in their laboratory for a period of 3 weeks. Later, phone calls allowed to discuss the question of research and to determine the human resources available to accompany me during the fieldwork.

One meeting with Mr. Thierry de Coster (ULB-Coopération), Mr. Boris Javeau (ULB-Coopération) and Dr. Dominique Perrin (Agence Wallonne de l'Air et du Climat) was organized in order to discuss the technical, organizational and financial points. Moreover, one meeting with Dr. Kauffmann (ULB) was held in order to discuss the sampling protocol.

As financial support was limited, it was necessary to find an economic way to perform the chemical analyses. Firstly, I contacted, Hach, a company renting portable spectrophotometers. Secondly, I contacted the *Société Wallonne des Eaux* and its director, Mr. Sébastien Ronkart, kindly offered to perform the analyses for scientific collaboration.

A.2. After the fieldwork

On meeting with Dr. Marc Elskens (Vrije Universiteit Brussel) was held in order to clarify the role of physicochemical properties of water on the availability of trace metals. It was necessary for the analyses of the results.

B. Team composition for the fieldwork

During the fieldwork I was accompanied by members of the laboratory GTVD of University of Lomé, Dr. Gnon Tanouayi, Dr. Kamilou Ouro-Sama and Dr. Dominique Solitoke as well as by Mr. Maurice Walker, director of the NGO *Action d'Aide Humanitaire pour le Développement* (AHD). Travels to the field zone were performed by motorcycle. Moreover, Mr. Daouda Sama, Master student in the laboratory GTVD, showed me how to process samples in the laboratory.

C. Authorisation request to perform the study

The study zone is showed in section (Introduction D.2). According to the hierarchical system of Togo, it was necessary to receive the permission to perform the study from different authorities. It was fully part of the work.

Firstly, as the study zone is under the prefecture *des Lacs* (Aného), we met the prefect of the prefecture des Lacs, who gave us the permission to go meet each village traditional chief. In addition, in order to perform the study in the western districts of Aného city, we met the Mayor of Aného who gave us the permission to go meet each neighbourhood traditional chief.

Next, we visited the traditional chiefs of Gbodjomé, Kpémé, Goumou-Kopé and Aglomé as well was the neighbourhood traditional chief of Habitat, Asukondji and Ahémé (west districts of Aného city) in order to receive the permission to sample well waters and perform a sociological survey in their respective village/district. These visits also allowed us to collect testimonies from the different local chiefs about the problem of phosphate treatment-related pollution (Figure 7).

Finally, in order to receive the permission to survey health centres, we wrote a letter to the Minister of Health. As we did not receive any answer from the Minister of Health, we met the Prefecture Director of Health who gave us the permission.

Figure 7. Visits of the traditional chiefs. On the left side, Mr. Togbé Ekouévi Biova Foligah V, chief of Kpémé. On the upper right side, Mr. Amey, chief of Ahémé. On the bottom right side, the field team at Mr. Togbui Kokou Togbé ATTI IV's, chief of Gbodjomé.

D. Well water analyses

D.1. Collect

Well waters were collected in the 4 zones of interest. 4 wells were sampled in zones A and D. 5 wells were sampled in zones B and C. Moreover, 2 wells were sampled in zone R used as a negative reference because it is too far away from the plant to be impacted by it. One water sample was collected per well. 500 mL of water were collected in plastic bottles (Figure 8), transported in a cooler and left to stand overnight at room temperature for decantation and removal of the heaviest particles (sand, …). GPS data of each well is found in Annexe 1. Figure 6 shows the map of the study area with the collect points.

Mud from the discharge point and dust from the chimney of the plant were collected and used as positive controls for the contaminants because they should be enriched with the different elements released by the phosphate treatment process. Moreover, they might help to understand the pathway followed by the potential contaminants of well waters. Mud was left to stand at room temperature for 2 days in order to separate supernatant from the organic matter. Both parts were used as positive control. Mud supernatant was used for ICP-MS. The organic matter of the mud was dried at 75°C for 3 days in order to obtain a solid matter. For mineralized samples, 1 g of either dried mud or dust were mixed with 1 ml of nitric acid 65% and 3 ml of hydrochloric acid 37%. The preparation was heated at 150°C until complete evaporation of the acids. The pellet was resuspended in 20 mL of distilled water. The solution was filtered with wattman paper N°1 and used for ICP-MS.





Figure 8. Well water sampling. Well waters were all sampled on the same day. 500 ml of water was collected in a plastic bottle. Wells were uncovered. It included wells without lid (middle left) and wells with a half lid (middle right). The picture at the bottom shows a household of Goumou-Kopé that we met during sampling. They explained to us that a lot of dust coming from the phosphate treatment plant deposits everywhere (on their skin, inside their house, …) almost continuously.

D.2. Physicochemical parameters

Physicochemical properties of water were analysed in the laboratory GTVD of University of Lomé. pH was measured with the pH meter BASIC 20+ (Crison). Total dissolved solids (TDS) and salinity were measured with the apparatus Portamess 913 (Knick).

D.3. Ionic chromatography and ICP-MS

For Inductively Coupled Plasma Mass Spectrometry (ICP-MS), well waters and mud supernatant were fixed with 1% nitric acid containing gold chloride and stored at 4°C. Moreover, mineralized mud and dust were also analysed by ICP-MS. For ionic chromatography analyses, well waters were not acidified and were stored at -20°C. Samples were transported in a cooler to Belgium and were analysed by *Société Wallonne des Eaux* (SWE). On the one hand, anions F^- and $oPO4^{3-}$ were quantified by ionic chromatography. As these samples were not acidified, this method allowed the detection of the dissolved phase only. On the other hand, total Ca, Al, Fe, Mn, Cu, Zn, Co, Ba, As, Cd, Cr, Hg, Ni, P, Se, Sr, U were analysed by ICP-MS. As these samples were acidified, this technique allows the detection of both dissolved and particulate phases (total element).

E. Sociological survey

A survey based on a questionnaire was performed in a door to door manner. 20 adults from each zone (A, B, C, D and R) were interviewed. One student volunteer originate from each zone was trained as surveyor. We organized a meeting in order to train them (Figure 9). The respondents were adults living at least for 10 years in their respective zone. Gender balance was respected. Surveyors covered uniformly their geographic zone. Only one person by household was interviewed. The questionnaire (Annexe 2) was divided into 3 parts: 1) water consumption habits, 2) personal perception of well water quality based on organoleptic properties, 3) health problems potentially related to phosphate treatment and to well water consumption.

Figure 9. Training of the surveyors. We organized a meeting in Kpémé and trained the future surveyors for the good understanding of the questionnaire. One surveyor interviewed 20 people from each of the study zones.

F. Survey in health centres

A survey based on a questionnaire (Annexe 3) was held in health centres of Kpémé (zone A), Goumou-Kopé (zone B), Habitat (western district of Aného city, zone D) and Gbodjomé (zone R) (Figure 10). Note that Aglomé doesn't have a health centre. Inhabitants of Aglomé mostly go to the health centre of Kpémé in case of need of basic health care. This survey aimed to 1) confirm the results of the sociological survey with the point of view of a health specialist, 2) bring other information about diseases not known by the population, 3) know the opinion of a health specialist whether these diseases might be due to the phosphate treatment plant activity and/or to well water consumption. One health specialist par centre was interviewed. We performed the interview ourselves.

Figure 10. Health centre of Kpémé. The survey was based on a questionnaire. We interviewed one health specialist in each health centre.

IV. RESULTS AND DISCUSSION

A. Physicochemical parameters of well waters

It is important to measure the physicochemical properties of waters because they help to better understand the potential contamination of well water with F^- and trace elements (see section Introduction C.4.b).

A.1. pH

pH influences the adsorption of elements on adsorbents. It therefore influences the relative abundance of one element between its dissolved and its particulate phases and therefore its bioavailability [27]. In our study, the reference zone presents a pH of 6.55 and the 4 zones of interest present mean pH values ranging from 7.00 to 7.49 (Figure 11). All these values are not significantly different and are all considered as optimal pH values according to the WHO [20]. The potential differences in contaminant concentrations between the zones would not be explained by a difference in pH.

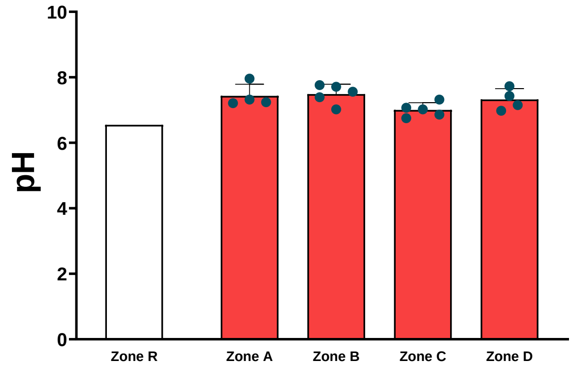

Figure 11. pH of well waters. pH influences the solubility of elements. Water was left to stand overnight for decantation and removal of the heaviest particles. pH is measured with the pH meter BASIC 20+ (Crison). Zone R = negative reference zone, Gbodjomé. The mean of 2 well waters was set as the zone R value. Zone A = Kpémé; zone B = Goumou-Kopé; zone C = Aglomé; zone D = west Aného. Each point represents the water sample of one well (N = 4 or 5). Results are expressed as mean ± SD.

A.2. Salinity

In the present study, salinity was used as an indicator of marine intrusion. Moreover, salinity increases the solubility of some elements. Mean salinity values of zone B (0.34) and C (0.56) are higher than the salinity in the reference zone (0.28) (Figure 12). This suggests that marine intrusion is particularly important in zones B and C. This is explained by their geographical localisations (Introduction D.2.). Moreover, the relatively high salinity in zones B and C might increase the solubility of contaminants [35], [43].

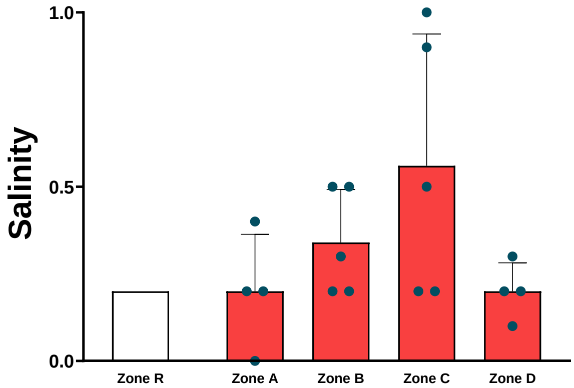

Figure 12. Salinity of well waters. Salinity influences the solubility of elements. Moreover, it is an indicator of marine water intrusion. Salinity is measured with the apparatus Portamess 913 (Knick). Water was left to stand overnight for decantation and removal of the heaviest particles. Zone R = negative reference zone Gbodjomé. The mean of 2 well waters was set as the zone R value. Zone A = Kpémé; zone B = Goumou-Kopé; zone C = Aglomé; zone D = west Aného. Each point represents water sample of one well (N = 4 or 5). Results are expressed as mean ± SD.

A.3. Total Dissolved solids, orthophosphates and calcium

Total Dissolved Solids (TDS), $oPO4^{3-}$ and total calcium were used as indicators of the presence of phosphate ore residues in water. Indeed, their values are high in the mud and dust positive controls.

TDS comprises inorganic salts (calcium, magnesium, …) and small quantities of organic matter dissolved in water [20]. In our study, mean TDS is higher in zones B (417.6 mg/L) and C (579.8 mg/L) than in the reference zone (340.8 mg/L) (Figure 13.1). This could be explained by the presence of phosphate ore residues in the well waters of zones B and C. However, one should bear in mind that TDS can also be due to other materials (tree leaves, sand…) [20]. Therefore, other indicators of the presence of phosphate ore residues should be evaluated together with TDS.

$oPO4^{3-}$ composes 29.55% of the crude phosphate ore of Togo [13]. $oPO4^{3-}$ concentrations in zones A (0.13 mg/L), B (0.06 mg/L), C (0.11 mg/L) and D (0.08 mg/L) are higher than in the reference zone (0.05 mg/L) (Figure 13.2). Zones A and zones C present the highest $oPO4^{3-}$ concentrations (Figure 13.2). This suggests that these zones contain phosphate residues coming from the treatment plant activity.

Calcium is abundant in the earth crust [44] and the crude phosphate ore of Togo is enriched (33.86%) with Ca [13]. Total Ca concentrations in zones B (78.74 mg/L), C (41.32 mg/L) and D (48.03 mg/L) are higher than in the reference zone (32.4 mg/L). Zone B presents the highest total Ca concentration (Figure 13.3), suggesting that phosphate ore residues would be mainly present in this zone.

Taken together these 3 indicators suggest that phosphate ore residues are mainly present in well waters of zones A, B and C. This is logical because they are located near the treatment plant. As explained in the section of introduction D.2, phosphate residues might come from solid waste storage followed by rainwater infiltration, mud discharge followed by marine water intrusion, or dust deposition.

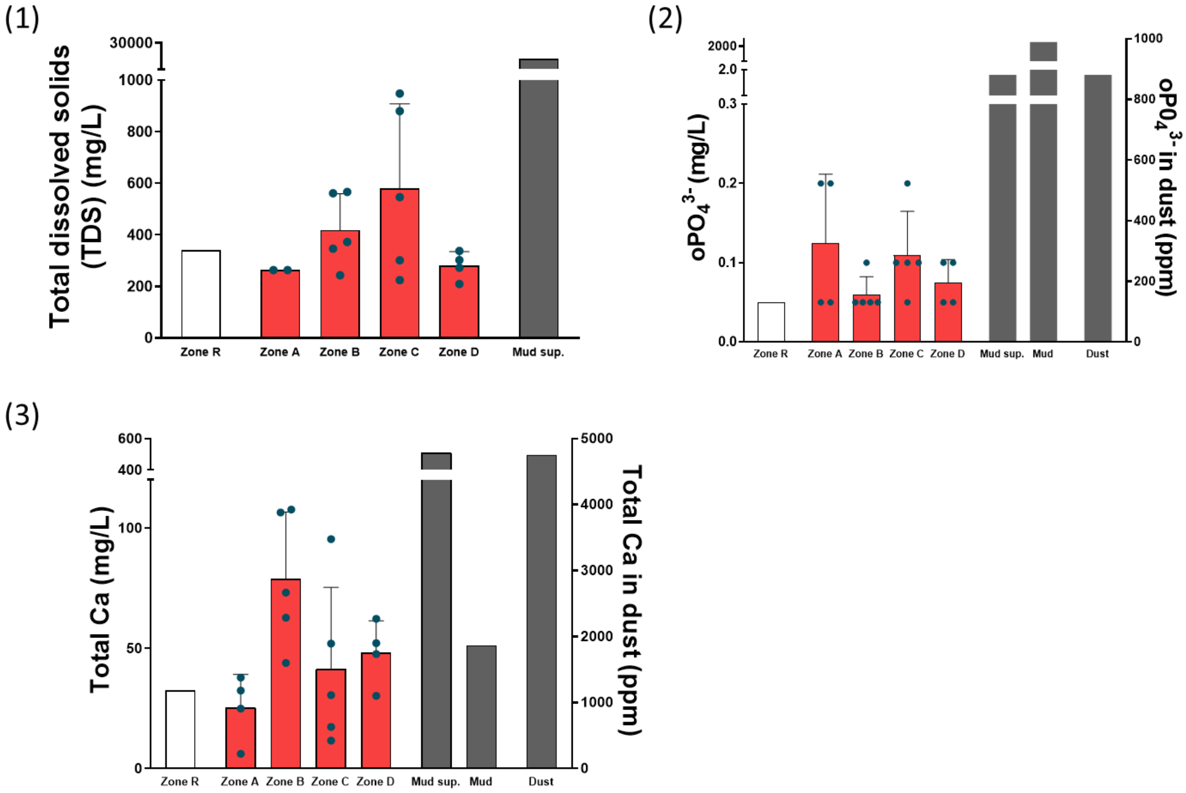

Figure 13. Total dissolved solids (1), orthophosphates (2) and total calcium (3) in well waters. These are indicators of the presence of phosphate ore residues in water. Water was left to stand overnight for decantation and removal of the heaviest particles. TDS was measured with Portamess 913 (Knick). $oPO4^{3-}$ was quantified by ionic chromatography. Because sample was not acidified, only the dissolved phase was detected. Total calcium was quantified by ICP-MS. Zone R = negative reference zone Gbodjomé. The mean of 2 well waters was set as the zone R value. Zone A = Kpémé; zone B = Goumou-Kopé; zone C = Aglomé; zone D = west Aného. These zones are differentially impacted by the activity of the phosphate treatment plant according to their geographical localisation. Each point represents one water sample (one well) (N = 4 or 5). Results are expressed as mean ± SD. Mineralized mud (Mud) and dust (Dust) coming from the plant are used as positive controls. Supernatant of mud (Mud sup.) is also used as a positive control. For $oPO4^{3-}$ quantification in the 3 positive controls, total phosphorus concentrations (data not shown) were multiplied by the factor 0.3261 as described by the company HACH.

