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SPATIAL DISTRIBUTION OF ARSENIC, BORON, FLUORIDE, AND LEAD IN SURFACE AND GROUNDWATER IN ARUMERU DISTRICT, NORTHERN TANZANIA

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Abstract: This study was carried out in Arumeru district, to provide the critically missing information that could aid in the improvement of water quality policies, management practices, and public health protection. The physico-chemical parameters and the fluoride concentration for springs, rivers, lakes, boreholes, and dug wells were determined on 101 samples while the arsenic, boron, and lead concentrations were determined on 90 samples. All data were subjected to cluster analysis and principal components analysis (PCA). Fluoride (F) was found to be high, above the recommended standard, in all the water sources with a median F value of 3 mg/L. The abundance pattern for F was similar to the total dissolved solids (TDS) pattern, of alkaline lakes>dug wells>boreholes>streams>fresh water lakes>springs. The lowest fluoride and TDS values were observed in springs (median F=1.3 mg/l, TDS=145 mg/L) and were attributed to a short water-rock interaction time and to the geology. Some lakes and dug wells were found to have low dissolved oxygen (DO) owing to high organic matter inputs and poor aeration. The highest median F value was found in leeward alkaline lakes (median=260 mg/L) and lowest in windward springs (median=1 mg/L). The fluoride and high TDS values in the water sources were found to be controlled by the geological materials, water-rock interaction time (short in mountainous areas due to a high hydraulic gradient in a slightly fractured formation), and the precipitation levels and evaporation rates which also control the formation and dissolution of salts. Arsenic and lead, which were present in water sources above the recommended standard in 14% of the analysed samples (As: median=0.3 mg/L, Pb: median=0.1 mg/L), were found to have a similar concentration profile. Boron was high and above the recommended standard in one sample only (1.65 mg/L in Lake Big Momella, 1% of the samples). The samples were clustered into 9 groups with the first four clusters characterized by high TDS and fluoride. PCA indicated that TDS, fluoride, boron, arsenic, lead, and pH were the major loading components accounting for 86.9% of the total variance. Spatially, fluoride and boron were associated with lahars, ash, and pyroclastic materials whereas arsenic and lead were associated with pyroclastics and nephelinitic to phonolitic lava. Communities in areas with high levels of these heavy metals are further exposed to health risks, in addition to those of fluoride, when such water is used for drinking. This finding, which has not been previously reported, calls for a detailed assessment to be made of the heavy metals in water used for consumption. Due to the toxicity of arsenic and lead, water sources with a high concentration of these, beyond the recommended standards, should either be treated, before being supplied as drinking water, or completely abandoned.

Keywords: Northern-Tanzania; Spatial distribution; Surface and groundwater; Volcanic areas; Water contamination.

INTRODUCTION

Water quality problems have been an issue of global concern, and because of this the 6th goal of the Sustainable Development Goals (Clean Water and Sanitation) has

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highlighted the need for every citizen of the planet earth to have access to safe and affordable drinking water.[1] The trend of water pollution is on an increase through anthropogenic activities (changes in land use, agriculture, mining activities, and mismanagement of wastes) and natural processes in many countries.[2-6] Natural pollution of water is related to the composition of geological materials through various processes such as the dissolution and dissociation of elements, where elements like arsenic, boron, fluoride, and lead may be enriched.[2,5,7-9] Owing to the high toxicity of some elements at a low concentration in water and food, their sources, levels, and liberation mechanisms need to be understood. Although the concentrations of highly toxic elements, such as fluoride, arsenic, boron, and lead, in surface and groundwater are well known in the developed world,[3,10,11] the levels of such elements in the developing countries, like those of East Africa, are poorly known.

The few available reports on water fluoride levels in East Africa have shown a wide distribution in the concentration of fluoride, ranging from values that are below the WHO recommended upper limit guideline of 1.5 mg/L to as high as 2800 mg/L.[2-4,12-23] Similarly, the information available on arsenic, lead, and boron levels in both surface and groundwater is scanty. The excessive ingestion by organisms of some elements, such as fluoride, arsenic, lead, and boron, may have severe health impacts.[8,24-28] For example, the population in areas with high fluoride concentrations in the surface and groundwater may experience dental, skeletal, and non-skeletal fluorosis.[26,29] However, not much attention has been paid to these areas by some governments, particularly in East Africa, to assist such communities in finding alternative water sources, probably because of lack of information on the levels and political sensitization in such areas at ward, district, regional, and national levels.

The distribution of fluoride in Tanzania has been reported by several workers.[4,12,18,22,23,30-32] Regions that have been reported to have high concentrations of fluoride in surface and ground water include Kilimanjaro, Arusha, Singida, Geita, Simiyu, Mara, Manyara, and Shinyanga,[12,15,18,21,23,24] most of which fall within the East African rift valley and Precambrian plateau (Figure 1). Although the levels of fluoride concentrations may be related to geological formations and thus have a high spatial variability, there is no detailed information available on the levels of fluoride concentration in relation to the geology at a district scale, particularly in areas studded with volcanic rocks. Thus, there is a need for assessing the fluoride concentrations in such areas as Arumeru district in order to provide science backed information to policy makers.

Arsenic (As) is among the potential toxic elements of global concern. Prolonged utilisation of water with arsenic can cause lung cancer, skin lesions, developmental effects, cardiovascular disease, gastro-intestinal effects, central and peripheral nervous system disorders, neurotoxicity, birth defects, and death.[26,27,33] The the WHO has adopted 0.01 mg/L as the maximum allowable concentration for arsenic in drinking water. In Ethiopia, along the East Africa rift (EAR) system, arsenic is known to be associated with fluoride.[34] In Tanzania, the arsenic concentration in water has been reported in mining areas, especially in the goldfields of Lake Victoria.[3] There has been little focus on arsenic studies along the EAR system in Tanzania where arsenic is likely to be associated with fluoride. In such areas, the lack

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of information on the levels of arsenic in drinking water at the regional, district, and ward levels could be adding more problems to communities that are currently highly impacted by fluoride. This creates an urgent need for arsenic research in Tanzania, particularly along the EAR system.

