

Assessment of Water Quality in a Catchment Draining a Fluorite Rich Region in Kenya

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ABSTRACT

Access to water in adequate quantity and of good quality is increasingly becoming elusive especially in underprivileged rural communities. The situation is exacerbated by point and/or non-point pollution sources especially from heavy metals. Fluoride ions have been reported to contaminate surface water sources causing dental and skeletal fluorosis particularly in areas with rocks that have been subjected to hydrothermal activity such as the Rift Valley. Kenya Fluospar Company has for over 35 years produced the acid grade fluorspar from a mining plant at Kimwarer, Kerio Valley in Kenya. Although groundwater is an important source of water for household use in this area, previous studies singled out the effects of mining activities on the parameters of surface water. Moreover, all earlier studies examined the parameters of the water when the mining activities were at full scale.

This study investigated the influence of mining activities on selected water quality parameters of surface water and groundwater sources at a time when mining activities were largely downscaled until complete closure. Water samples were collected from eight sites during high, intermediate and low flow periods. Fluoride, Manganese, Turbidity, Electrical Conductivity and pH were determined at Moi University Public Health Laboratories. The results were compared with previous findings obtained when the company was fully operational. The interaction between surface water and groundwater was explored by comparing the trends in ion concentrations of the parameters. At full operation, the ion concentrations of most of the parameters were way beyond the WHO recommendations for drinking water. Fluoride levels in the downstream water samples were about five times higher while that in the effluent streams was about 20 times higher than the recommended level. Waters from nearby groundwater sources were found to have higher average Fluoride ion concentrations (> 1.15 mgL⁻¹) as compared to the surface water sources when the company's activities were minimal. Lower ion levels were observed during the high flows and the phenomenon was attributed to dilution. However, higher turbidity values were recorded due to increased sediments in runoff. Except for pH, the variation in levels of all the other parameters could directly be linked to the presence or absence of mining activities. It was demonstrated that treating the water improved its physico-chemical characteristics. The similar response in ion concentration between surface water and groundwater sources in the study area suggested probable interaction that calls for further exploration using electrical sounding and/or environmental tracers.

Keywords: Fluoride, Groundwater, Ion concentration, Mining, Surface water

I. INTRODUCTION

The ever increasing worldwide pressure on water resources, under natural and anthropogenic conditions, calls for novel solutions to address the scientific and societal issues involving water resources [1]. The quality of waters is one of the most important criteria that determine its usefulness for a specific need. A large proportion of people in developing countries lack access to safe drinking water especially due to point and non-point source pollution. According to Karanja [2], almost 1 billion people lacked access to improved water quality while 2 million annual deaths were attributable to

unsafe water, sanitation, and hygiene. Muiruri [3] et al. identified the weathering of rocks as one of the natural factors that result into the presence of heavy metals in water sources. Human activities in water towers and in areas traversed by streams and rivers have contributed to deteriorating water quality standards in developing countries as most of the populace is dependent on unsustainable exploitation of natural resources. Arap-Chelal [4] highlighted the tremendous negative effects on water resources that were expected from human settlement in the headwaters of Kerio River.

Mining activities may cause a variety of environmental problems including deforestation and the deposition of

sediments having high concentrations of heavy metals on water and soils near the mining sites. Typically, mining activities are not subject to rational selection or advanced planning because mineral deposits exist in some prescribed locations dictated by geology. Thus, there is no choice about the characteristics of their ecological setting, biological and chemical features and mineral compositions. Kithiia [5] argued that the effects of industrial growth and their effluents have been a major contributing factor to water quality degradation in the vicinity of industrial activities. According to Ripley [6] et al., the pollution of environment with toxic materials from mining was gaining recognition and becoming a public concern. It is currently a globally important environmental health, economic and planning problem. The major substances that are found to contaminate water are Fluorides, heavy metals and organic waste.

Fluoride is a persistent and non-degradable poison that accumulates in soil, plants, wild life and in humans. Over exposure to Fluoride in drinking water causes dental and skeletal fluorosis in human beings [7]. Nair [8] et al., observed that dental fluorosis was endemic in Kenya and was considered as a major dental public health problem. Drinking water, especially in areas with volcanic rocks and hot springs, is the epidemiologically most important source of Fluoride [9]. According to WHO guidelines which have since been adopted by Kenya, the maximum permissible Fluoride level is 1.5 mgL⁻¹ [10]. Some experts have also suggested that rickets thrive in Fluoride stricken areas. Karanja [2] observed that rural communities are particularly vulnerable to poor water quality disease burden.