B. Fluorides and trace metals in well waters

Among the contaminants quantified in this work, results for F^-, Pb, Se, U, Al, Cu, As, Cr, Ni, Ba, Sr, Mn, Zn and Co are discussed because these elements present WHO or national guide values. A guide value represents the concentration of a constituent that does not result in any significant risk to health over a lifetime of consumption. Guide values represent concentration of the total element (dissolved and particulate). Table 2 summarizes the different guide values associated with these contaminants. All these contaminants were shown to be potentially associated with health disorders when ingested via drinking water [20].

Contaminant	Guide value (µg/L)	Source of guide value
F^-	1500	WHO [20]
Pb	10	WHO
Se	40	WHO
U	30	WHO
Al	900	WHO
Cu	2000	WHO
As	10	WHO
Cr	50	WHO
Ni	70	WHO
Ba	1300	WHO
Sr	7000	Canadian government [45]
Mn	120	Canadian government
Zn	3000	Australian Drinking Water Guideline [46]
Co	10	Assessment of Water Quality Management in Turkey [47]

Table 2. Guide values (µg/L) for F^- and trace metals in drinking water.

Enrichment of the mud (positive control) with these elements is calculated in annexe 4. This allows to understand whether the presence of the elements in water samples are due to the process of phosphate treatment or not. Moreover, it is an indicator of marine water intrusion. Mud is not enriched with Mn. Mud is significantly enriched with Sr. Finally, it presents an extremely high enrichment with Pb, Se, U, Al, Cu, As, Cr, Ni, Ba, Zn and Co.

Similarly, enrichment of dust (positive control) with these elements is calculated in annexe 5. This allows to understand whether the presence of the elements in water samples are due to the process of phosphate treatment or not. Moreover, it is an indicator of contamination via dust deposition. Dust is minimally enriched with Pb, Al, Cr, Ba, Mn. Dust is moderately enriched with Co. Finally, it is significantly enriched with Cu, Ni, Sr and highly enriched with Se, U, As, Zn.

B.1. Fluorides

Water was left to stand overnight for decantation and removal of the heaviest particles. Water was not acidified, allowing to **measure only the dissolved F^-**. F^- concentrations were measured by ionic chromatography.

In the zones of interest (A to D), mean F^- concentrations of well waters range from 0.11 to 0.16 mg/L. These values are higher than the negative reference zone (0.06 mg/L) (Figure 14). Zone B presents the highest F^- concentration. However, results are not significant. As explained in the section of introduction D.2, contamination of zone B can be explained by solid waste storage on the soils, dust deposition and marine water intrusion. The hypothesis of F^- contamination via marine water intrusion is also supported by the high salinity found in zones B and C. However, it should be noted that, even if all the values stand below the WHO guide value (1.5 mg/L), it doesn't mean that F^- would not induce any significant risk for health by ingestion via drinking water. Indeed, the low F^- concentrations detected in our samples could be explained by a lack of solubility of F^- in our pH conditions (pH=7). Indeed, in an experiment during which phosphate rock is dipped in water at pH 7, only about 10% of F^- is dissolved and about 90% of F^- is particulate (incorporated in phosphate rock) (Figure 15) [48]. Therefore, as ionic chromatography only allows the detection of the dissolved F^-, total F- might be underestimated. However, in case of ingestion of fluorides-containing particles, the low pH of the stomach might increase F^- solubility and toxicity. It is known that the addition of a mix of acid to the water samples lead to a significant increase if F^- detection [23] and would therefore allow to better evaluate the risks of intoxication. Finally, Tanouayi and colleagues highlighted an important F^- concentration in mud and dust coming from the plant, suggesting that phosphate treatment is the main source of F^- contamination in well waters in our study [23].

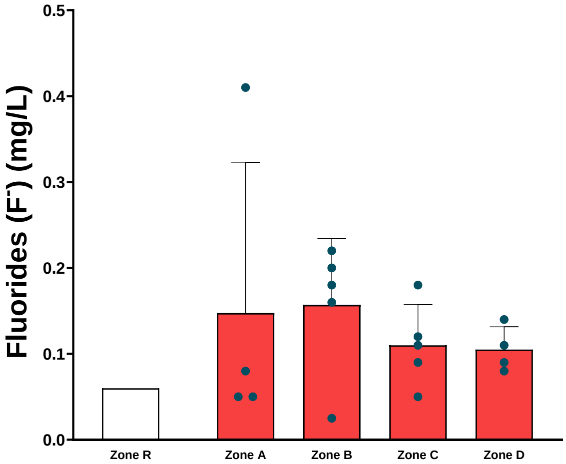

Figure 14. Fluoride concentrations in well waters. Well waters were collected in plastic bottles and left to stand overnight for decantation and removal of the heaviest particles. Water was not acidified. Therefore, only the dissolved F- were quantified by ionic chromatography. Zone R = negative reference zone, Gbodjomé. The mean of 2 well waters was set as the zone R value. Zone A = Kpémé; zone B = Goumou-Kopé; zone C = Aglomé; zone D = west Aného. These zones are differentially impacted by the activity of the phosphate treatment plant according to their geographical localisation. Each point represents one water sample (one well) (N = 4 or 5). Results are expressed as mean ± SD. The statistical analyses were conducted using paired t-tests between the zone R value and the mean of each zone of interest. Moreover, a one-way analysis of variance (ANOVA), followed by Tukey's test for multiple comparison were performed for the comparison of the 4 zones of interest. P≤0.05 values were considered statistically significant. All statistical analyses were carried out using GraphPad Prism (GraphPad Software).

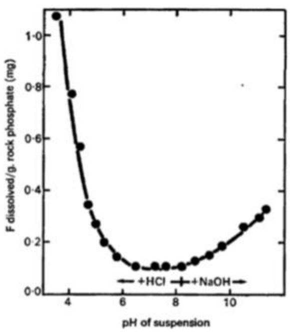

Figure 15. Effect of pH on the solubility of F^- of a phosphate rock (Ratio solid:solution 1:100) [48]

Similar results were obtained in 2006 in zones A, B and D (F^- concentration below 0.2 mg/L). However, in zone C, F^- concentration was 0.45 mg/L in 2006, which is about 4 times higher than our results [34]. Later in 2016, F^- concentrations were higher in zone A (0.38 mg/L), zone B (0.48 mg/L) and zone C (0.37 mg/L) compared to the present study. Note that zone B was already the site with the highest F^- concentration [23].

This difference in F^- concentrations between the previous studies (2006 and 2016) and 2019 might have different explanations:

1) The progressive decrease, since 2012, in the use of solid waste to repair the streets of the surrounding villages. This leads to a decrease in contamination through rainwater infiltration.
2) The difference in pH in zone A (6.39 in 2016 vs 7.43 in 2019) and zone B (7.19 in 2016 vs 7.49 in 2019). Well waters of these zones were more acidic in 2016 compared to 2019. Low pH increases F^- solubility.
3) Other, such as a change in the nature and size of suspended particles, influencing the availability of F^- (personal communication) [23].

B.2. Trace metals

Water samples for trace metal quantification were left to stand overnight for decantation and removal of the heaviest particles. Water was not filtrated, allowing small suspended particles to stay. Samples were then saturated with acid in order to decrease the pH at 2, inducing particles dissolution. It allowed to **measure total trace metals** (dissolved and particulate). It is therefore more representative of the health risk as we suppose that the population would not ingest big particles but, as we know that they do not filtrate well waters before consumption, (Results and discussion D.1) would therefore ingest smaller particles. These small particles can later be dissolved once in the stomach because of the low pH and become bioavailable and toxic.
Here, trace metals were divided into 2 categories according to the fact that they were previously detected or not in the study zone.

B.2.a. Trace metals already detected in the study zone in previous studies

In previous studies, Pb, Cu, Ni were quantified in well waters near the phosphate treatment plant. Here we aimed to confirm those results in 2019. Moreover, in previous studies, Al and As were detected in other environmental compartments of the study zone. Here we aimed to add information about well waters in 2019.

B.2.a.1. Pb, Cu, Ni

Results of the present study:

Mean Pb concentrations in the zones B and D (0.85 and 1 µg/L, respectively) are higher than in the reference zone (not detected). However, Pb is not detected in zones A and C. Results are not significant (Figure 16.1). As explained in the section of introduction D.2, contamination of zone B can be explained by solid waste storage on the soils, dust deposition and marine water intrusion. The hypothesis of Pb contamination via marine water intrusion is supported by the high salinity found in zone B and by the extremely high enrichment of the mud sample with Pb. However, all the values stand below the WHO guide value (10 µg/L) suggesting that Pb alone would not induce any significant risk for health by ingestion via drinking water.

Mean Cu concentrations in the 4 zones of interest (A to D) range from 0.65 to 1.7 µg/L. Only zone D presents a Cu concentration higher than the negative reference zone (1.4 µg/L). Results are not significant (Figure 16.2.). Even if dust and mud are enriched with Cu, it seems difficult to explain Cu contamination of zone D by dust deposition and marine water intrusion because of its geographical localisation. Cu could come from other sources (fertilizer, paint, …) [49]. Moreover, all the values stand below the WHO guide value (2000 µg/L) suggesting that Cu alone would not induce any significant risk for health by ingestion via drinking water.

Mean Ni concentration in the 4 zones of interest (A to D) range from 0.73 and 3.29 µg/L. Zones A and C present a Ni concentration higher than the negative reference zone (1 µg/L). Differences are not significant (Figure 16.3). Contamination of zones A and C can be explained by solid waste storage on the soils, dust deposition and marine water intrusion. The hypothesis of marine intrusion is also supported by the high salinity found in zone C and the extremely high enrichment of mud with Ni. The hypothesis of Ni contamination by dust deposition is supported by the significant enrichment of dust with Ni. However, all the values stand below the WHO guide value (70 µg/L) suggesting that Ni alone would not induce any significant risk for health by ingestion via drinking water.

Comparison with a previous study:

In 2015, well waters of zone B were evaluated for Pb, Cu and Ni. Cu concentration was around 100 µg/L, which is approximately 116 times higher than our results (0.86 µg/L). Similarly, Pb concentration was 258.9 µg/L, which is approximately 305 times more concentrated than in our study (0.85 µg/L). Ni concentration was 83.13 µg/L, which is approximately 114 times more concentrated than in our study (0.73 µg/L) [42]. The differences between the 2 studies might have different explanations:

1) The progressive decrease, since 2012, in the use of solid waste to repair the streets of the surrounding villages. This leads to a decrease in contamination through rainwater infiltration.
2) The rhythmic effect of salinity due to marine water intrusion. Salinity increases trace metals solubility.
3) Other, such as a change in the nature and size of suspended particles, influencing the adsorption of trace elements (personal communication) [42].

B.2.a.2. Aluminium and Arsenic

Mean Al concentration in the zones of interest (A to D) range from 15.94 to 62.52 µg/L. Zones A, C and D present Al concentrations higher than the negative reference zone (15.35 µg/L). The highest Al concentration is found in zone C. However, results are not significant (Figure 16.4). Al contamination of zones A and C can be explained by solid waste storage on the soils, dust deposition and marine water intrusion. The hypothesis of marine intrusion is also supported by the high salinity found in zone B and by the extremely high enrichment of mud with Al. The minimal enrichment of dust with Al doesn't support the hypothesis of contamination via dust deposition. However, all values stand below the WHO guide value (900 µg/L) suggesting that Al alone would not induce any significant risk for health by ingestion via drinking water. Finally, salinity increases Al solubility.

Mean As concentration in the zones of interest (A to D) range from 0.68 to 1.88 µg/L. Zones B, C and D present an As concentration higher than the negative reference zone (0.70 µg/L). The highest As concentration is found in zone B. However, the differences are not significant (Figure 16.5). As contamination of zones B and C can be explained by solid waste storage on the soils, dust deposition and marine water intrusion. The hypothesis of As contamination by marine water intrusion is also supported by the high salinity found in zones B and C and by the extremely high enrichment of mud with As. The hypothesis of As contamination by dust deposition is supported by the high enrichment of dust with As. However, all the values stand below the WHO guide value (10 µg/L) suggesting that As alone would not induce any significant risk for health by ingestion via drinking water.