Lead (Pb), one of the heavy metals, occurs naturally in a variety of metamorphic, igneous, and sedimentary rocks.[36] In nature, Pb-ores are commonly associated with the ores of arsenic, copper, silver, zinc, and antimony in complex vein deposits.[36] Although such deposits are not known in the EAR system, the genetic association of these deposits with igneous rocks is likely to favour the presence of Pb in EAR rocks. If Pb is present in a significant amount, it can be released to the groundwater systems; the systems which are already contaminated by fluoride.[4,18,22,31,32]

As with other heavy metals, long term exposure to Pb results in memory deterioration, a reduced ability to understand, a diminished intellectual capacity in children, and a prolonged reaction time.[8] Despite the occurrence of these severe impacts in humans, the levels of lead in water are poorly known in Tanzania. Little information has been published on the levels of Pb in the groundwater in the areas affected by natural pollutants, particularly fluoride, such as the EAR system and the volcanic regions of Tanzania. A few of the available reports have indicated elevated Pb concentrations, above the recommended WHO limit of 0.01 mg/L, in the surface and groundwater.[29,37-39] However, Pb contamination in Tanzania has been attributed to anthropogenic processes, specifically emissions from vehicles and waste disposal.[37-39] Despite the efforts made in finding water sources which are not contaminated by fluoride in the Arumeru district, attention has not been given to other natural pollutants such as Pb which is likely to be associated with fluoride/ volcanic materials.

Although, the water quality problems related to volcanic activities, specifically with fluoride pollution, are intensified in the Arumeru district, information on the levels of boron (B), which is among the contaminants with adverse effects in human body, is poorly known. Boron may cause effects on the stomach, liver, kidneys, and brain function, including cognitive performance in humans, and eventually can lead to death.[25] The WHO has adopted 0.5 mg/L[29] as the maximum allowable concentration for boron in water. Despite the occurrence all these effects, boron levels have not been well documented in Tanzania. Although boron is commonly associated with volcanic activities and hydrothermal springs,[40] attention has not been given to the occurrence of boron in volcanic areas such as the EAR system. Despite the observation by British Geological Survey[30] that the alkaline condition of some of the lakes and groundwaters of northern Tanzania might result in their having high concentrations of elements such as boron, no detailed work has been conducted to document the levels and distribution of boron in such areas. Therefore, in order to sustainably provide drinking water of an appropriate quality, the levels of some other natural pollutants, such as boron, needs to be carefully assessed.

The Arumeru district is experiencing serious water quality problems that have been related to the magmatic activities of the East African rift valley.[12] Also, water scarcity within the district is increasing with time due to population growth and climate change. In an attempt to reduce water scarcity, many boreholes and hand dug wells have been constructed to supplement the surface and spring water sources.

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Most of wells are utilized for domestic, agricultural, and other socio-economic activities without a detailed understanding of the levels of fluoride, arsenic, boron, lead, and associated natural contaminants. The local communities within the district continue to use polluted water unknowingly because of the lack of information on the levels and distribution of such elements in the water systems.

Various statistical techniques have been used to treat large data sets so as to better understand their salient features, to check if there are significant differences in the concentrations of various elements between water sources,[43,59] and also to classify or cluster parameters that have similar or related characteristics.[41-47] These techniques, particularly cluster analysis and principal component analysis, have employed a hierarchical and agglomerative approach, and varimax rotation, to highlight sensitive similarity relationships among the data sets.[41-47]

Therefore, the spatial distribution of fluoride, arsenic, boron, and lead as well as the physical parameters of pH, dissolved oxygen (DO), and total dissolved solids (TDS) were used to assess the suitability of drinking water within the Arumeru district, northern Tanzania, so as to provide critically needed scientific information to communities and to the policy and decision makers. The statistical techniques of cluster analysis, a non-parametric test (Kruskal Wallis test), and principal component analysis were used as tools for highlighting the salient features of the spatial distribution of these elements.

MATERIALS AND METHODS

Study area: The study was conducted in the Arumeru district, which is located in the Arusha region, northern Tanzania, between latitudes 3º0’ to 3º 40’ South and longitudes 36º 40’ and 37º 0’ East (Figure 1). The area is studded with volcanic materials that were deposited during several episodes of volcanic eruption, with the last eruption being in 1913.[48] Mount Meru is the second highest mountain in Tanzania (4565 m above sea level) and the ninth highest in Africa. It is considered to be a recharge zone of the groundwater for Arusha City and its environs. The climate of northern Tanzania is influenced by monsoon winds and the migration of the inter-tropical convergence zone.[49] Because of this, the area has a bimodal rainfall distribution with the shortest rainfall season being in October-December and the longer one in March-May. Climatically, the area can be subdivided into two zones, namely, a high rainfall zone found on the windward side of the mountain and a low rainfall zone found on the leeward side of the mountain[50] and in the low altitude areas (plain). Because of a marked change in the topography within a short distance, there is large temperature gradient, varying from low temperatures at the top of Mt. Meru to high temperatures in the lowland areas.[51]

Numerous streams, which are potential domestic water sources for the local people living on the mountain, are found on the slopes of the mountain. The density of the streams is controlled by the level of precipitation with the leeward side being characterized by few perennial streams/rivers (e.g., the Ngarenanyuki River). The windward side is characterized by many perennial streams/rivers with most of them joining the Themi ya Simba and Kikuletwa Rivers (Figure 1). Due to the large population living around the mountain, most of the water is utilized for various purposes before joining the Pangani River.