Nair [8] et al. enumerated a number of previous studies conducted to investigate the prevalence of Fluoride in surface and groundwater sources. Samples from the lakes in Rift Valley exhibited extremely high levels of Fluoride ion concentrations. In a follow up study focusing on groundwater, Nair [8] et al. tested 1286 samples of water collected from boreholes distributed across Kenya. Only about 40% of the samples were found to have Fluoride ion concentrations within the WHO recommendation while 20% had levels over 5% ppm. As was the case of surface waters, the high Fluoride levels in groundwater, were observed in boreholes whose location coincided approximately with the position of the Rift Valley. The high Fluoride areas showed quite a close association with the distribution of volcanic rocks. According to WHO [11], Fluoride is commonly associated with volcanic activity and fumarolic gases. Most Fluorite occurs as vein fillings in rocks that have been subjected to hydrothermal activity. In addition, sediments of marine origin in mountainous areas, granitic and gneissic rocks have been found to have high groundwater Fluoride concentrations in Kenya, Ethiopia, India, Pakistan, Malawi, Thailand, China, Sri Lanka, and Southern Africa [12,13, 11,7,8]. The San Rafael Massif (Argentina) is characterized by widespread Fluorite and Manganese epithermal ore deposits [14].

Fluorides are found at significant levels in a wide variety of minerals, including fluorspar, rock phosphate, cryolite, apatite, mica, hornblende and others [11]. Fluorite (CaF₂), also known as fluorspar, is a common Fluoride mineral of low solubility occurring in both igneous and sedimentary rocks. Fluorite deposits occur within the Basement rocks of the Mozambique Belt in the Kerio Valley. The Fluorite ore bodies occur along a tract some ten kilometres long and about three kilometres wide, at the foot of the Elgeyo escarpment, and stretch from Kimwarer ridge to Muskut. The Fluorspar Mining and Processing Plant, one of the largest capital investments in the Kerio valley [15], produce the acid grade fluorspar which contains an excess of 97% CaF₂[7] through open cast mining method. Fluorspar is the second most important mining commodity in Kenya after soda ash [16].

Kiptanui [17] reported that the impacts of mountaintop mining on stream and groundwater quality, biodiversity, and forest productivity were "pervasive and irreversible" and that existing strategies for mitigation and restoration were not compensating for the degradation. According to Mayher [16], mining activities by Kenya Fluorspar Company (KFC) at Kerio Valley have caused landslides, soil flows and rock falls that have blocked and destroyed waterways and water pipes consequently affecting the community's access to water. This has compelled the community to rely mostly on water from wells and surface water sources downstream of the mining area.

Osawa [15] determined the concentration of heavy metals in the water, soil and sediment samples from Kimwarer River and its environs. The mean Fluoride ion concentration of samples collected from streams upstream of the mining area was about 0.6 mgL⁻¹. This concurred well with Nair [8] et al. who reported that the Fluoride ion concentration for groundwater samples collected from Elgeyo Marakwet was below 1 mgL⁻¹. The concentration of Fluoride in the downstream river samples ranged from 5.9 to 6.3 mgL⁻¹ while those of the mining effluent water samples ranged from 29.1 to 32.8 mgL⁻¹. The levels of Fluoride in the downstream water samples were about five times higher while that in the effluent streams was about 20 times higher than the recommended level of 1.5 mgL⁻¹ by WHO for domestic water. Mayher [16] quoted a Ministry of Water and Irrigation investigation of 2005 which cautioned the mining company against discharging wastewater having high levels of Fluoride into the Kimwarer River.

While the dangers posed by the mining activities to the sources of drinking water seem to be well documented, concerted efforts to enforce existing legislation to compel the mining company to treat the effluent prior to discharge appears to be lacking. In fact, Mayher [16] argued that pleas to mining companies and governments by communities often result yield limited tangible improvements, if any. Further, water quality parameters from groundwater sources in the environs of the mining area have not been investigated. So far, there is no evidence of any attempt to explore the interaction between surface water and groundwater. This study examined selected water quality parameters of both surface water and groundwater in Kimwarer at a time when the mining activities had been largely downscaled due to administrative challenges.

II. MATERIALS AND METHODS

A. Study area

Water samples were collected from water sources within and around the KFC mining area in Kimwarer, Elgeyo Marakwet County, as illustrated in Fig. 1.