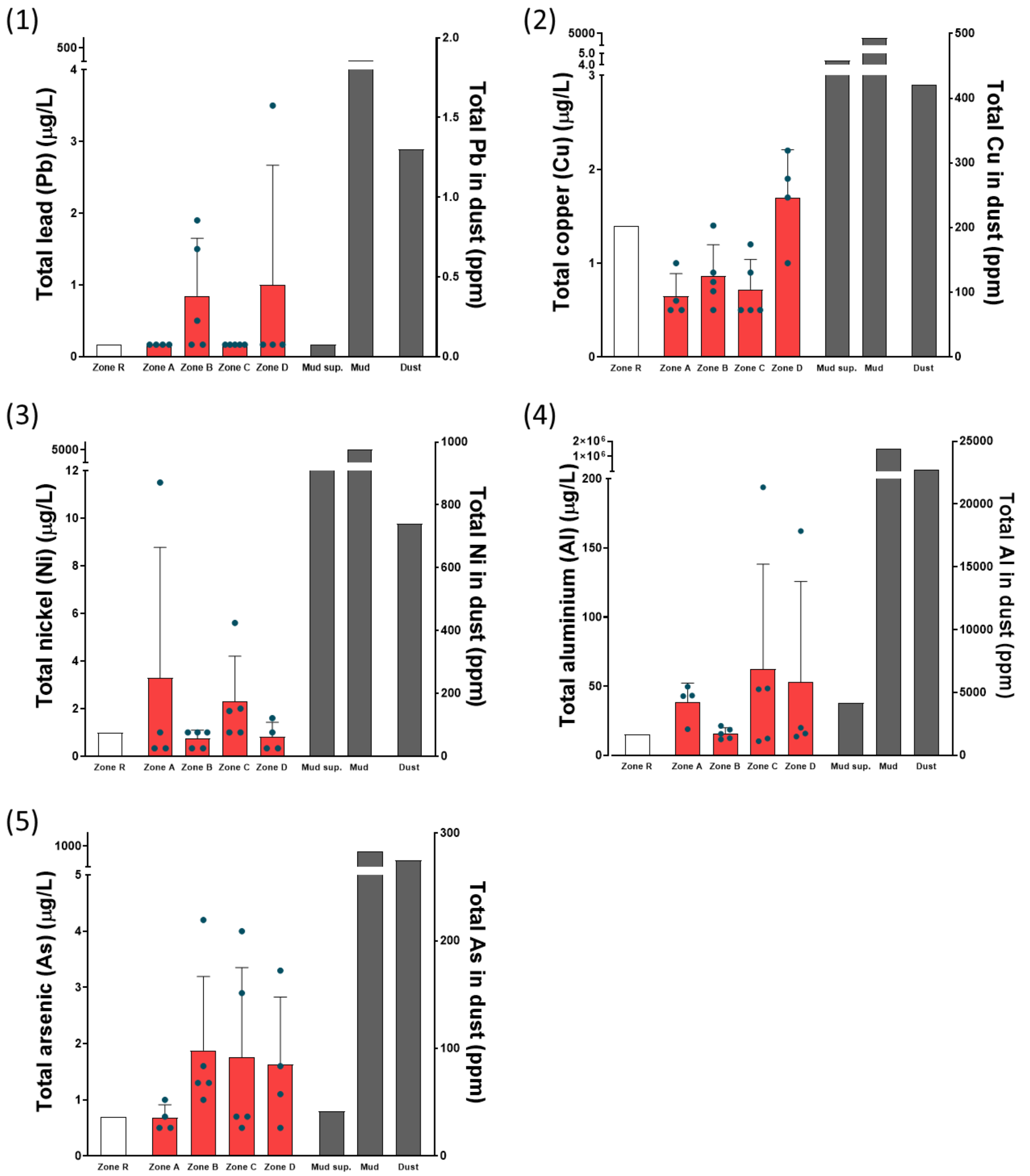

Figure 16. Concentrations of lead (1), copper (2), nickel (3), aluminium (4) and arsenic (5) in well waters. These trace elements were already detected in previous studies in different natural compartments. Well waters were collected in plastic bottles and left to stand overnight for decantation and removal of the heaviest particles. Water was not filtrated before analysis, allowing small particles to stay. Trace metals were measured by ICP-MS. Zone R = negative reference zone Gbodjomé. The mean of 2 well waters was set as the zone R value. Zone A = Kpémé; zone B = Goumou-Kopé; zone C = Aglomé; zone D = west Aného. These zones are differentially impacted by the treatment plant activities following their geographical localisation. Each point represents one water sample (one well) (N = 4 or 5). Results are expressed as mean ± SD. Mud supernatant (Mud sup.), mineralized mud (Mud) and mineralized dust (Dust) were used as positive controls for these trace elements. The statistical analyses were conducted using paired t-tests between the zone R value and the mean of each zone of interest. Moreover, a one-way analysis of variance (ANOVA), followed by Tukey's test for multiple comparison were performed for the comparison of the 4 zones of interest. P≤0.05 values were considered statistically significant. All statistical analyses were carried out using GraphPad Prism (GraphPad Software).

B.2.b. Trace metals newly detected in the study zone

Ba, U and Mn have not been pointed out as pollution coming from the phosphate treatment process of South Togo. However, they are present in the crude phosphate ore of Togo [13], [50]. This was therefore interesting to evaluate their potential presence in well waters of the study zone.

B.2.b.1. Barium

Mean Ba concentration in the zones of interest (A to D) range from 14.98 to 190.38 µg/L. Zones A and C present a Ba concentration higher than the negative reference zone (34 µg/L) (Figure 17.1). Differences are not significant. Ba contamination of zones A and C can be explained by solid waste storage on the soils, dust deposition and marine water intrusion. The hypothesis of Ba contamination by marine intrusion is supported by the high salinity found in well waters of zone C and by the extremely high enrichment of mud with Ba. The minimal enrichment of dust with Ba doesn't support the hypothesis of Ba contamination via dust deposition. However, all the values stand below the WHO guide value (1300 µg/L) suggesting that Ba alone would not induce any significant risk for health by ingestion via drinking water.

B.2.b.2. Uranium

Mean U concentration in the zones of interest (A to D) range from 0.07 and 0.37 µg/L. Zones B, C and D present a U concentration higher than the negative reference zone (0.05 µg/L) (Figure 17.2). The highest U concentration is found in zone C. However, differences are not significant. U contamination of zones B and C can be explained by solid waste storage on the soils, dust deposition and marine water intrusion. The hypothesis of U contamination of zones B and C by marine intrusion is supported by the high salinity found in well waters of these zones and by the extremely high enrichment of mud with U. The hypothesis of U contamination by dust deposition is supported by the high enrichment of dust with U. However, all the values stand below the WHO guide value (30 µg/L) suggesting that U alone would not induce any significant risk for health by ingestion via drinking water.

B.2.b.3. Manganese

Mean Mn concentration in the zones of interest (A to D) range from 2.13 to 344.48 µg/L. Zones A and C present a Mn concentration higher than the negative reference zone (6.35 µg/L) (Figure 17.3). However, differences are not significant. Mn contamination of zones A and C can be explained by solid waste storage on the soils and dust deposition. The minimal enrichment of dust with Mn doesn't support the hypothesis of Mn contamination via dust deposition. However, as mud is not enriched with Mn, marine intrusion doesn't seem to be involved in Mn contamination of well waters. However, all the values stand below the Canadian guide value (120 µg/L), suggesting that Mn alone would not induce any significant risk for health by ingestion via drinking water.

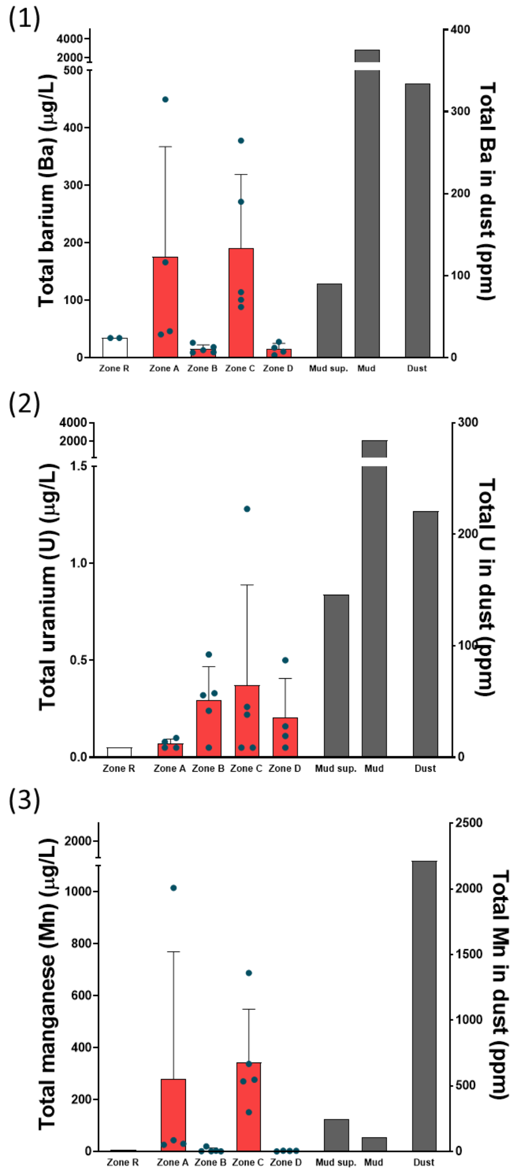

Figure 17. Concentrations of barium (1), uranium (2) and manganese (3) in well waters. These contaminants have not been detected before in the study area. Well waters were collected in plastic bottles and left to stand overnight for decantation and removal of the heaviest particles. Water was not filtrated before analysis, allowing small particles to stay. Trace metals were measured by ICP-MS. Zone R = negative reference zone Gbodjomé. The mean of 2 well waters was set as the zone R value. Zone A = Kpémé; zone B = Goumou-Kopé; zone C = Aglomé; zone D = west Aného. These zones are differentially impacted by the treatment plant activities following their geographical localisation. Each point represents one water sample (one well) (N = 4 or 5). Results are expressed as mean ± SD. Mud supernatant (Mud sup.), mineralized mud (Mud) and mineralized dust (Dust) were used as positive controls for these trace elements. The statistical analyses were conducted using paired t-tests between the zone R value and the mean of each zone of interest. Moreover, a one-way analysis of variance (ANOVA), followed by Tukey's test for multiple comparison were performed for the comparison of the 4 zones of interest. P≤0.05 values were considered statistically significant. All statistical analyses were carried out using GraphPad Prism (GraphPad Software).

Results for Cr, Zn, Co, Se and Sr are in annexe 6.

B.3. Concluding remark

Firstly, our study showed that the 3 positive control materials (mud supernatant, mineralized mud and mineralized dust) are enriched with Pb, Cu, Ni, Al, As, Ba and U. Similarly, Mn is present in the dust. This highlight that these contaminants are released by the phosphate treatment process. It suggests that their presence in well waters are a direct consequence of the plant activity, confirming the findings of previous studies [42]. Moreover, Gnandi and colleagues showed that F^- contamination of well waters was also a direct consequence of the plant activity [34].

Secondly, in the present study, the concentrations of F^-, Pb, Cu, Ni, Al, As, Ba, U and Mn in well waters stand below their guide values used as references in this work. Firstly, at pH 7, the majority of trace metals are adsorbed [51]. It could explain the low levels of trace metals detected in our samples. Indeed, even if these trace metals are present in the wells, they would be mainly adsorbed on the sediments in the bottom of the well and would therefore not be available for living organisms, limiting their toxicity. However, it should not be concluded that there is no risk for health due to ingestion of F^- and trace elements via drinking water. Indeed, local populations drink this water without filtration during their whole life. There is therefore a risk of bioaccumulation of these elements in the organism, highlighting the importance to calculate risk indexes.

C. Measurement of risk indexes

C.1. Enrichment factor and Ecological risk index of well waters

C.1.a. Enrichment factor

The enrichment factor (EF) is a widely used indicator for assessing trace element enrichment in soil. Here we used it for assessing enrichment in waters. The trace element concentration of a given element is normalized to the concentration of a reference element, generally chosen because the latter is of natural origin. Typical reference elements are Al or Fe [52].

$EF = [(C_{metal}/C_{Fe})_{sample}] / [(C_{metal}/C_{Fe})_{background}]$

EF values are ranked into five categories: minimal (EF<2); moderate (2<EF<5); significant (5<EF<20); very high (20<EF<40) and extremely high (EF>40) [53].

Table 3 shows the EF of well waters of the 4 zones of interest for Pb, Cu, As, Cr, Ni, Zn and Al. Well waters of zone R were used as water background. Fe was used for normalization.

Element	C_{zoneA}	C_{zoneB}	C_{zoneC}	C_{zoneD}	$C_{background}$	EFzoneA	EFzoneB	EFzoneC	EFzoneD
Pb	0,00	0,85	0,00	1,00	0,00	**0,00**	**0,00**	**0,00**	**0,00**
Cu	0,65	0,86	0,72	1,70	1,40	**0,12**	**1,31**	**0,01**	**0,48**
As	0,68	1,88	1,76	1,63	0,70	**0,24**	**5,73**	**0,07**	**0,92**
Cr	0,50	0,45	0,68	0,80	0,50	**0,25**	**1,92**	**0,04**	**0,64**
Ni	3,29	0,73	2,30	0,82	1,00	**0,83**	**1,56**	**0,06**	**0,33**
Zn	10,00	2,20	5,60	5,50	4,50	**0,56**	**1,04**	**0,04**	**0,49**
Al	38,73	15,94	62,52	52,9	15,35	Reference: Fe			
Fe	57,5	6,8	513,8	36,5	14,5				
Cpb/Cfe	0,00	0,13	0,00	0,03	0,00				
Ccu/Cfe	0,01	0,13	0,00	0,05	0,10				
Cas/Cfe	0,01	0,28	0,00	0,04	0,05				
Ccr/Cfe	0,01	0,07	0,00	0,02	0,03				
Cni/Cfe	0,06	0,11	0,00	0,02	0,07				
Czn/Cfe	0,17	0,32	0,01	0,15	0,31				

Table 3. EF of well waters with Pb, Cu, As, Cr, Ni, Zn, Al and Fe

EF < 2 for each element in each zone, supporting a minimal enrichment of well waters. As an exception, well waters of zone B present a significant enrichment with As (EF = 5.73). As zone B is enriched with at least one element, it is interesting to calculate the Ecological Risk Index of well waters.

C.1.b. Ecological Risk Index

The Ecological Risk Index (ERI), described by Hakanson in 1980, considers the potentially harmful elements As, Cd, Cr, Cu, Ni, Pb and Zn and is calculated as followed:

$$\mathbf{ERI = \sum TEF_i \times CF_i}$$

Where $\mathbf{CF_i}$ is the concentration of one element in the water sample normalized by its concentration in the background water: $Ci_{sample} / Ci_{background}$

TEFi is the dimensionless toxic equivalent factor for a given element: Cd - 30, As - 10, Ni and Pb - 5, Cu and Cr - 2 and Zn - 1

ERI are classified into low (ERI < 150); moderate (150 < RI < 300); considerable (300 < RI < 600) and very high (RI < 600) [52].

Table 4 shows the ERI calculated for each zone of interest. Zone R was used as background.

Element	C_{zoneA}	C_{zoneB}	C_{zoneC}	C_{zoneD}	$C_{background}$	TEFi
Pb	0,00	0,85	0,00	1,00	0,00	**5**
Cu	0,65	0,86	0,72	1,70	1,40	**2**
As	0,68	1,88	1,76	1,63	0,70	**10**
Cr	0,50	0,45	0,68	0,80	0,50	**2**
Ni	3,29	0,73	2,30	0,82	1,00	**5**
Zn	10,00	2,20	5,60	5,50	4,50	**1**
Cf Pb	0,00	0,00	0,00	0,00		
Cf Cu	0,46	0,61	0,51	1,21		
Cf As	0,96	2,69	2,51	2,32		
Cf Cr	1,00	0,90	1,36	1,60		
Cf Ni	3,29	0,73	2,30	0,82		
Cf Zn	2,22	0,49	1,24	1,22		
ERI Pb	0,00	0,00	0,00	0,00		
ERI Cu	0,93	1,23	1,03	2,43		
ERI As	9,64	26,86	25,14	23,21		
ERI Cr	2,00	1,80	2,72	3,20		
ERI Ni	16,45	3,65	11,50	4,10		
ERI Zn	2,22	0,49	1,24	1,22		
ERI total	**31,24**	**34,02**	**41,64**	**34,17**		

Table 4. ERI of well waters of the study zone, using zone R as background water.

ERI of each zone is below 150 supporting a low ecological risk associated with well waters. ERI calculated using tap water of Uccle (Belgium) in 2016 was also used as background for comparison. Results are found in annexe 7. ERI are also below 150, supporting a low ecological risk as well.

C.2. Target hazard quotient for non-carcinogenic risk

Trace metals are not excreted by the body and are bioaccumulated. Therefore, health risks are likely in populations that drink contaminated waters during their whole life. Target Hazard Quotient (THQ) aims to express the non-carcinogenic risk for a population exposed to a contaminant. THQ is the ratio of the potential exposure to a substance and the level at which no adverse effects are expected [42].

THQ = EDI / RfD

Where **EDI** is the estimated daily intake

RfD is the oral reference dose (mg/kg/d)

EDI = (CxQ)/Bw

Where **C** is the concentration of the substance in water

Q is the daily water quantity consumed per person. In our case, adults drink 2.6L of well waters daily (results of the sociological survey, data not shown). The average daily consumption of water for a child is estimated at 1.5L [42].

Bw is the body weight. The average body weight of a child from 0 to 15 years old is estimated at 28 kg. The average body weight of an adult is estimated at 70 kg according to the US Environmental Protection Agency (EPA) [42].

If THQ < 1, no adverse health effects are expected as a result of exposure.