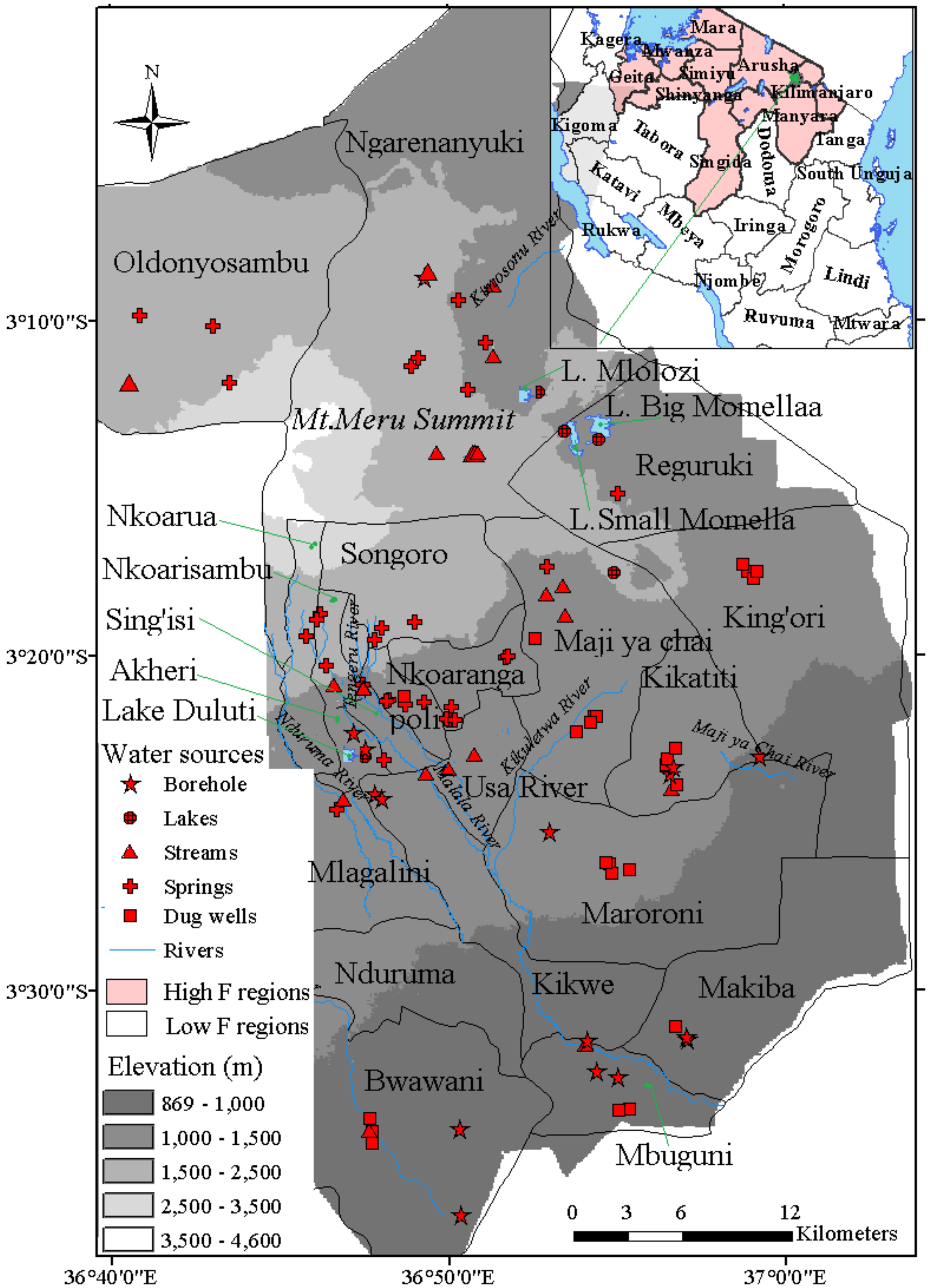

Figure 1. A map of the Arumeru district showing the study area and the sampling points.

Sampling and analytical methods: A total of 101 water samples were collected within the Arumeru district between May and July, 2015. These samples were collected from hand dug wells (27), boreholes (16), springs (31), rivers (21), lakes

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(Big Momella, Small Momella, Duluti, Mlolozi, and Ngurdoto crater) (5), and rain water.[52]

Water was allowed to mix thoroughly before sampling and *in-situ* measurements of pH, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS), and temperature were made using the Hanna-HI 9829 multi-parameter meter after calibration. The water samples were filtered using 0.45 µm membrane filters and collected in triplicate in 1000 mL polyethylene bottles. Two bottles of water samples from each site were acidified by adding few drops of concentrated HNO_3 and H_2SO_4 to a pH<2 and kept in cool boxes before transportation to the laboratory for storage in a refrigerator. Untreated (not acidified) samples were used in determining the concentration of fluoride in the water.

The determination of the concentration of fluoride in the water was carried-out at the Nelson Mandela African Institution of Science and Technology (NM-AIST) for all the collected samples within seven days of sampling using a fluoride ion selective electrode. Ninety samples were analysed for arsenic, boron, and lead. The selection of 90 out of 101 samples was based on: (i) the fluoride concentration—for full coverage of low to high fluoride zones in all water types; (ii) the depth of the boreholes or dug well—for representation of shallow to deep wells/boreholes; (iii) Rainfall difference—for full coverage of the leeward side (semiarid) and the windward side; (iv) the altitude—for representation of lowland areas to mountainous areas (altitude variation from ~900–2500 m above sea level); and (v) the importance of water source—the samples were selected based on the importance of the sampled water source (population dependent on the water source, e.g, market, village, school, hospital, and hotel). The analyses of the levels of arsenic, boron, and lead were performed at the Southern and Eastern African Mineral Centre using ICP-OES, and the detection limit was 0.01 mg/L.

Statistical analysis (non-parametric test and multivariate statistical analysis): The fluoride differences between the various water sources were assessed using a non-parametric test, specifically the Kruskal-Wallis test. The Kruskal-Wallis test was used since the data were not normally distributed[43,59,88] and the number of samples in each water source was not large enough to qualify for a parametric test (ANOVA)/[43,88] A non-parametric test is said to be less fussy and does not have stringent assumptions as compared to its parametric counterpart[89].