Figure 1: Location of Kenya Fluospar Company and sampling sites

Table 1: Water sampling points

S. No.	Sampling point	Description of site
1.	BT	A point just before the water treatment plant.
2.	AT	A point just after the water treatment plant.
3.	Spring	A water source at the upstream area of the mining area.
4.	R1	A stream upstream of the mining area which drains into Kimwarer River; any change in parameters is due to the mining activities.
5.	R2	A point just after the mining area to monitor any changes on surface water of Kimwarer River as a result of the Company's operations.
6.	R3	A point farther downstream of Kimwarer River aimed at investigating self-regulation and influence of inflows.
7.	W1	A source of groundwater located upstream of the mining area.
8.	W2	A source of groundwater located downstream of the mining area.

B. Sampling

This study focused on Fluoride, turbidity, Manganese, Electrical Conductivity and pH as the parameters of interest. Water samples were collected from sources shown in Fig. 1 at weekly intervals for period of three months to coincide with both high and low flows. The water levels in the wells were also monitored during this period. From Fig. 1, the sampling sites were defined as shown in Table 1.

C. Laboratory tests

Laboratory tests were done at the Public Health Laboratory (PHE) at Moi University. The Fluoride and Manganese tests were carried out using the Palintests [19].

i) Fluoride test

The Fluoride tests were done by the Photometer method using automatic wavelength selection. Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) and Eriochrome Cyanine R ($C_{23}H_{15}Na_3O_9S$) were reacted in acidic solution to form a red colored complex. This color is destroyed by Fluoride ions to give the pale yellow color of the Eriochrome Cyanine. Different amounts of Fluoride thus produce a range of colors from red to yellow.

In the test, two tablet reagents were used. The first tablet (Fluoride #1) was crushed and added to a 10 ml water sample. The second tablet (Fluoride #2) was also crushed and added into the sample. The mixture was then left to stand for about five minutes to allow for full colour to develop. The colour produced in the test was measured using the Palintest Comparator and Disc. The disc reading represented the Fluoride concentration in mgL^{-1} .

ii) Manganese test

As was the case of Fluoride test, Manganese was similarly tested using the Palintest procedure. The first tablet (Manganese #1) was crushed and added to a 10 ml water sample. The second tablet (Manganese #2) was also crushed and added into the sample. The mixture was then left to stand for exactly 20 minutes. Any continuing colour change after this period was ignored. The colour produced in the test was measured using the Palintest Comparator and Disc. The disc

reading represented the Manganese concentration present in the sample in mgL^{-1} .

iii) Testing for pH

The test was done using a pH meter. A water sample was put in a beaker to a level that the sensor of the pH meter could be immersed. Stable readings were then recorded from the pH meter for each water sample. The mean values were computed for samples from the same source.

iv) Electrical Conductivity test

The Electrical Conductivity meter (Fig. 4b) was used to carry out the Electrical Conductivity tests of the water samples. The meter was set to the highest range. Distilled water was used as the standard for the range provided by the Electrical Conductivity meter. Stable values of Electrical Conductivity were then recorded for each sample. The probe was rinsed well between samples and standards. The mean values were computed for samples from the same source.

v) Turbidity test

The test was done using a turbidity meter. The samples were poured into measuring cylinders and the meter was inserted in each of the samples until a stable value of turbidity was observed and recorded. The probe was rinsed well between samples. The mean values were computed for samples from the same source.

III. RESULTS AND DISCUSSION

This study started when the activities of KFC were being scaled down and completed after the company had finally shut down. To understand the entire effect of fluospar mining on water resources at KFC, the results of this study were compared to that of Osawa [15]. This earlier attempt investigated levels of Fluoride and other ions in the Kimwarer River during low and high stage as well as in the soil around the mining area. The mean values obtained from laboratory analyses for Fluoride (mgL^{-1}), Manganese (mgL^{-1}), Turbidity (NTU), Electrical Conductivity ($\mu s.cm^{-1}$) and pH are tabulated in Table 2.