If THQ > 1, adverse health effects as a result of exposure are possible. In other words, there is a sanitary risk.

Table 5 shows the THQs for the contaminants of interest calculated for children and adults. For each element, one zone with one of the highest levels was chosen for example.

Element	Zone	C (mg/L)	EDI child	EDI adult	RfD (mg/kg/j)	THQ child	THQ adult
F-	B	0.157	0.0084	0.006	0.05 [20]	**0.168**	**0.116**
Pb	B	0.00085	0.0000455	0.00003	0.0035	**0.010**	**0.009**
Ni	A	0.00329	0.00018	0.0001	0.02	**0.009**	**0.006**
Cu	D	0.0017	0.000032	0.00006	0.01	**0.009**	**0.006**
Al	C	0,063	0,00338	0,00231	1 [54]	**0,003**	**0,002**
As	B	0,002	0,00010	0,00007	0.0003 [55]	**0,338**	**0,232**
U	C	0,000	0,00002	0,00001	0.0002 [55]	**0,100**	**0,069**
Mn	C	0,344	0,01860	0,01275	0.046 [55]	**0,404**	**0,277**
Ba	C	0,190	0,01028	0,00704	0.2 [56]	**0,051**	**0,035**

Table 5. THQs for F^-, Pb, Ni, Cu, Al, As, U, Mn and Ba calculated for children and adults.

THQ for each studied element is lower than 1, suggesting that there is no health effects expected as a result of exposure. It suggests that there is no sanitary risk associated with F^-, Pb, Ni, Cu, Al, As, U, Mn and Ba in well waters. This is in contrast with the findings of Tanouayi and colleagues [42]. Indeed, they calculated a THQ for Pb of 3.48 for children and of 1.86 for adults. They concluded that the sanitary risk linked to Pb was probable. This difference in THQ between 2015 and 2019 is explained by the difference of Pb concentration between 2015 (258.9 µg/L) and 2019 (0.85 µg/L) [42].

C.3. Target cancer risk (TR)

Arsenic is also a potent carcinogen [57]. The Target cancer Risk (TR) measures the carcinogenic risk associated with the consumption of As over a prolonged exposure.

TR = EDI x OSF

Where **EDI** is the estimated daily intake calculated as above.

OSF is the oral slope factor [52].

According to New York State Department of Health, the TR categories are: TR ≤ 10^{-4} = Low; 10^{-4} to 10^{-3} = moderate; 10^{-3} to 10^{-1} = high; ≥10^{-1} = very high [58].

Table 6 shows the TR for As calculated for children and adults in each zone.

Element	Zone	Concentration (mg/L)	EDI child	EDI adult	Oral slope factor	TR child	TR adult
As	R	0,0007	0,000038	0,000026	1,5	5,63E-05	3,90E-05
	A	0,0007	0,000038	0,000026	1,5	5,63E-05	3,90E-05
	B	0,0019	0,000102	0,000071	1,5	1,53E-04	1,06E-04
	C	0,0018	0,000096	0,000067	1,5	1,45E-04	1,00E-04
	D	0,0016	0,000086	0,000059	1,5	1,29E-04	8,91E-05

Table 6. Target cancer Risk from As of well waters.

In zones B and C, TR of As is moderate for children and adults. Moreover, in zone D, it is moderate for children. This indicates that there is a cancerogenic risk associated with As in well waters.

C.4. Effects of a mix of elements: Index of Rodier

Each element taken separately presents a concentration lower than its guide value, suggesting that, alone, it doesn't have an effect on health. However, there could be a health risk associated with a mix of elements. According to Rodier, the importance of the effect caused by a mix of elements is the sum of the effects that they would provoke separately:

$$\sum(C_i / CLA_i) \leq 1$$

Where C_i = Concentration of element i in water

CLA_i = concentration limit authorized for element i.

If the sum ≤ 1, there should not be any health effect of the mix of elements [13][59].

Table 7 shows the index of Rodier calculated for each zone for the mix of F^-, Pb, Se, U, Al, Cu, As, Cr, Ni, Ba, Zn, Mn, Sr and Co. Note that the results of the concentrations of Se, Cr, Zn, Sr and Co are found in annexe 6.

Element	Guide value (GV) µg/L	C_{zoneR}	C_{zoneA}	C_{zoneB}	C_{zoneC}	C_{zoneD}	C_R/GV	C_{zoneA}/GV	C_{zoneB}/GV	C_{zoneC}/GV	C_{zoneD}/GV
F	1500	60,00	147,50	157,00	0,11	0,11	0,040	0,098	0,105	0,000	0,000
Pb	10	0,00	0,00	0,85	0,00	1,00	0,000	0,000	0,085	0,000	0,100
Se	40	2,80	1,27	0,64	3,44	1,03	0,070	0,032	0,016	0,086	0,026
U	30	0,05	0,07	0,29	0,37	0,21	0,002	0,002	0,010	0,012	0,007
Al	900	15,35	38,73	15,94	62,52	52,90	0,017	0,043	0,018	0,069	0,059
Cu	2000	1,40	0,65	0,86	0,72	1,70	0,001	0,000	0,000	0,000	0,001
As	10	0,70	0,68	1,88	1,76	1,63	0,070	0,068	0,188	0,176	0,163
Cr	50	0,50	0,50	0,45	0,68	0,80	0,010	0,010	0,009	0,014	0,016
Ni	70	1,00	3,29	0,73	2,30	0,82	0,014	0,047	0,010	0,033	0,012
Ba	1300	34,00	175,50	14,98	190,38	14,75	0,026	0,135	0,012	0,146	0,011
Zn	3000	4,50	10,00	2,20	5,60	5,50	0,002	0,003	0,001	0,002	0,002
Mn	120	6,35	278,53	5,32	344,48	2,13	0,053	2,321	0,044	2,871	0,018
Sr	7000	280,65	173,13	385,44	427,32	267,30	0,040	0,025	0,055	0,061	0,038
Co	10	0,33	3,68	0,00	2,26	0,00	0,033	0,368	0,000	0,226	0,000
SUM							**0,38**	**3,15**	**0,55**	**3,70**	**0,45**

Table 7. Index of Rodier representing the health effect caused by a mix of elements.

$\sum(C_i / CLA_i)$ are < 1 for the reference zone as well as for zones B and D, suggesting that there is no risk of the mix of these elements in these zones. However, zone A and zone C present a sum of ratios of 3.15 and 3.70 respectively. This highlights the presence of a possible health effect of the mix of these elements in these zones.

C.5. Concluding remark

The measure of different risk indexes allowed us to better understand the impact of the presence of F^- and trace elements in well waters.

To summarize, well waters of zone B are significantly enriched with As. Moreover, the ecological risk associated with As, Cd, Cr, Cu, Ni, Pb and Zn in well waters is low. In addition, THQs of F^- and trace elements are below 1, suggesting that there is no health effect expected as a result of exposure.

However, the measure of TR suggests that As is associated with a risk of cancer, mainly in zones B and C. Note that well waters of zone B are significantly enriched with As. Moreover, there is a possible effect on health associated with a mix of elements in zones A and C.

In the next section, we aimed to study the correlation between well water contamination with F^- and trace elements and the prevalence of health problems in the same zones. Therefore, we performed a sociological survey aiming to highlight the big health concerns observed by the population. Moreover, we performed a survey in health centres in order to add the experience of health specialists.

D. <u>Sociological survey</u>

The sociological survey is divided into 3 parts: water use habits; perception of water quality according to organoleptic properties; and health problems potentially caused by the consumption of well waters contaminated with F^- and trace metals.

The survey was written for the present study. Questions were based on existing surveys [30], [60]–[64], on the symptoms of intoxication with F^- and trace elements [20], [31] and on a personal communication with Dr. Arun Kumar (Mahavir Cancer Sansthan & Research Centre, Patna, Bihar, India).

<u>D.1. Well water uses</u>

Questions on water use habits were particularly interested in the origin of drinking water, the utilisations of well waters and the eventual treatment of well waters before consumption.

Uncovered wells are the main source of drinking water in the households of the reference zone (80%) as well as in zone B (85%), zone C (70%) and zone D (80%) (Figure 18). Uncovered wells, mainly in zones B and C are prone to receive dust coming from the phosphate treatment activity. However, in zone A, the households take 30% of their drinking water from uncovered wells and 40% from covered wells. Taken together well water is the main source of drinking water in zone A. It might suggest that the population of zone A is more sensitized to the issue of dust deposition than in the other zones and use lids to avoid well water contamination by dust. However, this difference could also be due to a bias of the survey. Indeed, the notion of "covered well" can vary from a surveyor to another: as some wells present a half lid, we don't know if surveyors included them in "covered" or "uncovered" wells.

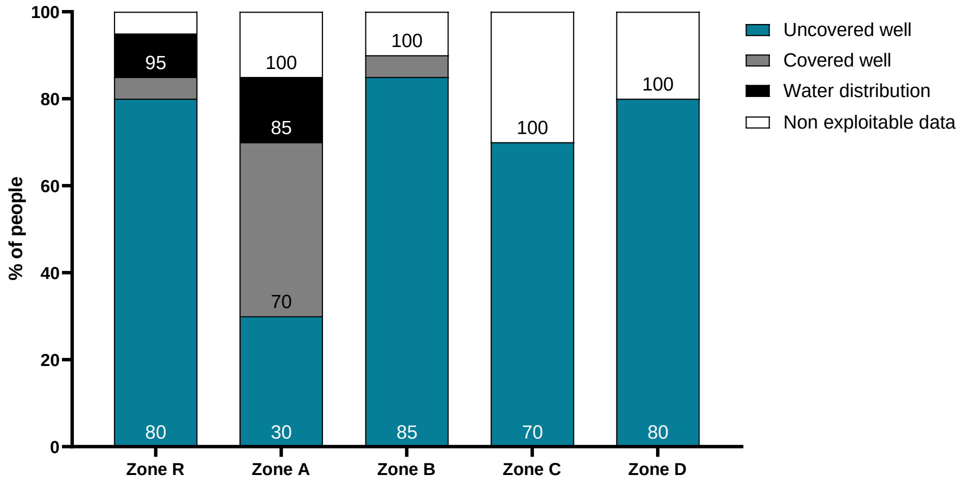

Figure 18. Drinking water source. Percentage of the population answering "uncovered well", "covered well", "water distribution" to the question 1 "**What is the main drinking water source of your household?".** Zone R = Gbodjomé, zone A = Kpémé, zone B = Goumou-Kopé, zone C = Aglomé; zone D = west Aného.

The main part of the population uses well waters for drinking: 85% in the reference zone, 80% in zone A, 90% in zone B, 70% in zone C and 80% in zone D (Figure 19). This confirms the results of Figure 18. Drinking water containing pollutants might lead to intoxication [23]. Moreover, the populations of the reference zone and the zones of interest also use well water for cooking, washing aliments, washing dishes and for body hygiene. These actions may also be vectors of contamination through water (personal communication).

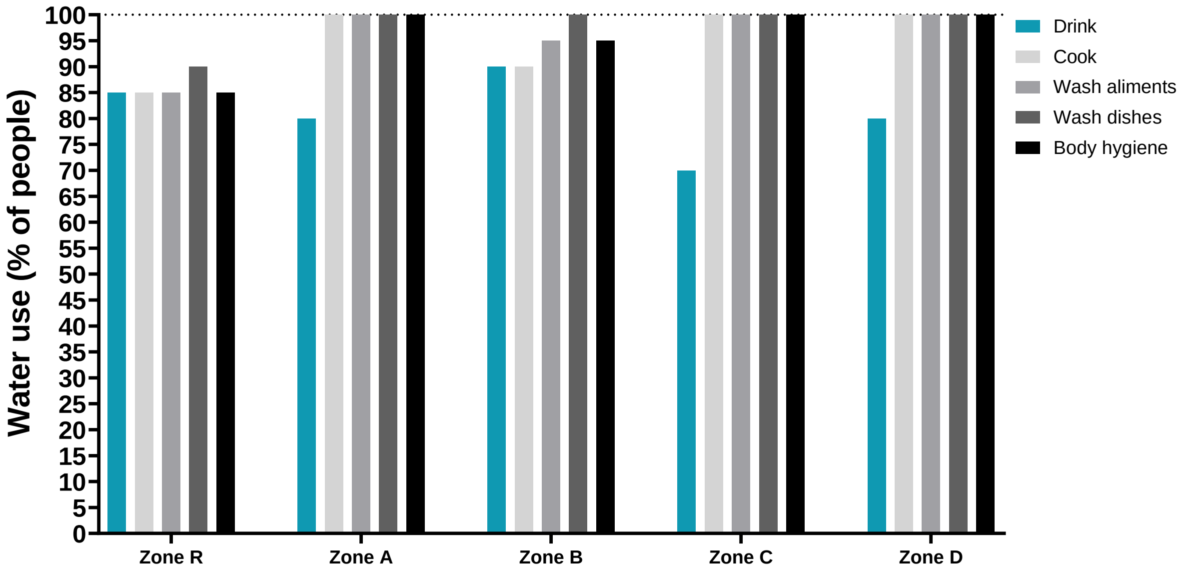

Figure 19. Well water uses. Percentage of the population answering "drink", "cook", "wash aliments", "wash dishes", "body hygiene" to the question 5 "**For which uses do you use well water**?". Zone R = Gbodjomé, zone A = Kpémé, zone B = Goumou-Kopé, zone C = Aglomé; zone D = west Anécho.

The main part of the populations of the reference zone (75%) and zone B (75%) and zone C (95%) do not perform any treatment before using (including drinking) well waters (Figure 20). In zone A, only 40% of the population do not perform any treatment. Moreover, in zone A and zone D, 60% and 50% of the population uses a product (chlorides, bleach) to disinfect well waters, respectively. This might suggest a higher sensibilisation of the population of zone A about drinking water quality. However, zone C seems to be the less sensitized to drinking water quality. Finally, in all the zones, nobody let water decant or filtrate water before consumption. There is an exception in zone B, where 5% of the population filter water through tissue. Decantation and filtration would remove suspended particles from water. These particles could contain F^- and trace metals (particulate phase) because of adsorption and precipitation at the pH conditions of our study (pH=7). Decantation and filtration are therefore good behaviours to reduce the potential F^- and trace elements ingestion via ingestion of small suspended particles (personal communication).

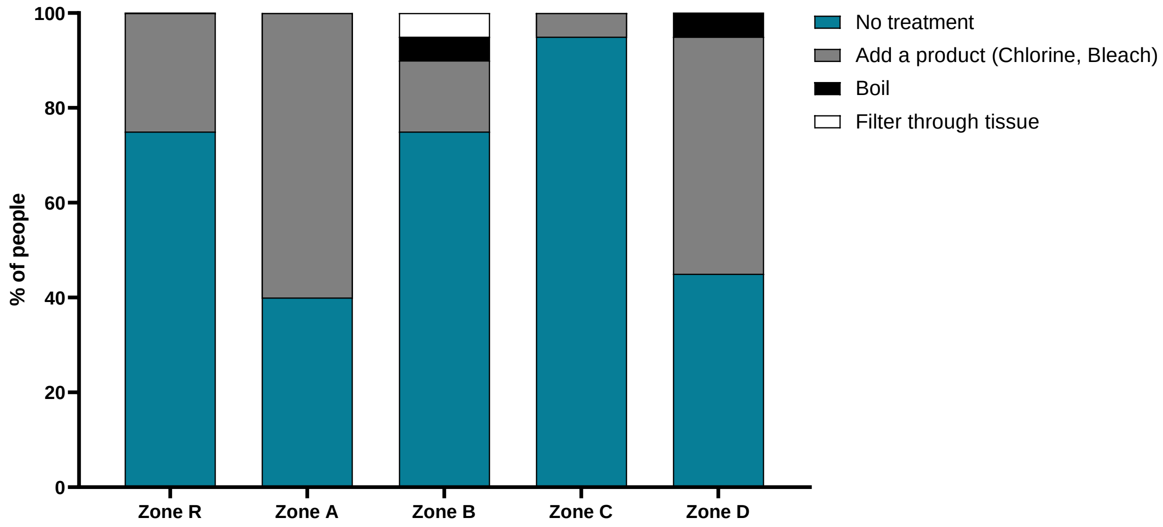

Figure 20. Well water treatment. Percentage of population answering “no treatment”, “add a product”, “boil”, “filter through tissue” to the question 4 “**Do you treat well water before using it? If yes, how?**”. Zone R = Gbodjomé, zone A = Kpémé, zone B = Goumou-Kopé, zone C = Aglomé; zone D = west Aného.