All data were subjected to cluster and principal component analysis using SPSS version 21 software. Cluster analysis was executed, based on the normalized data set by means of the Ward's method in which Euclidean distances are used as the measure of similarity. The data were standardized through the range of –1 to 1 transformation; this was done to avoid misclassification due to wide differences in the dimensionality of the data.[47,53,54] Similarly, the factors with the highest Eigenvalues obtained during the PCA were used to assess the most loading parameters.[55] Also, the varimax rotation was performed to simplify the data structure for ease of analysis.[44-46,56-58]

RESULTS

Spatial distribution and differences in the physico-chemical parameters among the water sources: The values of the TDS, which ranged from 23–19,620 mg/L with a

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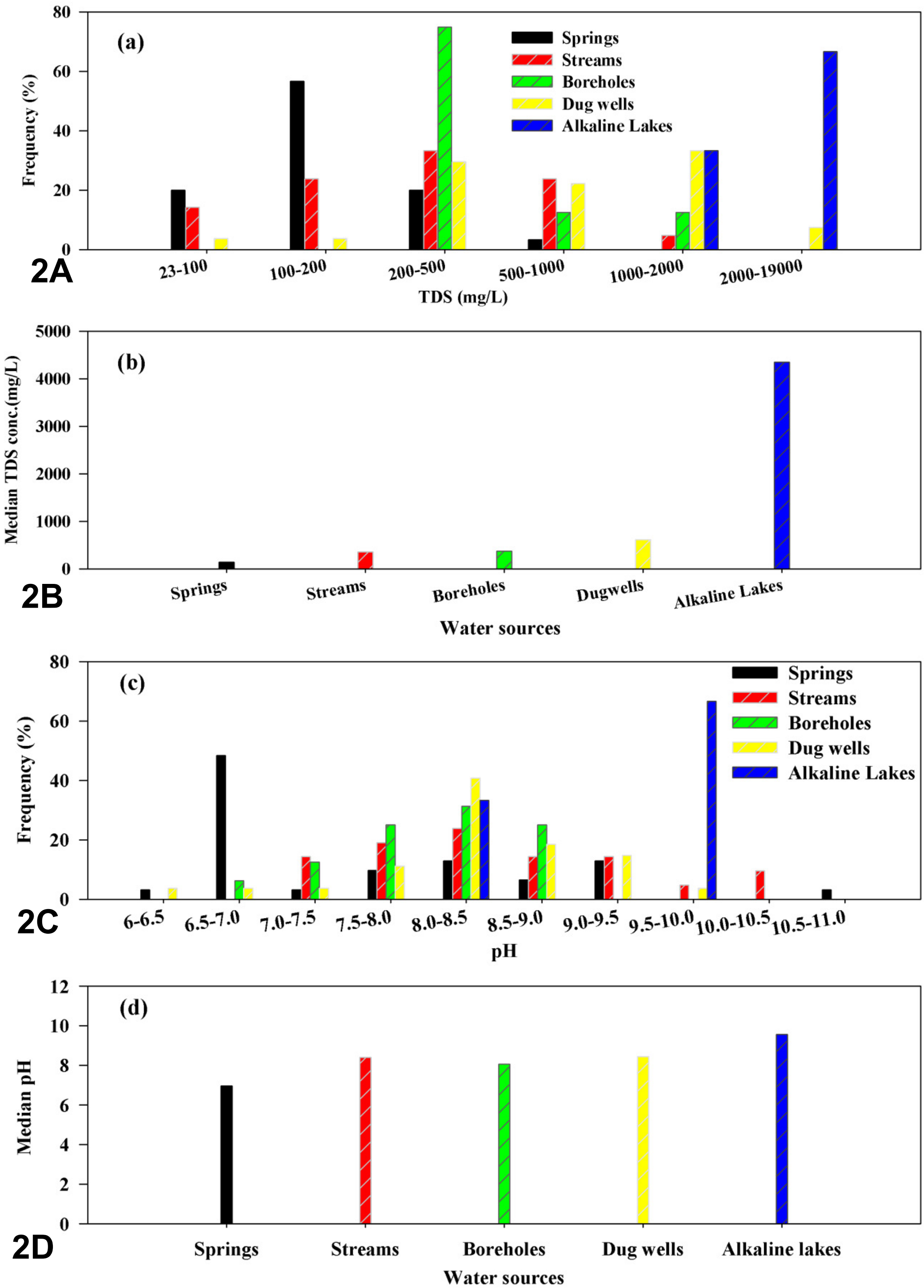
median of 365 mg/L, were high in the alkaline lakes and dug wells relative to the other water sources (Figure 2A).



Figures 2A-2D. Frequency and the median distribution of TDS and pH in all the water sources. 2A: Frequency of total dissolved solids (TDS) (mg/L) in the various water sources; 2B: Median TDS in the various water sources; 2C: Frequency of pH in the various water sources; and 2D: Median pH in the various water sources.

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The dominance pattern was alkaline lakes>dug wells>boreholes>streams>springs. A similar trend was observed for the median values (Figure 2B). The springs were found to have low dissolved ions with 57% of all springs falling in the range of 100–200 mg/L (Figure 2A). Some springs (20%), streams (14%) and dug wells (3%) had very low TDS (23–100 mg/L) (Figure 2A).

The pH values for all the water sources ranged from 6.4 to 10.9 with a median value of 8.2. Although the pH values for the springs were distributed throughout the range, the highest frequency was observed between 6.5 and 7.0 and this represented the highest frequency for all the water sources (Figure 2C). The 6.5–7.0 pH range (15% of all the samples) represented 50% of all springs. The median pH values of all the water sources ranged from 7.6 to 8.6 and showed an increasing trend from springs, boreholes, streams, and dug wells to alkaline lakes (Figure 2D). About 41% of the dug wells (equivalent to 11% of all the samples analysed) had a pH falling within the range of 8.0–8.5 and had the highest frequency relative to the other water sources (Figure 2C). Generally, the streams, and springs in the leeward side of Mt. Meru were typically more alkaline with a pH>8.5 (Figures 3A and 3B).

Generally, the median DO values showed an increasing trend from fresh water lakes, dug wells, boreholes, and springs to streams (Figure 3C). A very low DO (0–2 mg/L—anoxic conditions) was found in 7% of the dug wells and in all the fresh water lakes whereas a high DO (5–6 mg/L) was found in the streams (71%) and a very high DO (6–8.5 mg/L) was present in the springs (30%) (Figure 3D). Interestingly, the boreholes were found to have a high DO relative to the dug wells (Figures 3C and 3 D).