Table 2: Mean levels of the measured parameters (a = current study; b = Osawa[15])

Parameter/Site	R1 ^a	R1 ^b	R2 ^a	R2 ^b	R3 ^a	R3 ^b	Well1	Well2	Spring	BT	AT
Fluoride	0.48	0.61	0.60	30.9	0.57	5.09	0.91	0.82	0.91	0.92	0.44
Manganese	0.02	0.02	0.03	0.07	0.02	0.04	0.02	0.02	0.02	0.02	0.01
Turbidity	4.4	4.5	4.7	66	4.4	13	4.0	3.9	2.9	3.0	0.6
Conductivity	73.6	75.5	82.1	205	77.8	101.5	93.5	88.7	81.4	76.3	48.2
pH	7.8	7.3	7.5	7.8	7.7	7.5	8.2	8.3	8.0	8.0	7.2

A. Fluoride levels

From Table 2, the average concentration of Fluoride was extremely higher when the company was still in full operation especially immediately downstream of the processing plant

(R2b). This was attributed to effluent discharge from the wastewater treatment facilities at the plant. However, the concentration decreased by about 600% from R2 to R3, a distance of approximately 2000 m owing to dilution from tributaries and natural mixing. When the company activities

were downscaled until closure, the average Fluoride concentrations reduced drastically to levels below the recommended WHO threshold of 1.5 mgL⁻¹ as seen in Fig. 2. This underscored the enormous negative health effects that KFC has continuously meted on the community around the plant.

In almost all sites, the ion concentration was highest during low flows and vice versa. Waters from nearby groundwater sources (Well 1, Well 2, Spring and BT) had higher average ion concentrations (> 1.15 mgL⁻¹) as compared to the surface water sources. This could have been occasioned by recharge that flows through geological formations that contain soluble Fluoride ions as well as leachate from mining waste. Thus, explained why the ion concentrations during high flow were higher than when the flow was regarded intermediate.

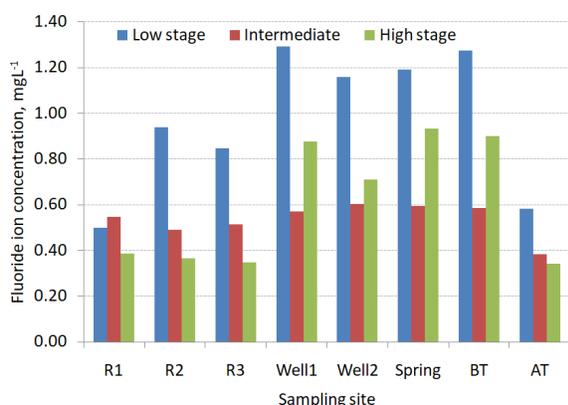


Figure 2: Fluoride ion concentration (mgL⁻¹) during low, intermediate and high flows

The high ion concentration during low flow was caused by lowered water table/phreatic surface leading to a drop in water levels in the wells during the dry season. Since groundwater flow is considered slow, although there are no mining activities currently, the elevated levels of ion concentrations could present for quite a while. As much as possible the community is advised to avoid certain sources of water during dry season. Three sites viz. R2, Well1 and BT had maximum sample values of 1.61, 1.87 and 1.61 mgL⁻¹, respectively, which exceeded the WHO limit. In this study, water treatment was recommended for it was demonstrated to lower the ion concentrations by up to 70%.

B. Manganese levels

The concentration of Manganese in all water sources was within the WHO drinking water guidelines of 0.05 mgL⁻¹ except for R2 which had a maximum concentration of 0.093 mgL⁻¹ in one of the samples and an average of 0.055 mgL⁻¹ during the dry season (Fig. 3). Osawa [15] reported mean concentrations ranging from 0.967 to 1.772 mgL⁻¹ and 0.071 to 0.122 mgL⁻¹ for effluent water samples (R2) and

downstream river samples (R3), respectively. The mean value of 0.07 mgL⁻¹ (Table 2) suggested that Manganese remained a health hazard throughout the time when the plant was in operation.

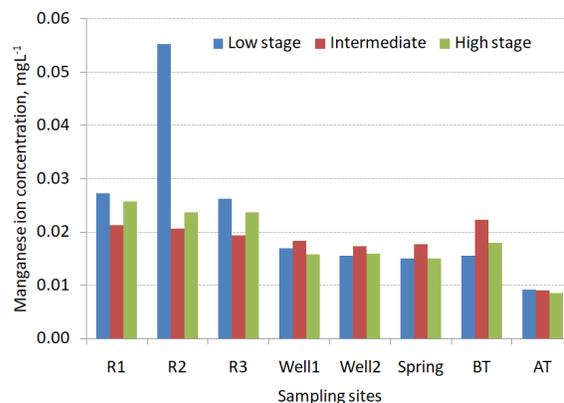


Figure 3: Manganese ion concentration (mgL⁻¹) during low, intermediate and high flows

Groundwater sources exhibited low concentrations (maximum sample concentrations of 0.02 mgL⁻¹) compared to surface sources (maximum sample concentrations of about 0.03 mgL⁻¹) and could be regarded as better options in terms of Manganese ion concentration. This excludes R2 whose elevated concentration was associated with mining effluents and leachate from the waste. Treating the water reduced the Manganese ion concentration by up to 65% and thus was a recommended approach to ensure that the community has water for household use that meets the WHO regulations on Manganese levels.