D.2. Perception of well water quality

This part aims to understand how population percept their well waters (quality, health risk, …)

First, water quality perception was evaluated based on organoleptic properties. Suspended particles are more observed in zone B (25%), zone C (5%) and zone D (25%) compared to the reference zone (10%) (Figure 21). Suspended particles refer to small particles in suspension that might contain F^- or trace metals and are probably ingested with water because the population do not decant or filtrate water. Yellow colour is observed in zone A (30%), in zone B (5%), in zone C (90%) and in zone D (15%). Deposits on the bottom of the wells are observed in zone B (45%), zone C (100%) and zone D (30%). They refer to bigger particles that probably decant rapidly and should therefore not be ingested by the people even if they do not filtrate or let decant their waters. However, deposits in the bottom can be a marker of contamination from the phosphate treatment. They are important in zone B and C. Yellow colour might be a marker of water contamination with phosphorite residues. Indeed, at the site of mud discharge in the sea, a phenomenon called “yellow tide” happens. It suggests that zone A and particularly zone C receive phosphorite residues in their wells (marine infiltration and dust deposition). However, it should be taken into consideration that the yellow colour of water could also come from other particles such as tree leaves and sand. Taken together, zone C presents the water the most yellow and the most charged with particles, suggesting that it could contain a lot of phosphate residues.

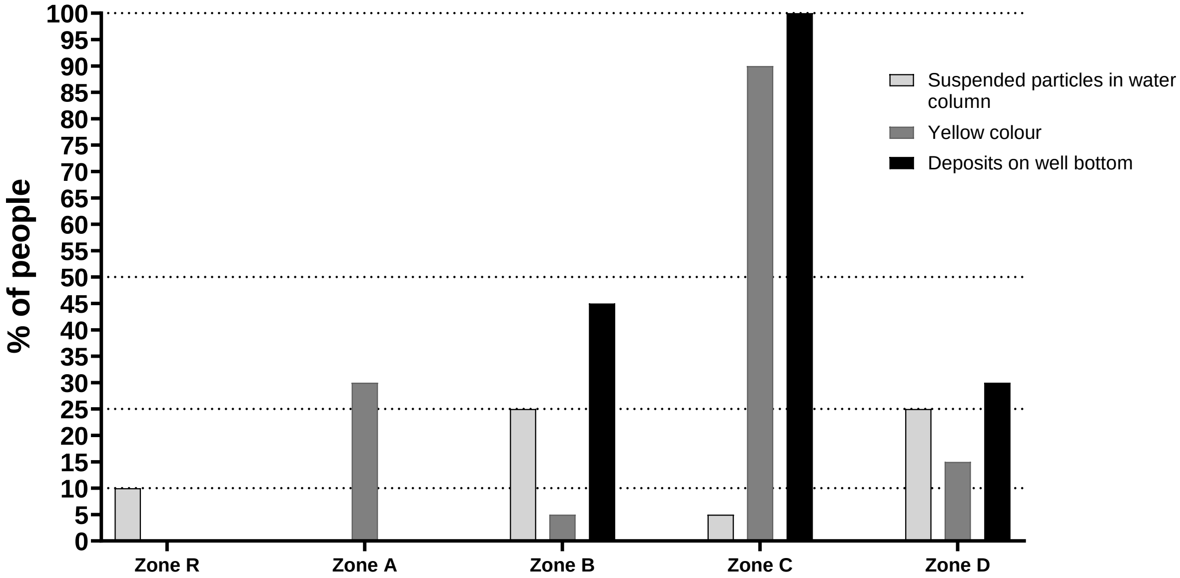

Figure 21. Qualitative perception of well waters. Percentage of the population observing “suspended particles”, “yellow colour”, “deposits on well bottom” in their well waters to the question 6 “**What are the characteristics of the well water you use?**”. Zone R = Gbodjomé, zone A = Kpémé, zone B = Goumou-Kopé, zone C = Aglomé; zone D = west Anécho.

Next, we aimed to understand whether well waters could be a source of health problems. Figure 22 shows the opinion of the population. The percentage of the population thinking that well waters can cause health problems “a lot” is 20% in the reference zone, 30% in zone A, 70% in zone B, 45% in zone C and 5% in zone D. The answer “a lot” was mainly given in the 3 zones receiving a significative amount of waste (dust deposition, marine water intrusion, solid waste storage on soils) from the phosphate treatment plant: zones A, B and C. More particularly, zones B and C are highly impacted by dust deposition and marine intrusion (Introduction D.2). This suggests that the phosphate treatment activity would be the cause of these health problems. As the main health problem easily observable by the population is dental fluorosis, we suggest that they refer to this disease in particular.

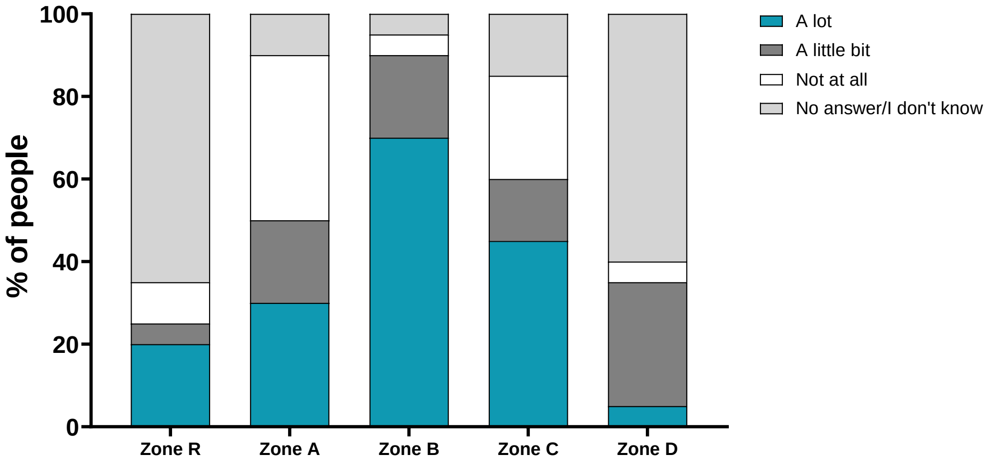

Figure 22. Health problems. Percentage of population answering “a lot”, “a little bit”, “not at all” to the question 8 “**Do you think well water you use can cause health problems?**”. Zone R = Gbodjomé, zone A = Kpémé, zone B = Goumou-Kopé, zone C = Aglomé; zone D = west Anécho.

In order to evaluate which diseases are present in the populations, medical symptoms were surveyed in the next section.

D.3. Medical symptoms

This part aims to understand the health problems encountered by the population, as well as their potential link to well water contamination with F^- and trace metals. Note that only the problems that can be observed by the population (without medical background) is surveyed.

Dental fluorosis is a disease caused by F^- accumulation in teeth [34]. There are more cases of dental fluorosis observed in zone A (5% often; 5% sometimes; 50% rarely), zone B (85% often; 15% rarely), zone C (90% often; 5% sometimes) and zone D (5% sometimes; 45% rarely) compared to the reference zone (15% rarely). Zones B and C are the zones where dental fluorosis is the most observed (Figure 23).

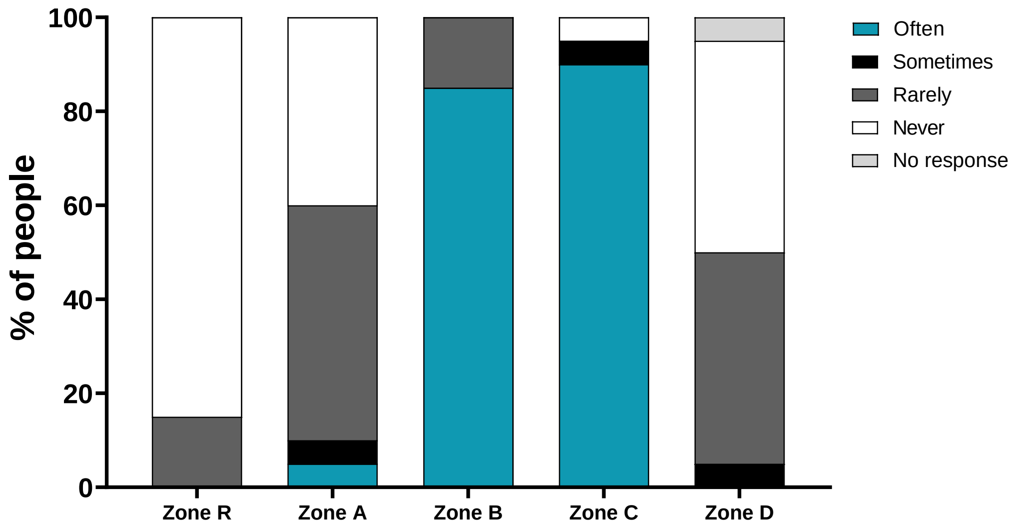

Figure 23. Dental fluorosis. Percentage of the population answering "often", "sometimes", "rarely", "never" to the question 9 **"Are there cases of dental fluorosis in your village? If yes, how often?"**. Zone R = Gbodjomé, zone A = Kpémé, zone B = Goumou-Kopé, zone C = Aglomé; zone D = west Aného.

When exposed in the longer term to a high level of F^-, people may develop skeletal fluorosis. In the question 10 , the term "skeletal system problems" was used as reference to skeletal fluorosis because the population might not know the name of this disease. One limitation is that other skeletal problems not related to skeletal fluorosis could be taken into account by the surveyed people. There are more cases of skeletal problems observed in zone A (5% often; 10% sometimes) and zone C (5% often; 20% sometimes) compared to the reference zone (10% sometimes) (Figure 24). No more cases of skeletal problems were described in zone B and zone D compared to the reference zone. The prevalence of skeletal problems is way lower than for dental fluorosis which is normal because teeth are impacted earlier than bones by F^-. The symptoms of skeletal problems observed in zones A and C were general skeletal pain, leg and back pain as well as articulation problems. Moreover, 5% of the people interviewed in zones A and C observed skeletal structural change (data not shown). It should be taken into consideration that interviewed people are not health specialists and can sometimes not make the difference between skeletal problems caused by fluorosis and by other causes such as normal aging.

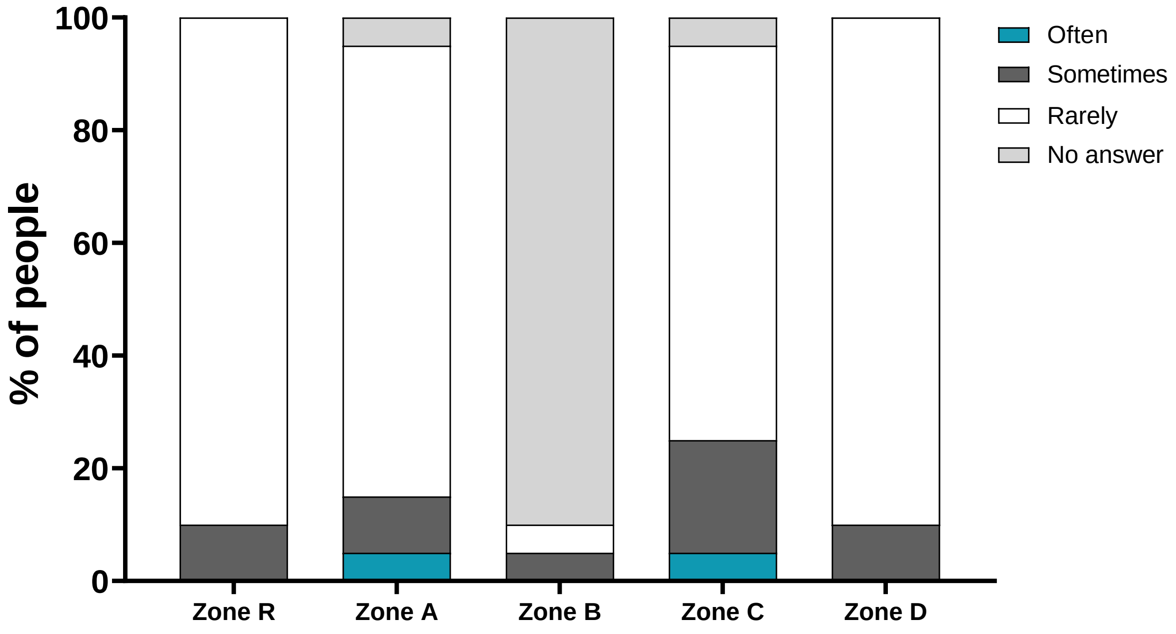

Figure 24. Skeletal fluorosis. Percentage of the population answering “often”, “sometimes”, “rarely”, “never” to the question 10 “**How often happen the problems of skeletal system in your village?**”. Zone R = Gbodjomé, zone A = Kpémé, zone B = Goumou-Kopé, zone C = Aglomé; zone D = west Aného.

The question 11 referred to arsenicosis. The main symptoms are skin lesions such as hyperpigmentation or hyperkeratosis in hand palm, foot palm as well as spotted hyperpigmentation on the whole body [30] (personal communication). Our results don’t show clearly the presence of arsenicosis in the population of all the zones. However, in zone C, 10% of the population observed cases of skin problems in their population compared to 5% in the reference zone (Figure 25). Skin problems encountered in zone C are mainly lesions on feet palm and spotted hyperpigmentation on the whole body (data not shown) which are symptoms of arsenicosis. However, in should be taken into consideration that the interviewed people could confuse symptoms of arsenicosis with broader skin symptoms, even if pictures were shown during the survey in order to avoid this bias.

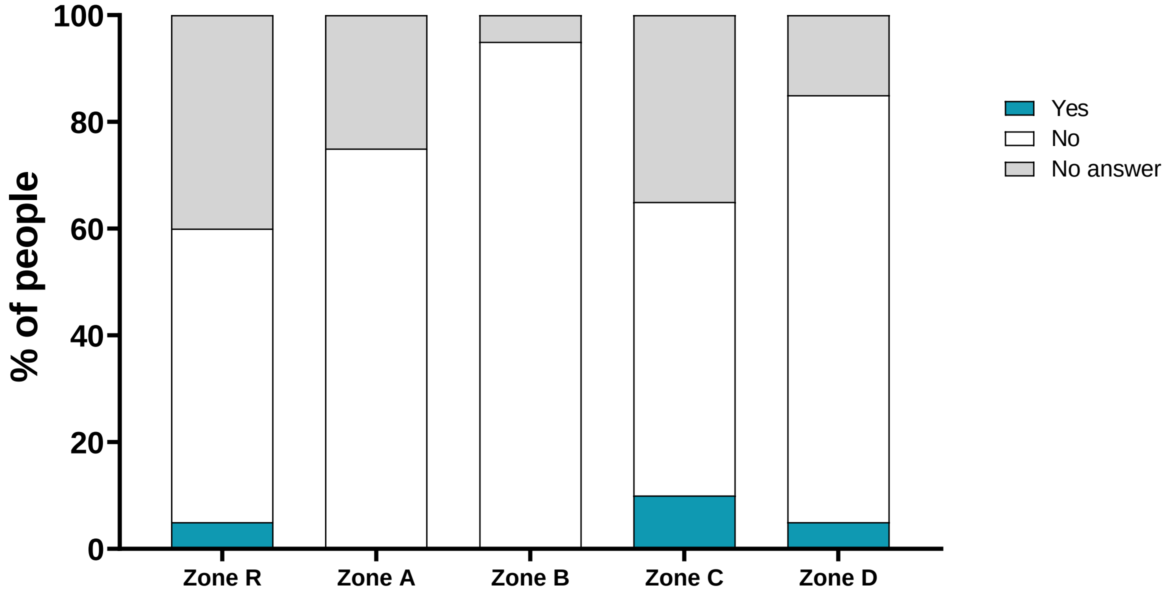

Figure 25. Arsenicosis. Percentage of the population answering “yes”, “no”, “rarely” to the question 11 “**Do you personally encounter skin problems?**”. Zone R = Gbodjomé, zone A = Kpémé, zone B = Goumou-Kopé, zone C = Aglomé; zone D = west Aného.