Chemical parameters: The fluoride concentrations were grouped in 6 groups namely; (i) low fluoride (0–1.5 mg/L), that is within the acceptable WHO standard of 1.5 mg/L;[29] (ii) intermediate fluoride which is within the current Tanzania standard (1.5–4 mg/L);[86] (iii) slightly high fluoride, that is within the former Tanzania standard (4–8 mg/L);[87](iv) high fluoride (8–20 mg/L); (v) very high fluoride (20–100 mg/L); and (vi) extremely high fluoride (100–1500 mg/L). A low fluoride concentration (0–1.5 mg/L) was found in most of the springs (55% of springs, 17% of all samples) (Figure 4A); an intermediate fluoride (1.5–4 mg/L) was found in most of the boreholes (63% of boreholes, 10% of all samples); a very high fluoride (20–100 mg/L) was found in the dug wells (37% of dug wells, 10% of all samples); and an extremely high fluoride (100–1500 mg/L) was found in the alkaline lakes (66% of lakes, 2% of all samples) (Figure 4A). The fluoride variation among the water sources was observed to be statistically significant ($p<0.05$) (Table1) with the dominance pattern of the fluoride levels being alkaline lakes>dug wells>boreholes>streams> fresh water lakes>springs.

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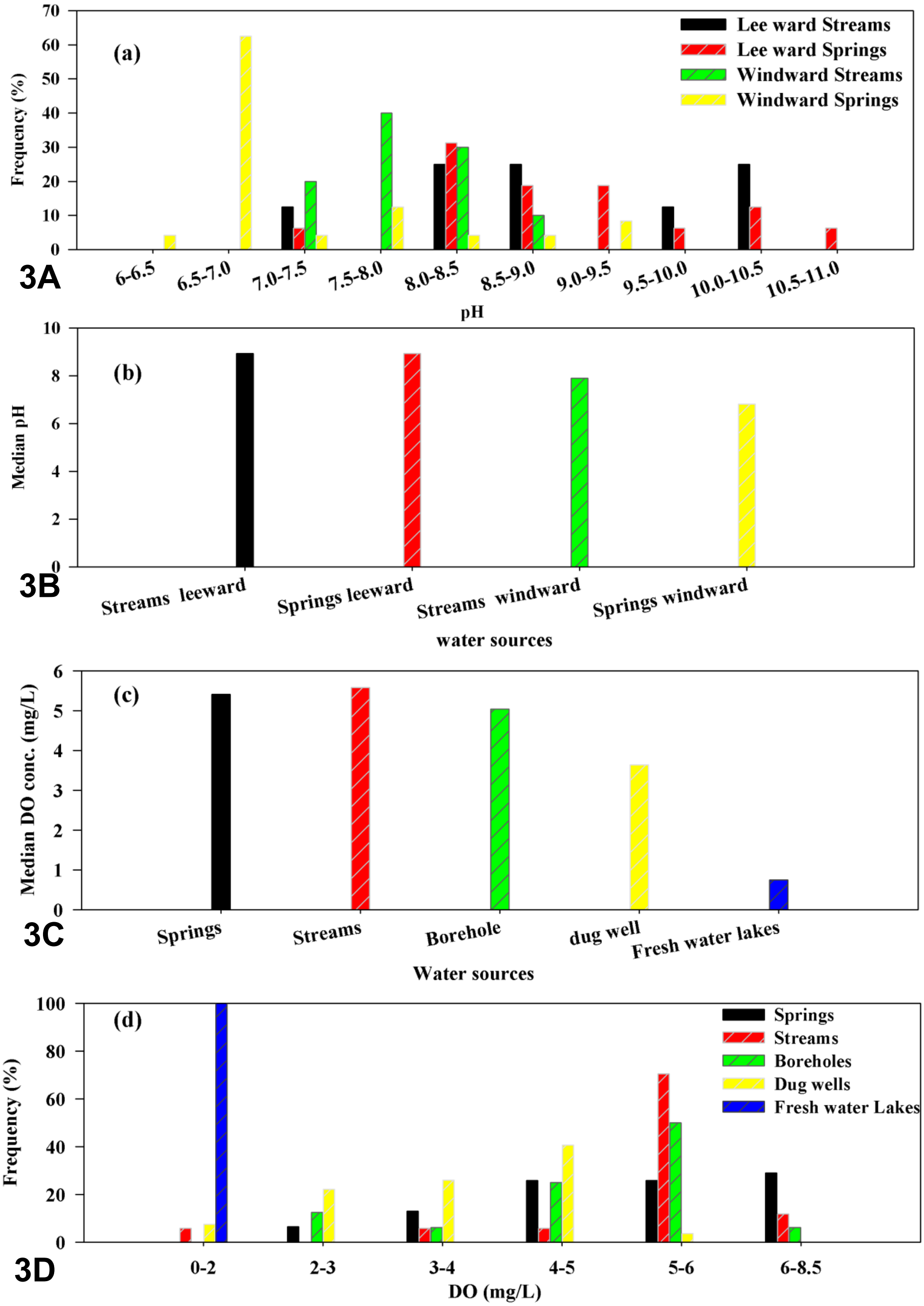
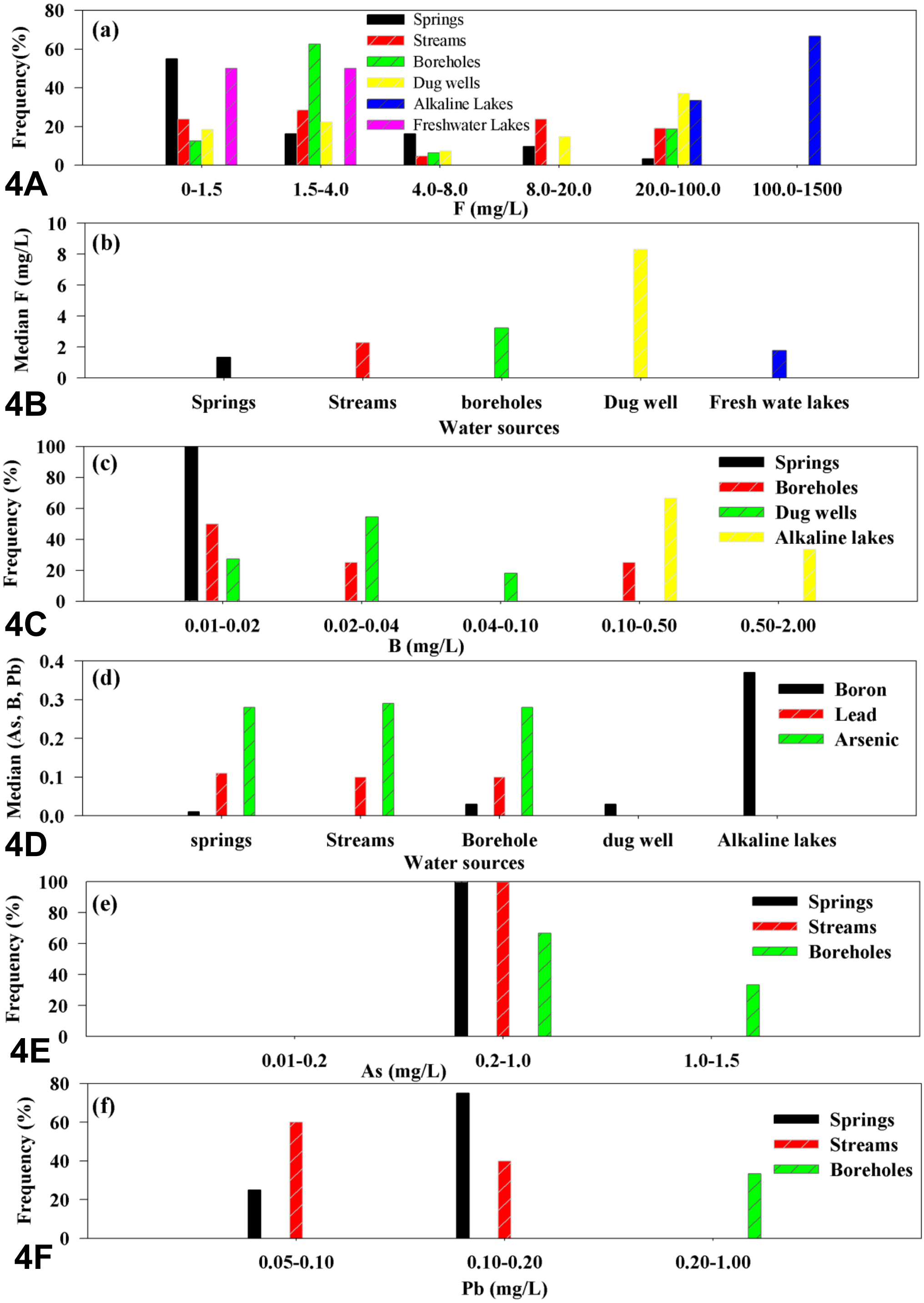