C. Turbidity levels

Although the level of turbidity upstream (R1) when the company was in full operation averaged 4.5 NTU as shown in Table 2, the average levels after the mining plant were between 66 NTU and 13 at R2 and R3, respectively [15]. The values below the plant were much higher than the WHO recommended threshold of 5 NTU. The high turbidity levels were attributed to runoff loaded with sediments that end up into the water sources. The mining operations and movement of heavy machinery escalated this especially during the rainy season. Even when the operations were minimal and eventual closure, the turbidity levels were higher during the wet season that coincided with high flows in all cases except after treatment (Fig. 4).

The maximum sample turbidity levels beyond the WHO recommendation were 5.36, 5.61, 5.65, 7.34 and 5.84 NTU from R1, R2, R3, Well1 and Well2, respectively. There were no samples that exceeded 5 NTU in all sources during the intermediate and low flow periods accentuating the contribution of runoff to higher turbidity. Furthermore, most surface water sources had lower average NTU values during the dry season. While the water source BT met the WHO

requirements in all periods, the treatment still lowered the turbidity levels by up to 87% to levels below 1 NTU which is desired by WHO. In fact, the KFC should allow and find means to supply water from this source to the entire community in the mining area.

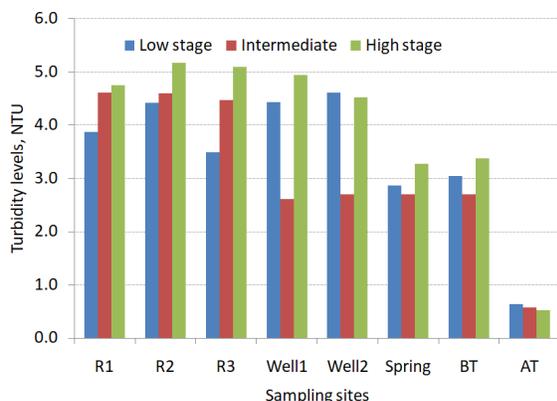


Figure 4: Turbidity levels (NTU) during low, intermediate and high flows

The three groundwater sources (Well1, Well2 and Spring) demonstrated a close similarity with higher values during the wet and dry seasons and lower turbidity values being recorded during the intermediate flow period. Interflow, considered to be responsible for recharge in shallow groundwater sources such as those under investigation, was attributed to the higher turbidity values during the wet season. The higher values during the dry season was explained by reduced water quantity in the groundwater sources thus raise the concentration. Lower levels of turbidity during the intermediate flow period were associated with less sediments getting into these sources owing to diminished surface runoff and interflow. Moreover, due to decreased disturbance from inflows, the sediments in the wells tended to settle at the bottom.

D. Electrical Conductivity levels

According to WHO standards, Electrical Conductivity values should not exceeded 400 $\mu\text{S}/\text{cm}$ [18]. The maximum Electrical Conductivity value obtained by Osawa [15] during the dry season was about 275 $\mu\text{s}.\text{cm}^{-1}$ and an average of 205 $\mu\text{s}.\text{cm}^{-1}$ for site R2. However, in this study which was conducted when mining activities were minimal, Well1 registered the maximum value of 123 $\mu\text{s}.\text{cm}^{-1}$ and an average of 93.5 $\mu\text{s}.\text{cm}^{-1}$. Even though there was no cause of alarm as the Electrical Conductivity values under both cases were way below the recommended threshold, the influence of mining activities on increasing Electrical Conductivity was evident. The average Electrical Conductivity values are displaced in Fig. 5.

During the dry season, generally higher Electrical Conductivity values were recorded as a consequence of elevated concentration of various ions as earlier discussed. In most sites, there was no obvious difference between values

observed during the intermediate and high flow periods. These results clearly indicate that water in the study area was not considerably ionized and has the lower level of ionic concentration activity due to low dissolved solids. Nonetheless, water treatment has been shown to farther improve the water quality by reducing the Electrical Conductivity by up to 51%.