Neurological problems can happen in children exposed to Pb, Cr, Ni, Mn and As [31]. The observation of neurological problems in children was assessed. Our results do not show the presence of neurological problems in children due to trace metals (Annexe 8).

In addition, the general state of the population was also evaluated in the survey with a list of symptoms to check (cardiac problems, headache, fever, cold, dizziness, muscular and general pain). There is a high prevalence of headache, fever and cold in the population of zone C (more than 80% for each symptom) compared to the other zones of interest and the reference zone (Figure 27). Cardiac problems (including chest pain) fatigue (general and muscular) and dizziness have the highest prevalence in zone A, with 40%, 60% and 50%, respectively. Cardiac problems have been notified only in zone A, zone B and zone C. The general state of people of zone C seems to be worrying.

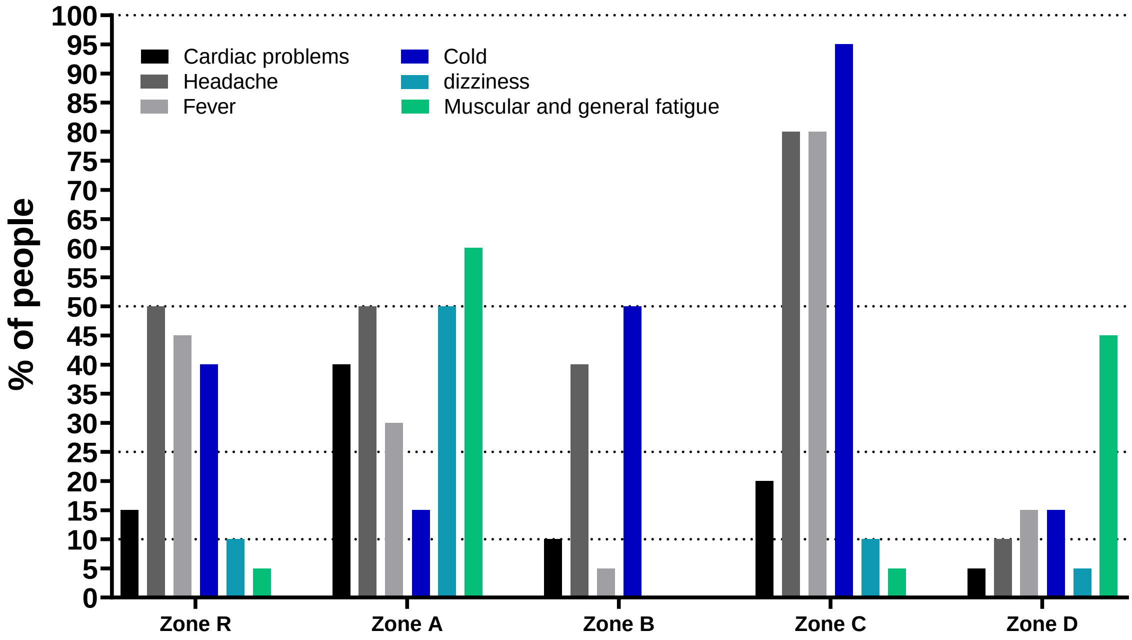

Figure 27. General state-related health troubles. Percentage of the population that encounters personally cardiac problems, headache, fever, cold, dizziness, muscular and general fatigue (question 13). Zone R = Gbodjomé, zone A = Kpémé, zone B = Goumou-Kopé, zone C = Aglomé; zone D = west Aného.

Finally, dust coming from the chimney of the phosphate treatment plant might also lead to health problems via direct contact in the eyes and the respiration tract [65]. Moreover, ingestion of F^- and trace element via water and food might cause acute digestive problems [31]. Question 13 aimed to evaluate these effects via assessment of eye, respiration and digestive problems (Figure 26). Eye problems happen more in zone A (65%), zone B (85%), zone C (100%) and zone D (70%) compared to the reference zone (30%). Eye problems are mainly vision-related problems, eye pain, redness, and to a smaller extent presence of crust in the eyes (data not shown). Respiration problems happen more in zone C (95%) compared to the reference zone (30%). Symptoms pointed out are mainly general lung problems, breathing difficulties, cough and respiratory infection (data not shown). Taken together zones A, B, D, and mainly zone C suffer from dust. The geographical localisation of zones A, B and C explain that they receive dust from the plant. Zone C is indeed the zone that receives the most important quantity of dust because it is situated north-east of the plant and that the wind blows in that direction most of the time. However, we should note that eye problems can have other sources such as too long exposure to sun without sunglasses. This could explain the relatively high % of eye problems already found in the reference zone. The prevalence of digestion problems is higher in zone A (45%), C (75%) and D (55%) compared to the reference zone (25%). Digestion problems pointed out are mainly in abdominal pain, diarrhea, gastrointestinal irritation, and to a smaller extend constipation (data not shown).

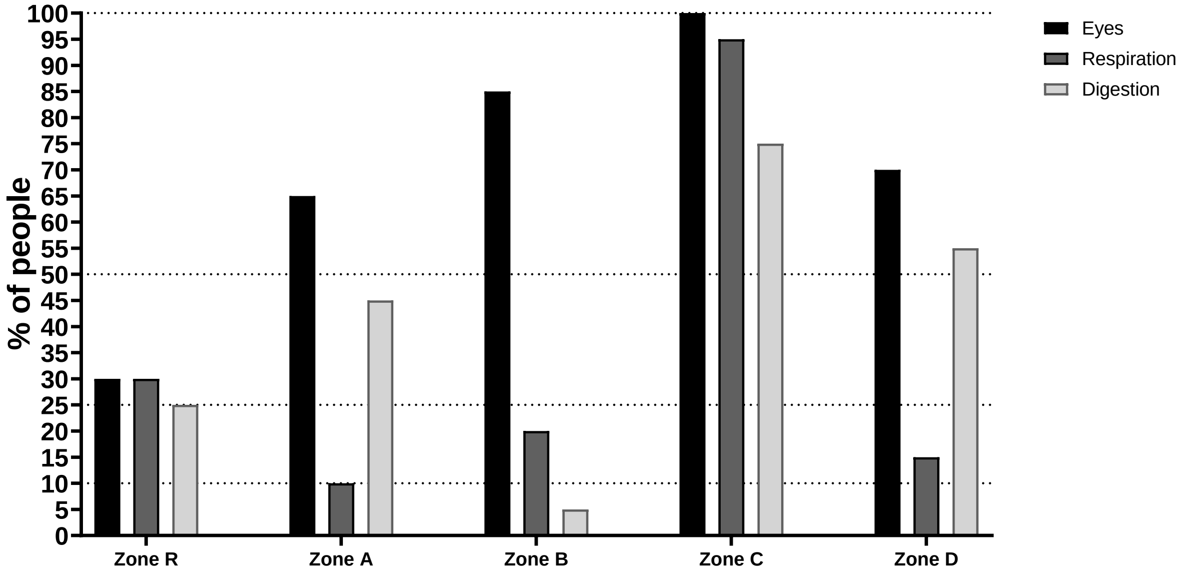

Figure 26. Health problems related to eyes, respiration and digestion. Percentage of population that encounter personally eyes, respiration and digestion problems (question 13). Zone R = Gbodjomé, zone A = Kpémé, zone B = Goumou-Kopé, zone C = Aglomé; zone D = west Aného.

As the inhabitants interviewed were no health specialists, it was important to confirm those results and to add other information with the opinion of health specialists.

E. <u>Health centre survey</u>

The survey in health centres aimed to 1) confirm the results of the sociological survey with the point of view of a health specialist, 2) bring other information about diseases not known by the population, 3) know the opinion of a health specialist whether these disease might be due to the phosphate treatment plant activity and/or to drinking of well waters. One specialist was interviewed per health centre. 4 health centres were surveyed: Centre of zone R (= centre R); centre of zone A (= centre A); centre zone B (= centre B); centre zone D (= centre D). Note that zone C doesn't have a health centre, and that its population mainly goes to the health centre A. Table 8 summarizes the prevalence of consultations for different pathologies in these 4 health centres. Answers are classified as "never", "sometimes" or "often".

Pathologies	Centre R	Centre A	Centre B	Centre D
Dental fluorosis				
Skeletal fluorosis				
Arsenicosis				
Cerebral troubles in children				
Skin allergies				
Digestion				
Respiration				
Eyes				
Hypertension				

Table 8. Prevalence of consultations for different types of pathologies in health centres: centre R = Gbodjomé, centre A = Kpémé, centre B = Goumou-Kopé, centre D = west Aného. Note that zone C doesn't have a health centre and its population goes mainly to the health centre of zone A. Legend: Light grey = never; dark grey = sometimes; orange = often

Health centres A and B often receive patients with dental fluorosis. In contrast, centres R and D never receive patients with dental fluorosis. This confirms the results of the sociological survey showing a higher prevalence of dental fluorosis in zones A, B and C than in zone R. Centres A and B receive sometimes patients with skeletal fluorosis. Results of the sociological survey suggests that skeletal fluorosis is present in zones A and C. As patients living in zone C go to the health centre of zone A, the results of the two surveys point out that zones A and C present cases of skeletal fluorosis. In contrast, the sociological survey fails to show the presence of skeletal fluorosis among the population of zone B. However, as the population is not well informed about skeletal fluorosis, the input of the health specialists helps to better represent the real prevalence of skeletal fluorosis. Cases of skeletal fluorosis are therefore present in zones A, B and C.

The 4 health centres surveyed do not receive patients with arsenicosis, nor children with cerebral troubles. As the sociological survey didn’t show any cerebral problems in children, the 2 surveys are in agreement. In contrast, the sociological survey could suggest that arsenicosis might be present in zone C. However, this result should be taken carefully and is not confirmed by the health centre survey. We will confirm that arsenicosis is not observed in the study area.

Finally, the centre A often receive patients with skin allergies. However, in the sociological survey, skin allergies were not observed in the population of zone A.

Centre A often receives patients with digestive troubles. This is in agreement with the results of the sociological survey, showing a high rate of digestive problems among the population of zones A and C.

Centres A and B often receive patients with respiration and eye-related problems. This confirms the results of the sociological survey pointing out these troubles among the populations of zones A, B and C.

In general, the health centre survey confirms results of the sociological survey. According to the health specialists, well water might be a vector of intoxication with F^- and trace metals. However, the main vector would be dust released from the plant and depositing in water or directly on people skin, eyes and lungs. More particularly, dental and skeletal fluorosis might be due to well water consumption but are mainly due to dust. Skin allergies would be due to well water consumption and dust. Digestive troubles are due to consumption of well waters. However, one should bear in mind that, in water, not only the F^- and trace metals can cause digestive problems. Other potential candidates can be bacteria, parasites, … Finally, respiration and eye problems are due to the dust.

In contrast, hypertension is highly present in the populations of all the zones, including the reference zone. This suggests that the phosphate treatment is not the cause. Indeed, according to health specialists, hypertension is due to bad eating habits. However, according to the sociological survey, cardiac problems would mainly occur in zones A and C. As cardiac problems can englobe different troubles, other than hypertension, it is difficult to compare both information. Moreover, patients with cardiac problems might go to an hospital to have a consultation with a cardiologist, without going to the local health centre.

F. General discussion

In the present study, we aimed to compare the results of the element quantification in well waters with the surveys, together with facts in the literature. Therefore, we can evaluate potential correlations and understand whether the health problems are due to the activity of the plant or not.

There is a correlation between the F^- concentration in well waters and the prevalence of dental and skeletal fluorosis. Remember that, even if F^- levels are below the WHO guide value (1500 µg/ml), the analytic method might have underestimated the real F^- concentration. Moreover, there is a correlation between the phenomenon of dust deposition and the occurrence of dental and skeletal fluorosis. This confirms the results of previous studies highlighting that dental fluorosis is a direct consequence of the phosphate treatment plant activity. More precisely, fluorosis is due to consumption of well waters, sea products and agricultural products contaminated with F^-, as well as to the direct inhalation of dust [23], [34]. Well waters consumption is therefore one vector of contamination among others.

Kumar and colleagues showed a correlation between As concentration in well waters and the prevalence of arsenicosis in India. Indeed, in their study, almost all of the water samples presented an As concentration higher than 10 µg/ml and the rate of arsenicosis in the population was high. Moreover, there was also 2 cases people with cancer together with arsenicosis symptoms [30]. The present study is in accordance with this correlation because levels of arsenic in well waters are below 10 µg/ml and it seems that there is no case of arsenicosis in the population. However, we pointed out that well waters of zone B present a significant enrichment with As and that there is a carcinogenic risk associated with As contamination in zones B and C. Therefore, even if symptoms of arsenic intoxication are not clearly observed in the population, it would be worth it to pay attention to As in well waters.

Pb, Cr, Ni, Mn and As may be toxic for the central nervous system and induce neurobehavioral troubles, already detectable in children [31], [63]. In the present study, no neurobehavioral troubles were highlighted in children. It correlates with the low levels of Pb, Cr, Ni, Mn and As detected in well waters (below respective guide values).

Nickel is associated with skin allergies [66]. Even if Ni concentrations are below the guide value in all the samples, mean Ni concentration is the highest in zone A. Moreover, skin allergies were highlighted in zone A by the health specialist. It suggests that there could be a correlation between Ni in well waters and the prevalence of skin allergies. Therefore, skin allergies might be due to Ni in water. However, it should be taken carefully because the population of zone A do not complain about skin allergies.

Cadmium intoxication is associated with high blood pressure [31]. However, in our study, there is an absence of correlation between Cd concentration in well water (not detected) and the prevalence of hypertension (high in all the zones). This strongly suggests that hypertension in the study area is not due to the plant activity. It would be due to bad eating habits as explained by the health specialists.

Health problems can be caused by the mix of different trace elements [13]. We showed that there is a possible health effect of trace elements in zones A and C. This correlates with the prevalence of general state-related problems. Indeed, cardiac problems, headache, fever, cold, dizziness, muscular and general fatigue are mostly present in zones A and C. Moreover, acute intoxication with F^- or trace metals might cause digestive problems [20], [30], [31]. In the present study, digestive troubles are mainly present in the populations of zones A and C. Except for zone B, there is a correlation between the concentrations of the studied contaminants (taken as a whole) in well waters and the prevalence of digestive troubles. Note that the absence of digestive problems pointed out in zone B could be due to a bias of the surveys. This suggests that the digestive problems would be due to the activity of the plant. However, one should bear in mind that digestive problems related to water consumption could be due to other things such as parasites and bacteria.