Figures 3A-3D. Frequency and mean distribution of dissolved oxygen (DO) and pH. 3A: Frequency of pH in the streams and springs in relation to the windward and leeward sides of Mt. Meru; 3B: Median pH in the streams and springs in relation to the windward and leeward sides of Mt. Meru; 3C: Median DO (mg/L) in the various water sources; and 3D: Frequency of DO (mg/L) in the various water sources.



Figures 4A-4F. Frequency and median distribution of fluoride (F), boron (B), arsenic (As), and lead (Pb) in all the water sources with the exception of the high median F in the alkaline lakes (260 mg/L) 4A: Frequency of F (%) in the various water sources; 4B: Median F (mg/L) in the various water sources; 4C: Frequency of B (%) in the various water sources; 4D: Median B, Pb, and As (mg/L) in the various water sources; 4E: Frequency of As (%) in the various water sources; 4F: Frequency of Pb (%) in the various water sources.

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Table 1. Test Statistics[a,b]

Statistical value	F	As	Pb	B
Chi square	22.826	6.337	5.831	26.881
df	5	5	5	5
Asymptotic significance	0.000	0.275	0.323	0.000

[a]Kruskal Wallis test; [b]Grouping variable: water source.

The results for the rivers (Malala and Tengeru) that were sampled from the head points to the foot of the mountain showed a lack of major changes in the fluoride concentrations. For instance, the fluoride concentration in the Malala river waters changed from 1.5 to 1.3 mg/L over a distance of about 7 km with a gradient change of 0.04. However, notable changes were observed when tributaries with different fluoride concentrations joined the main stream. For instance for the Kikuletwa River, the average fluoride of 2.3 mg/L is the result of the concentrating and diluting effects of the fluoride levels in the main tributaries joining it (Maji ya Chai: mean fluoride 18 mg/L, Tengeru stream: mean fluoride 1.3 mg/L, and Malala stream: mean fluoride 1.4 mg/L).

Boron was detected in 23 samples out of the 90 analysed samples with dug wells having the highest number (Figure 4D). Its concentration was low (within the acceptable WHO standard of 0.5 mg/L) in all the water sources except for the lake Big Momella (1.7 mg/L; Figure 4C). The median values were found to increase from springs, boreholes and dug wells, to alkaline lakes (Figure 4D).

Arsenic was detected in 13 out of the 90 analysed samples (14%) and was present in all the water sources apart from the lakes. Based on the grouping system of high arsenic (0.01–0.2 mg/L), very high arsenic (0.2–1.0 mg/L), and extremely high arsenic (1.0–1.5 mg/L), 12 samples out of 13 fell in the group of high As (Figure 4E). The stream and springs samples dominated this group (Figure 4E). Only one borehole sample was found to fall in the group of very high arsenic (1.3mg/L) (Figure 4E).

Lead was detected in 13 out of the 90 samples that had arsenic above the detection limit. Based on the WHO recommended standard for Pb of 0.01 mg/L[29] and the Pb results (0.07–0.96 mg/L) we obtained, the samples were grouped into three groups, namely; high lead (0.05–0.1 mg/L), very high lead (0.1–0.2 mg/L), and extremely high lead (0.2–1.0 mg/L). The high Pb group was dominated by streams, the very high Pb group was formed mainly by springs, and the extremely high Pb group was represented by one borehole sample (Figure 4F).

Factors controlling water chemistry: After performing PCA, the measure of sampling adequacy, the Kaiser Meyer Olkin test (KMO), was applied and gave a value of 0.6 which is considered to be adequate for the analysis.[59] The PCA results indicated that there were three main factors which controlled the water chemistry and accounted for 86.9% of the total variance in all the data sets (Tables 2A and 2B).