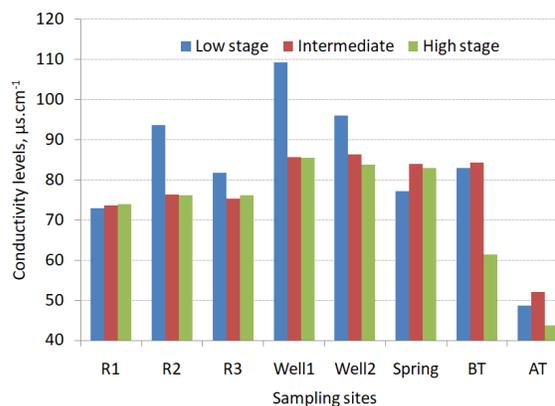


Figure 5: Electrical Conductivity level (μs) during low, intermediate and high flows

During the dry season, generally higher Electrical Conductivity values were recorded as a consequence of elevated concentration of various ions as earlier discussed. In most sites, there was no obvious difference between values observed during the intermediate and high flow periods. These results clearly indicate that water in the study area was not considerably ionized and has the lower level of ionic concentration activity due to low dissolved solids. Nonetheless, water treatment has been shown to farther improve the water quality by reducing the Electrical Conductivity by up to 51%.

E. pH levels

For drinking water, WHO recommends a pH range of between 6.5 - 8.5. In this study, three samples indicated pH values higher than the recommended level i.e. 8.9, 8.7 and 8.5 recorded for Well1, Spring and BT, respectively. Nevertheless, all the average values during all the flow periods were below 8.3 as illustrated in Fig. 6. Similarly, Osawa [15] reported pH values lower than 8 but also greater than 7.

Except after treatment, all samples recorded pH values greater than 7 yet the type of Fluoride being mined was largely acidic. The higher pH values could be explained by the liming performed on the factory effluents before being released to the river (R2). However, this would only affect downstream sources and cannot explain higher values observed upstream viz. R1, Well2, Spring and BT. Thus it was assumed that the observed elevated pH values were not exclusively as a result of mining activities but could be

attributed to the presence of alkaline deposits. Even so, water treatment reduced the pH of the water by up to 19%.

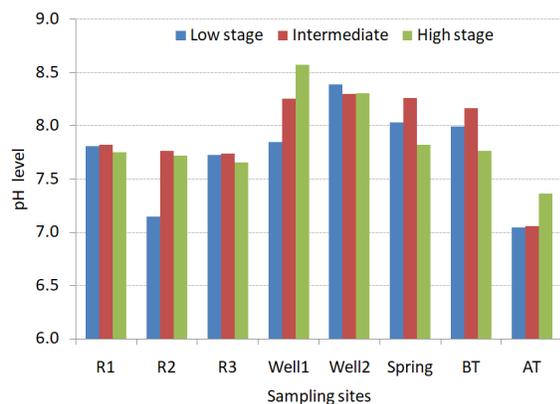


Figure 6: pH levels during low, intermediate and high flows

IV. CONCLUSIONS AND RECOMMENDATIONS

This study investigated changes in selected water quality parameters of both surface water and groundwater sources around KFC at a time when the mining activities had been largely downscaled and finally completely closed. The results were compared with previous findings [15] obtained when the company was in full operation. Five parameters viz. Fluoride, Manganese, Turbidity, Electrical Conductivity and pH were examined at periods considered to represent dry, intermediate and wet seasons.

Lower ion levels were observed during the high flows and the phenomenon was attributed to dilution. However, higher turbidity values were recorded due to increased sediments in runoff. Except for pH, the variation in levels of all the other parameters could directly be linked to the presence or absence of mining activities. Lower ion concentrations, below WHO thresholds, were recorded after complete closure of mining. Thus, for the parameters under consideration, as long as there are no mining activities, the community around the mining area could use both surface water and groundwater sources as they meet the WHO standards. However, it was demonstrated that treating the water improved its physico-chemical characteristics.

The similar response in ion concentration between surface water and groundwater sources in the study area suggested probable interaction that calls for further exploration using electrical sounding and/or environmental tracers. It is important to continue monitoring these and more parameters when the company is still out of operation to provide an indication of longer term trends of the ions. Should the company activities resume, the management ought to be compelled to strictly adhere to stipulated safety, occupational and environmental health regulations, standards and guidelines governing fluorspar mining activities.

Efforts need to be geared towards water supply infrastructure so that each household access treated water at reasonable distance and cost. Since this study focused on only a few physico-chemical parameters, there is need to further consider assessment of possible microbial contaminants in the water sources.

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