Finally, dust enriched with F^- and trace metals was shown to have harmful effects on the human body, especially when inhaled via the respiratory system. Some authors even suggested that dust was a vector of contamination more important than drinking water [33], [34], [65]. In our study zone, dust released from the chimney deposits on the neighbouring villages. Once deposited in water or on vegetables (where it accumulates vie foliar absorption) via dust, pollutants are consumed by human. Dust also deposits directly in the skin, the eyes or in the respiratory tract of people. In the present study, there is a correlation between the phenomenon of dust deposition and the prevalence of respiratory and eye problems. This suggests that these problems are directly due to the activity of the plant. Therefore, EF and ERI associated with dust were calculated in annexe 6. Dust is minimally enriched with Pb, Al, Cr, Ba, Mn. Dust is moderately enriched with Co. Finally, it is significantly enriched with Cu, Ni, Sr and highly enriched with Se, U, As, Zn. However, ERI = 34.63 < 150, supporting a low ecological risk due to dust.

Taken together these results show that, even if the level of the elements quantified stand below their respective guide values, well water consumption as drinking water might induce a risk for health. However, dust seems to be a vector of contamination more important than well water. Finally, zone C appears to be the zone the most impacted by the pollution. This leads to advices that could be given to the population.

G. Advices to the riparian population of the phosphate treatment plant:

Some advices could be given to the populations of zones A, B and C:

- Covering wells with lids would avoid dust deposition in the waters and therefore the potential intoxication by F^- and trace metals concentrated in the dust.
- Well water filtration would remove particles that are in suspension in water. These are probably phosphate residues containing F^- or other particles on which trace metals are adsorbed.

These 2 actions would decrease the risk of intoxication by F^- and trace elements via well waters.

V. CONCLUSION

In the present work, we aimed to study the eventual sanitary problems caused by the phosphate treatment plant of Kpémé. Particularly, we studied the risk induced by the vector of well water consumption as drinking water. Indeed, uncovered well are the main source of drinking water in the populations of the study zone and people do not filter their water before consumption. Moreover, well water is also used for cooking and wash aliments. Therefore, well water might be a vector of contamination with F^- and trace elements. The study zone was divided into zone A, zone B, zone C and zone D because these zones are differentially impacted by the activity of the plant according to their geographical localisation. Zone R was used as the negative reference zone. On the one hand, we aimed to quantify F^-, Pb, Se, U, Al, Cu, As, Cr, Ni, Ba, Sr, Mn, Zn and Co in well waters. On the other hand, we aimed to study the prevalence of different health problems potentially linked with F^- and trace metals intoxication among the populations.

First, the results of TDS, $oPO4^{3-}$ and total Ca indicated the presence of phosphate ore residues in well waters of zones A, B and C. The 3 ways of contamination of well waters with contaminant from the plant are 1) solid waste storage followed by rainwater infiltration, 2) mud discharge followed by marine water intrusion and 3) deposition of dust released from the plant.

Next, F^- was quantified in well waters. Even if F^- concentrations in well waters are below the guide value, it doesn't mean that there is no risk for health. Indeed, the technic of analysis could have underestimated the real F^- concentration. The comparison of F^- levels between the zones shows that levels are higher in the 4 zones of interest than in the reference zone. More particularly, zones A and B present the highest F^- concentrations. Finally, as Tanouayi and colleagues showed the enrichment of mud and dust with F^-, the phosphate treatment would be the main source of F^- contamination in well waters in our study [23].

Moreover, trace metals were quantified in well waters. All the trace metal concentrations stand below the respective guide values. Zone A presents higher levels of Ni, Al, Ba and Mn compared to the reference zone. Zone B presents higher levels of Pb, As and U compared to the reference zone. Zone C presents higher levels of Ni, Al, As, Ba, U and Mn compared to the reference zone. Zone C is the zone the most polluted of all because of its geographical localisation. The enrichment of mud with Sr, Pb, Se, U, Al, Cu, As, Cr, Ni, Ba, Zn and Co and the enrichment of dust with Co, Cu, Ni, Sr, Se, U, As and Zn indicate that the presence of these elements in well waters is a direct consequence of the phosphate treatment.

Levels of F-, Cu, Pb and Ni in this study were lower than in previous studies. This can have different explanations: the decrease in the use of solid waste to repair the streets of the surrounding villages; the rhythmic effect of salinity due to marine water intrusion; the difference in pH between the studies; a difference in nature and size of suspended particles, influencing the adsorption of elements.

Even if F^- and trace metal concentrations in well waters stand below their respective guide value, this doesn't mean that they would not induce a risk for health. Indeed, the population drink well water during their whole life without filtration. Moreover, trace metals are known to bioaccumulate in the organisms. Therefore, the measure of risk indexes allowed to better understand the health risks. The ecological risk associated with As, Cd, Cr, Cu, Ni, Pb and Zn in well waters is low. Moreover, THQs of F^- and trace elements were all below 1, suggesting that there is no health effect expected as a result of exposure. In contrast, the measure of TR suggests that there is a cancerogenic risk associated with As, mainly in zones B and C. Note that well waters of zone B are significantly enriched with As. Moreover, there is a possible effect of a mix of elements on health in zones A and C.

Next, we evaluated the correlations between the quantifications of the contaminants in well waters and the prevalence of different health troubles in the populations. Dental fluorosis and skeletal fluorosis present a higher prevalence in zones A, B and C than in the reference zone. This correlates with F^- levels in waters. Digestive problems happen in the populations of zones A and C. This correlates with the concentration of contaminants (F- and trace elements, taken as a whole) in well waters. Respiration and eyes problems are present in zones A, B and C. This correlates with the phenomenon of dust deposition. Results of previous studies even suggested that dust is a vector of contamination more important than well water consumption. However, the calculation of RI failed to show an ecological risk associated with dust.

In conclusion, the data of this study allowed us to better understand the sanitary problems linked with the phosphate treatment plant. Even if the levels of F^- and trace metals in well waters are below the guide values, they could induce a risk for health. Moreover, dust seems to be a vector of contamination more important than well waters. Finally, zone C seems to be the zone the most impacted by the pollution because:

- It presents the highest concentration of some of the contaminants in well waters.
- It presents the highest prevalence of fluorosis, digestive problems, respiratory problems and eyes problems.
- It presents a cancerogenic risk associated with As in well waters
- It presents a risk for health associated with a mix of elements
- It receives the highest quantity of dust.

Covering the wells and filtering well waters would decrease the quantity of F^- and trace metals ingested and would therefore decrease the risk of intoxication.

VI. PERSPECTIVES

First, it would be interesting to evaluate the different strategies of water sanitation that could be settled. Water sanitation should be focused on F^-, because of the presence of fluorosis, and As, because of its association with a cancerogenic risk. Moreover, as we pointed out the risk associated with a mix of element, it would be interesting to develop a technique able to remove a set of elements.

Next, it would be interesting to perform a study based on medical consultations. Disease that could be assessed are skeletal fluorosis, arsenicosis, cancer, respiration troubles and eye-related troubles.

Finally, as dust is enriched with many trace elements and with F^-, it would be interesting to evaluate more precisely the risk for health associated with dust in the treatment zone.

VII. STUDY LIMITATIONS

Firstly, water samples were collected in Togo and analysed in Belgium. Between the collect and the analysis there was a time lapse. It could be a problem for the non-acidified samples used for ionic chromatography because of the instability of phosphate and F^-. These results should therefore be taken with precautions.

Secondly, the sociological survey presents several limitations:

- Each zone was surveyed by a different surveyor. Therefore, answers could depend on whether the surveyor insists on a question or not.
- Surveyors were asked to cover uniformly their geographic zone. However, it is subjective. Ideally, we should have been representative of the sex and age ratios of each population.

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VIII. ANNEXES

<u>Annexe 1:</u> Latitudes and longitudes of the well from which were collected the samples

Well number	Site	Latitude	Longitude
1	Gbodjomé	6° 11' 35,33"	1° 24' 56,91"
2	Gbodjomé	6° 11' 20,84"	1° 24' 47,82"
3	Kpémé	06°13’23.7’’	001°30’13.2’’
4	Kpémé	06°13’12.9’’	001°30’19.4’’
5	Kpémé	06°12’50.6’’	001°30’25.0’’
6	Kpémé	06°12’55.4’’	001°30’12.2’’
7	Goumou-Kopé	06°12’47.6’’	001°31’48.1’’
8	Goumou-Kopé	06°12’46.6’’	001°31’49.3’’
9	Goumou-Kopé	06°12’51.9’’	001°32’08.4’’
10	Goumou-Kopé	06°12’55.2’’	001°32’10.7’’
11	Goumou-Kopé	06°13’00.4’’	001°32’12.7’’
12	Aglomé	06°13’05.2’’	001°31’24.5’’
13	Aglomé	06°13’12.3’’	001°31’11.2’’
14	Aglomé	06°13’12.2’’	001°30’56.5’’
15	Aglomé	06°13’07.9’’	001°30’50.6’’
16	Aglomé	06°13’29.5’’	001°30’50.3’’
17	West Aného	06°13’29.2	001°34’11.9
18	West Aného	06°13’26.2’’	001°33’12.3’’
19	West Aného	06°13’27.8’’	001°34’18.6’’
20	West Aného	06°13’36.3’’	001°34’34.5’’

Annexe 2: **Questionnaire for the sociological survey**

Questionnaire N° : … Date : ……./……./ …… Village:… Name of surveyor :…………….

Questionnaire on water quality

Socio-economic data

Name: ………… Sex: M/F Age :…… Job :……….

Scholarship level: None/primary/highschool/university Number of years lived in the village :…

Part 1 : Water use

Question 1. What is the main drinking water source of your household ?

Uncovered well ☐ covered well ☐ Dwell ☐ Private tap (TDE) ☐ Public tap ☐

Water bottles or bag ☐ Rainwater collect ☐ Surface water (stream, lake) ☐

Tanks brought to the village ☐ Other:……

Question 2. In the drinking water consumption of your household, what is the part of well water?

Less than half ☐ Half ☐ More than half ☐ Percentage (%) : …

Question 3. How many litres of well water do you drink daily?

Question 4. Do you treat well water before drinking/using it? If yes, how?

No treatment ☐ Boil ☐ Add a product (Bleach, chlorine,…) ☐

Filter through a tissue ☐ Use a filter (ceramics, sand, stone, …) ☐

Solar disinfection ☐ Let decant ☐ Dilution with another source ☐

I don't know ☐ other (specify):________

Question 5. For which uses do you use well water? (Check as many cases as you want)

Drink ☐ Cook ☐ Wash food ☐ Wash dishes ☐ Body hygiene ☐

House hygiene ☐ Wash clothing ☐ Animals ☐

Other :…………….

Part 2 : Evaluation of water quality

<u>Question 6.</u> What are the characteristics of well water that you use? (Check as many cases as you want)

Colour :
Colourless ☐ brown-red ☐ blue-green ☐ yellow ☐

Other:______

Taste:
Tasteless ☐ good taste ☐ bitter ☐ salty ☐

Other :_____

Other :
Particular smell: ______________ Transparent ☐ Not transparent ☐

Debris in the bottom ☐ Suspended particles ☐ Presence of mucus ☐

Foam ☐ Other:_____

<u>Question 7.</u> Are you concerned about the well water quality that you use?

Not at all ☐ A little bit ☐ A lot ☐ I don't know ☐

Explain :

<u>Question 8.</u> Do you think that the well water that you use could cause health problems ?

Not at all ☐ A little bit ☐ A lot ☐ I don't know ☐

Explain :

Part 3 : Medical symptoms

Question 9. Dental fluorosis is an affection that causes marbled stains on teeth. Stains can be white, yellow, brown or black (see picture N°1).

A) Are there any cases of dental fluorosis in your village? If yes, how often?
Never ☐ Rarely ☐ Sometimes ☐ Very often ☐

Explain :

B) Do you personnally encounter this phenomenon?

If yes, explain :

C) According to you, which would be the cause?................

Question 10.

A) Are there any problems of the skeletal system in your village? Which ones? (Check as many cases as you want)

Fracture ☐ Structural change (arched legs, …) ☐ General pain ☐

Leg pain ☐ Back pain ☐ Articulation pain (knees, elbows, wrist, hips) ☐

Articulation problems ☐ Atrophied feet ☐ Walking difficulties ☐

Other : _______ None of these ☐ I don't know ☐

B) How often are observed those problems in your village?
Rarely ☐ Sometimes ☐ Often ☐

Explain :

C) Do you personally encounter one of more of these problems?

Explain :

D) According to you, what is the cause?......................

Question 11.

A) Are there any skin problems in your village? Which ones? (Check as many cases as you want) (see picture N°2 and N°3)

Hand palms lesions ☐ Foot palm lesions ☐ Lesions on other body parts : _________

Hyperpigmentation of hand palm ☐ Hyperpigmentation on other body parts : __________

Allergies☐ Gangrene ☐ Other : ________ None of these ☐

I don't know ☐

B) How often are observed those phenomenons?
rarely ☐ Sometimes ☐ Often ☐

C) Do you personally encounter one or more of these symptoms?

If yes, explain :

D) According to you what would be the cause? ……………………

Question 12.

A) In the following list, are there some symptoms observed in the children of your village? (check as many cases as you want)

Dizziness, nausea, muscular weakness, fatigue☐ no appetite, anorexia ☐ Hyperactivity, inattention ☐

Often with and cold ☐ Behaviour troubles, impulsivity, irritability, grumpy☐

Learning and listening difficulties, delay in language learning ☐ Sleeping problem ☐

Other:_______ None of these ☐ I don't know ☐

B) How often are observed these phenomenon's?
Rarely☐ Sometimes☐ Often ☐

Explain :

C) According to you what would be the cause?………………………..

<u>Question 13.</u> Do you <u>personally</u> encounter problems in the following list? (Check as many cases as you want)

General state:

Heart problems ☐ Paralysis ☐ Headache ☐ Fever ☐ Cold ☐

Hypertension ☐ Low tension ☐ Diabetes ☐ Jaundice ☐

Loss of appetite/weight loss ☐ Dizziness/malaise ☐ General fatigue/ weakness ☐

Muscular fatigue ☐ ☐ Tremors ☐ Chronical infections ☐ Nausea ☐

Anaemia ☐ cough ☐ Memory loss ☐ Numbness of the limbs ☐

Depression ☐ Teeth problems ☐ Other:_______

Eyes:

Vision trouble/blindness ☐ Eye pain ☐ red eyes ☐

Crust in eyes ☐ Other:_________

Digestion:

Abdominal/gastric/intestinal pain ☐ Diarrhea ☐ Constipation ☐

Gastrointestinal irritation/acidity ☐ Other:_________

Respiration:

Lung problems ☐ Chest pain ☐ Breathing difficulties/asthma ☐

Respiratory infection/bronchitis ☐ Superior respiratory tract irritation ☐

Other:______

Explain if necessary :

Question 14. Other remark?

…..……..………………………………………………………………………………………………………
……
……………………………………………………………………………………………………..………
……
……………………………………………..

Picture n°1 = Dental fluorosis (for QUESTION 9)

Picture n°2 = hyperpigmentation of back (for QUESTION 11)

Picture n°3 = hand palm and foot palm lesions (for QUESTION 11)

Annexe 3: Questionnaire for the health centre survey

Questionnaire N° : …….. Date : …..../…..../ ……
Village/District:………..

Questionnaire for health centres

Name of health centre **:……………** *Name and function of the respondent:***…………**

Question 1. Have you been sensitized about sources and effects of trace metals on human health?

Yes/ No.

If yes,how?..