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These factors, which are represented by the principal components (PC_1, PC_2, and PC_3), are solubility, ionic radius, and the hydrogen ion concentration. The principal component one (PC_1) had strong positive loadings on fluoride, boron, and TDS and explained 44.4% of the total variance (Tables 2A and 2B). The PC_2 had strong positive loadings on arsenic and lead and explained 28.4% of the total variance while PC_3 had a strong positive loading on pH and explained 14.1% of the total variance (Tables 2A and 2B).

Table 2A. Total rotated component matrix[a] for the parameters of F, As, B, and Pb, and the values for all the parameters (F, As, B, Pb, pH, DO, and TDS (PC=principal component, F= fluoride, As=arsenic, B=boron, Pb=lead, DO=dissolved oxygen, TDS=total dissolved solids)

PC	Parameters				Values for all the parameters (F, As, B, Pb, pH, DO, and TDS)		
	F	As	B	Pb	Eigenvalue	% Total variance	Cumulative % variance
PC1	0.99	–0.02	0.981	–0.003	3.107	44.382	44.382
PC2	–0.03	0.984	0.113	0.988	1.989	28.408	72.79
PC3	0.02	–0.02	0.04	0.026	0.989	14.131	86.921

[a]Extraction method: principal component; Rotation method: varimax with Kaiser normalization, rotation converged in 4 iterations.

Table 2B. Total rotated component matrix[a] for the parameters of pH, DO, and TDS, and the values for all the parameters (F, As, B, Pb, pH, DO, and TDS (PC=principal component, F= fluoride, As=arsenic, B=boron, Pb=lead, DO=dissolved oxygen, TDS=total dissolved solids)

PC	Parameters			Values for all the parameters (F, As, B, Pb, pH, DO, and TDS)		
	pH	DO	TDS	Eigenvalue	% Total variance	Cumulative % variance
PC1	0.037	-0.384	0.983	3.107	44.382	44.382
PC2	0.068	0.159	–0.051	1.989	28.408	72.79
PC3	0.962	–0.314	0.1	0.989	14.131	86.921

[a]Extraction method: principal component; Rotation method: varimax with Kaiser normalization, rotation converged in 4 iterations.

Cluster analysis: The cluster analysis grouped the samples into a 9 cluster dendrogram (Figure 5 and Table 3).

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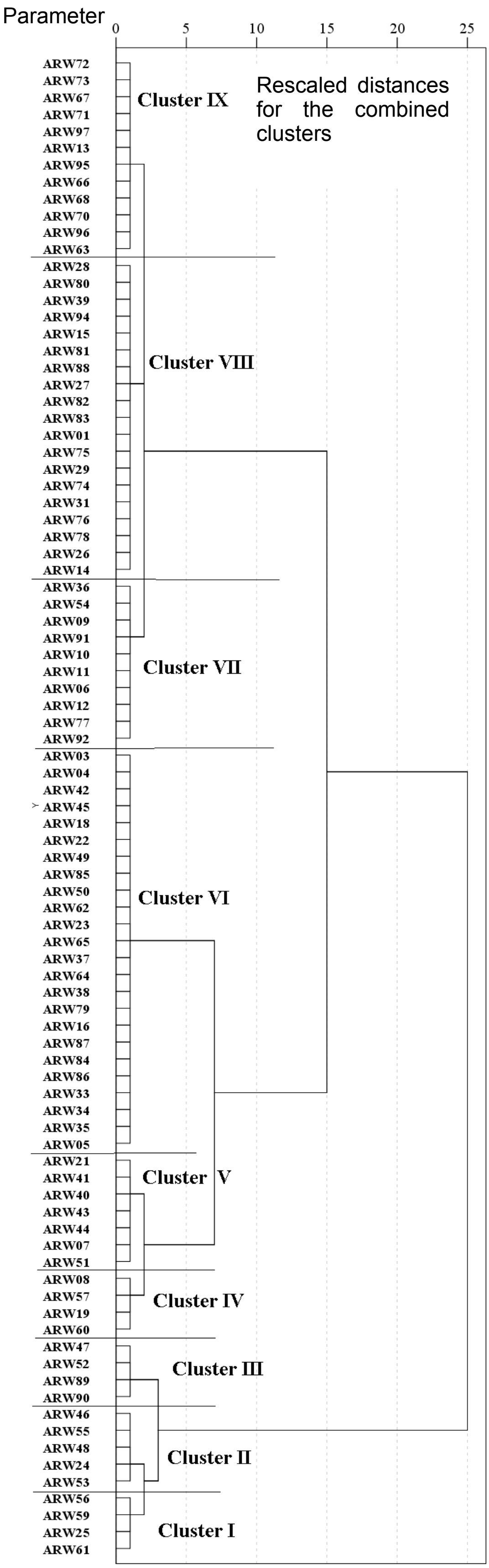

Figure 5. Cluster analysis dendrogram using the Ward linkage and showing the rescaled distances for the combined clusters

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Table 3. Major cluster characteristics
(F=fluoride, As=arsenic, B=boron, Pb=lead, TDS=total dissolved solids)

Parameter (concentration of F, B, As, Pb and TDS in mg/L)	Total number of samples in cluster	Minimum–Maximum	Median	Characteristic	Cluster
F	4	25-42	28	Very high	C_I
B	4	0.02-0.03	0.03	Slightly elevated	
pH	4	8-9.5	8.6	High	
TDS	4	1250-1550	1400	High	
F	5	8-52	32	Very high	C_II
B	5	0.04-0.05	0.04	Slightly elevated	
pH	5	8-9	8.3	High	
TDS	5	1710-1910	1800	High	
F	4	24-1460	171	Extremely high	C_III
pH	4	9-10	9.5	Very high	
TDS	4	2100-19600	3390	Extremely high	
F	4	17-47	27	Very high	C_IV
B	4	0.01-0.19	0.03	Slightly elevated	
TDS	4	830-1190.00	1010	High	
F	7	1.5-30	2.5	Slightly high	C_V
TDS	7	530-872	590	Slightly high	
F	24	1.2-25	3.5	Intermediate	C_VI
As	24	0.02-1.27	0.29	High	
B	24	0.01-0.27	0.02	High	
Pb	24	0.07-0.96	0.1	High	
TDS	24	260-566	400	Low	
F	10	0.93-15.33	2.5	Slightly low	C_VII
TDS	10	197-376	250	Slightly low	
F	19	0.9-14	1.3	Low	C_VIII
TDS	19	100-255	138	Low	
F	12	0.08-3.9	1	Very low	C_IX
TDS	12	23-105	80	Very low	

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Despite the fact that there are some scattered samples, there is a defined spatial distribution of the water sources according to the physical and chemical characteristics of the study area (Figure 6).