Question 2. Do you think well water is a vector of contamination by trace metals ?
Never/sometimes/often. If yes, explain :…………………………………………………………………

Question 3. Is there any consciousness of the population about the effect of the phosphate treatment plant activity on their health ? Yes/No. If yes, explain :…………………………………………………

Question 4. Do you receive patients with dental fluorosis? Never/sometimes/Often

- Precise de prevalence of consultations:…………..
- How many new cases were diagnosed for the last 5 years ?
- Do you think it could be linked with the activity of the SNPT? Yes/No
  If yes, explain………………………………………………………………………………………
- Do you think it might be linked with well water consumption? Yes/No
  If yes, explain : ……………………………………………………………………………………
- According to you, what would be the cause?

Question 5. Do you receive patients with skeletal fluorosis ? Never/sometimes/Often

- Precise de prevalence of consultations :……………..
- How many new cases were diagnosed for the last 5 years ?
- How is it diagnosticated?
- Do you think it could be linked with the activity of the SNPT ? Yes/No
  If yes, explain……………………………………………………………………………
- Do you think it might be linked with well water consumption? Yes/No
  If yes, explain : …………………………………………………………………………………
- According to you, what would be the cause ?

Question 6. Do you receive patients with cardiovascular diseases? Never/sometimes/Often

- Precise de prevalence of consultations :……………..
- How many new cases were diagnosed for the last 5 years ?
- How is it diagnosticated?
- Do you think it could be linked with the activity of the SNPT? Yes/No
  If yes, explain……………………………………………………………………………
- Do you think it might be linked with well water consumption? Yes/No
  If yes, explain : ……………………………………………………………………………………
- According to you, what would be the cause ?

Question 7. Do you receive patients with hepatic diseases? Never/sometimes/Often

- Precise de prevalence of consultations :……………..
- Which diseases?
- How many new cases were diagnosed for the last 5 years ?
- How is it diagnosticated?
- Do you think it could be linked with the activity of the SNPT? Yes/No

If yes, explain………………………………………………………………………………………

- Do you think it might be linked with well water consumption? Yes/No
  If yes, explain : ……………………………………………………………………………………………
- According to you, what would be the cause ?

Question 8. **Do you receive patients with bladder pathologies?** Never/sometimes/Often

- Precise de prevalence of consultations :……………..
- How many new cases were diagnosed for the last 5 years ?
- How is it diagnosticated?
- Do you think it could be linked with the activity of the SNPT ? Yes/No
  If yes, explain………………………………………………………………………………
- Do you think it might be linked with well water consumption as drinking water ? Yes/No
  If yes, explain : ……………………………………………………………………………………………
- According to you, what would be the cause ?

Question 9. **Do you receive patients with arsenicosis?** Never/sometimes/Often

- Precise de prevalence of consultations :……………..
- How many new cases were diagnosed for the last 5 years ?
- How is it diagnosticated?
- Do you think it could be linked with the activity of the SNPT ? Yes/No
  If yes,
  explain……
- Do you think it might be linked with well water consumption as drinking water ? Yes/No
  If yes, explain : ………………………………………………………………………………
- According to you, what would be the cause ?
- Which symptoms: foot palm lesion; hand palm lesion; lesion on other body part; hyperpigmentation of hand palms; hyperpigmentation on other body part; other: …
- What symptoms often occur?

Question 10. **Do you receive kids with cerebral troubles ?** Never/sometimes/Often

- Precise de prevalence of consultations :……………..
- How many new cases were diagnosed for the last 5 years ?
- How is it diagnosticated?
- Do you think it could be linked with the activity of the SNPT? Yes/No
  If yes, explain…………………………………………………………………………………………
- Do you think it might be linked with well water consumption as drinking water ? Yes/No
  If yes, explain : ………………………………………………………………………
- According to you, what would be the cause ?
- What symptoms?

Question 11. **Do you receive patients with the following health problems?** (Check as many cases as you need)

General state :

Heart problems ☐ Paralysis ☐ Headache ☐ Fever ☐ Cold ☐

Hypertension ☐ Low tension ☐ Diabetes ☐ Jaundice ☐

Loss of appetite/weight loss ☐ Dizziness/malaise ☐ General fatigue/ weakness ☐

Muscular fatigue ☐ Tremors ☐ Chronical infections ☐ Nausea ☐

Anaemia ☐ cough ☐ Memory loss ☐ Numbness of limbs ☐

Depression ☐ Teeth problems ☐ Other :_______

Eyes :

Vision trouble /blindness ☐ Eye pain ☐ red eyes ☐

Crust in eyes ☐ Other :________

Digestion :

Abdominal/gastric/intestinal pain ☐ Diarrhea ☐ Constipation ☐

Gastrointestinal irritation/acidity ☐ Other :________

Respiration :

Lung problems ☐ Chest pain ☐ Breathing difficulties/asthma ☐

Respiratory infection/bronchitis ☐ Superior respiratory tract irritation ☐ Other :______

Fertility and development

Fertility troubles ☐ Pregnancy fail ☐ Babies/kids mortality ☐

Growth/development trouble ☐ Mental disturbance ☐

Memory loss in the elderly ☐

- In the symptoms you checked, which ones are frequent? …… …………………………………
- Do you think it could be linked with the activity of the SNPT ? Yes/No
  If yes, explain……………………………………………………………………………………
- Do you think it might be linked with well water consumption as drinking water ? Yes/No
  If yes, explain : ……………………………………………………………………………………
- According to you, what would be the cause ?

Question 12. **Other Remark** ?……………………………………………………………….

Annexe 4. Enrichment factors (EF) of mud

The enrichment factor (EF) is a widely used indicator for assessing trace element enrichment in soil. Here we used it for assessing enrichment in mud tailings discharged directly from the plant into the sea. The trace element concentration of a given element is normalized to the concentration of a reference element, generally chosen because the latter is of natural origin. Typical reference elements are Al or Fe [52].

$EF = [(C_{metal}/C_{Fe})_{sample}] / [(C_{metal}/C_{Fe})_{background}]$

EF values are ranked into five categories: minimal (EF<2); moderate (2<EF<5); significant (5<EF<20); very high (20<EF<40) and extremely high (EF>40) [53].

Mud is not enriched with Mn. Mud is significantly enriched with Sr. Finally, it presents an extremely high enrichment with Pb, Se, U, Al, Cu, As, Cr, Ni, Ba, Zn and Co. Mud is used as a positive control in this study. Its enrichment with some elements strongly suggests that their presence in well waters come from the phosphate treatment. Moreover, it is an indicator that the contaminant come via marine water intrusion in the phreatic nappe.

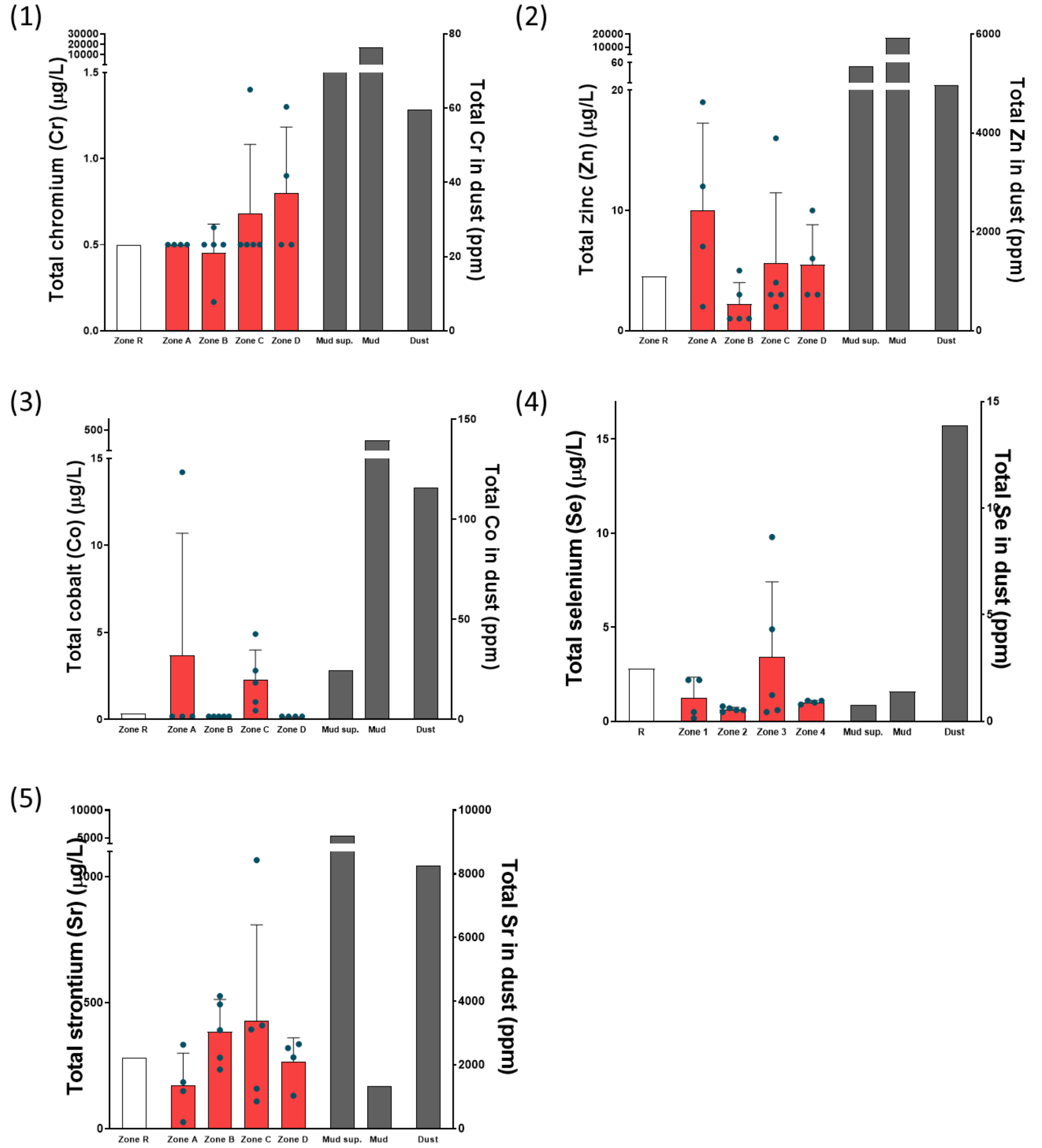
Element (ppm)	Mud Togo	Element/Mn (togo)	Upper earth crust	Element/Mn (earth)	**EF**
Pb	134,7	2,47	17	0,03	**76,62**
Se	1,6	0,03	0,083	0,00	**186,40**
U	2070	37,98	2,5	0,00	**8006,53**
Al	1486000	27266,06	77440	146,94	**185,55**
Cu	3205	58,81	14,3	0,03	**2167,24**
As	787,6	14,45	2	0,00	**3807,94**
Cr	16800	308,26	35	0,07	**4641,47**
Ni	5200	95,41	18,6	0,04	**2703,36**
Ba	2830	51,93	668	1,27	**40,97**
Zn	17200	315,60	52	0,10	**3198,45**
Mn	54,5	1,00	527	1,00	**1,00**
Sr	168	3,08	316	0,60	**5,14**
Co	302,6	5,55	11,6	0,02	**252,25**
Fe	867400	15915,60	30890	58,61	**271,53**

Enrichment factors of mud. Upper earth crust was used as background.

Annexe 5. Enrichment factors (EF) and Ecological Risk Index (ERI) of dust

Element (ppm)	Dust Togo	Dust Togo/50	Element/Mn (togo)	Upper earth crust	Element/Mn (earth)	**EF**	Cdust/Cearth	TEFI	TEFIxCFI	RI
Pb	1,3	0,026	0,00	17,00	0,03	**0,02**	0,001529412	5,00	0,01	**34,63**
Se	13,9	0,278	0,01	0,08	0,00	**39,84**	3,34939759			
U	220,76	4,4152	0,10	2,50	0,00	**21,01**	1,76608			
Al	22750	455	10,27	77440,00	146,94	**0,07**	0,005875517			
Cu	420,8	8,416	0,19	14,30	0,03	**7,00**	0,588531469	2,00	1,18	
As	274,9	5,498	0,12	2,00	0,00	**32,70**	2,749	10,00	27,49	
Cr	59,6	1,192	0,03	35,00	0,07	**0,41**	0,034057143	2,00	0,07	
Ni	739,5	14,79	0,33	18,60	0,04	**9,46**	0,79516129	5,00	3,98	
Ba	334,5	6,69	0,15	668,00	1,27	**0,12**	0,01001497			
Zn	4975	99,5	2,25	52,00	0,10	**22,76**	1,913461538	1,00	1,91	
Mn	2215	44,3	1,00	527,00	1,00	**1,00**	0,084060721			
Sr	8250	165	3,72	316,00	0,60	**6,21**	0,522151899			
Co	115,8	2,316	0,05	11,60	0,02	**2,38**	0,199655172			
Fe	18,68	0,3736	0,01	30890,00	58,61	**0,00**	1,20945E-05			

<u>Annexe 6.</u> Concentrations of chromium (1), zinc (2) and cobalt (3), selenium (4) and strontium (5) in well waters.



Annexe 6. Concentrations of chromium (1), zinc (2) and cobalt (3), selenium (4) and strontium (5) in well waters. Well waters were collected in plastic bottles and left to stand overnight for decantation and removal of the heaviest particles. Water was not filtrated before analysis, allowing small particles to stay. Trace metals were measured by ICP-MS. Zone R = negative reference zone Gbodjomé. The mean of 2 well waters was set as the zone R value. Zone A = Kpémé; zone B = Goumou-Kopé; zone C = Aglomé; zone D = west Aného. These zones are differentially impacted by the treatment plant activities following their geographical localisation. Each point represents one water sample (one well) (N = 4 or 5). Results are expressed as mean ± SD. Mud supernatant (Mud sup.), mineralized mud (Mud) and mineralized dust (Dust) were used as positive control for these trace elements. The statistical analyses were conducted using paired t-tests between the zone R value and the mean of each zone of interest. Moreover, a one-way analysis of variance (ANOVA), followed by Tukey's test for multiple comparison were performed for the comparison of the 4 zones of interest. P≤0.05 values were considered statistically significant. All statistical analyses were carried out using GraphPad Prism (GraphPad Software).

Annexe 7. Ecological Risk Index of well waters using Belgian tap water as reference

Element	CzoneR	CzoneA	CzoneB	CzoneC	CzoneD	Cbackground	TEFi
Pb	0,00	0,00	0,85	0,00	1,00	0,2	**5**
Cu	1,40	0,65	0,86	0,72	1,70	5	**2**
As	0,70	0,68	1,88	1,76	1,63	1	**10**
Cr	0,50	0,50	0,45	0,68	0,80	2	**2**
Ni	1,00	3,29	0,73	2,30	0,82	2	**5**
Zn	4,50	10,00	2,20	5,60	5,50	9	**1**
Cf Pb	0,00	0,00	4,25	0,00	5,00		
Cf Cu	0,28	0,13	0,17	0,14	0,34		
Cf As	0,70	0,68	1,88	1,76	1,63		
Cf Cr	0,25	0,25	0,23	0,34	0,40		
Cf Ni	0,50	1,65	0,37	1,15	0,41		
Cf Zn	0,50	1,11	0,24	0,62	0,61		
ERI Pb	0,00	0,00	21,25	0,00	25,00		
ERI Cu	0,56	0,26	0,34	0,29	0,68		
ERI As	7,00	6,75	18,80	17,60	16,25		
ERI Cr	0,50	0,50	0,45	0,68	0,80		
ERI Ni	2,50	8,23	1,83	5,75	2,05		
ERI Zn	0,50	1,11	0,24	0,62	0,61		
ERI total	**11,06**	**16,85**	**42,91**	**24,94**	**45,39**		

Table X. ERI of well waters of the study zone, using tap water of Uccle, Belgium (2016) as background water [67]**.**

Annexe 8. Frequency of neurological problems in kids