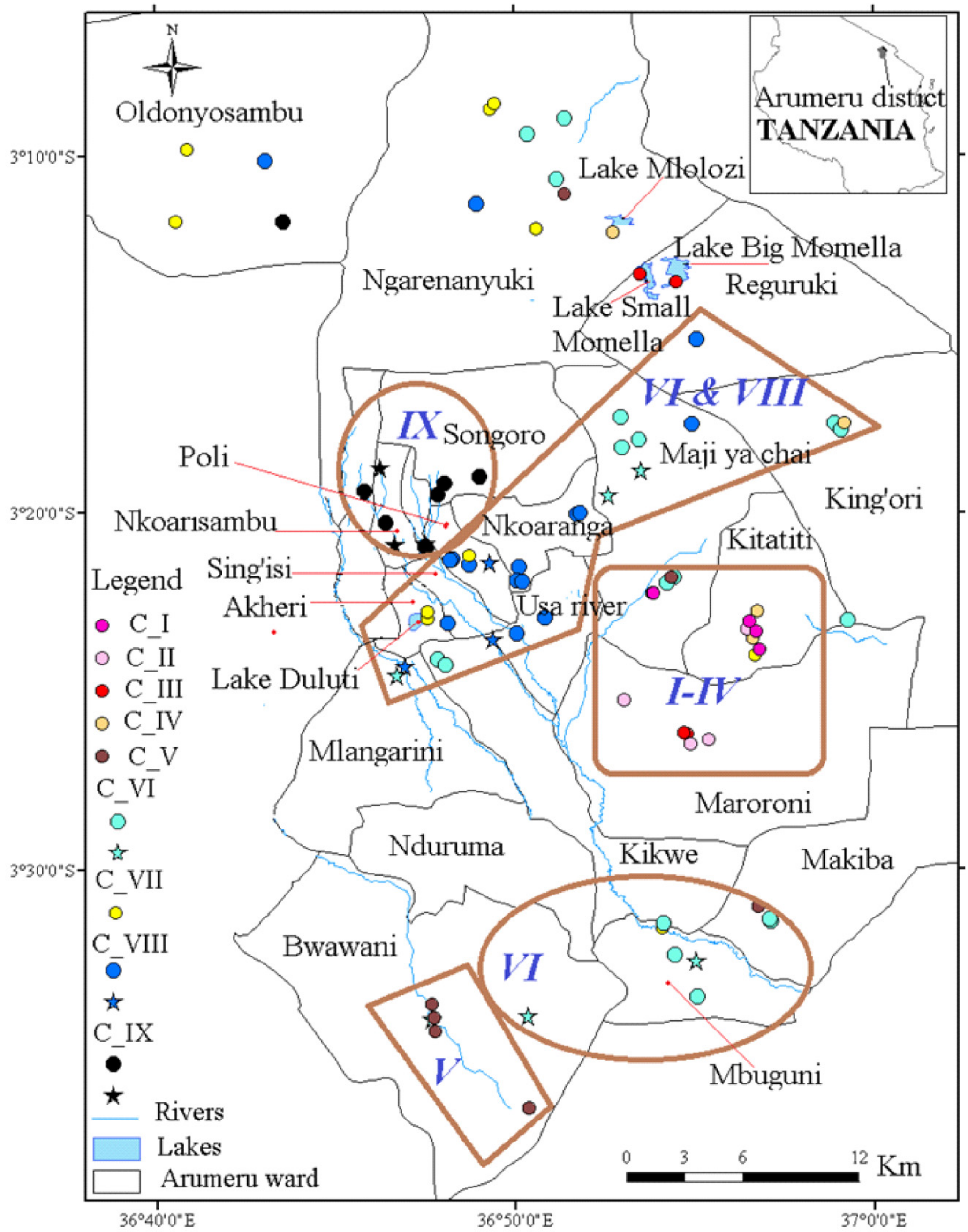

Figure 6. Spatial distribution of the clusters (all samples had F while the star symbol represents samples with high As)

Clusters I to IV, which were generally characterized by a high fluoride level (median>25 mg/L) and TDS (median>1000 mg/L), represented the alkaline lakes, dug wells, and boreholes that are located around the Kikatiti-Maroroni area and on

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the leeward side of Mt. Meru (Figure 6 and Table 3). A few distinctive characteristics differentiate one cluster from another. Cluster I encompasses 4 sampling sites (3 boreholes and 1 dug well) which are characterized by alkaline water with a high fluoride level (median= 28 mg/L) and TDS (mean=1400 mg/L) (Table 3). The boron concentration (median=0.03 mg/L) differentiates cluster II from cluster I. These are mostly dug well samples from around Maji ya Chai, Kikatiti, and Maroroni. Cluster III is the group with alkaline water with an extremely high fluoride level (median=171 mg/L) and a high TDS (median=3390 mg/L) (Table 3). These are 2 leeward alkaline lakes and 2 dug well samples from around Kikatiti-Maroroni. Cluster IV is characterized by a low fluoride level (median=27 mg/L) and TDS (median=1010mg/L), relative to cluster III, with a boron concentration between 0.01 and 0.19 mg/L. This group is composed of two dug wells, one borehole and one alkaline lake.

Cluster V is the intermediate cluster separating the first four clusters (clusters I to IV) with a high TDS and fluoride level and the last four clusters (clusters VI to IX) with a high DO, a low TDS, and a low fluoride level. Most of the samples in cluster V were in the southern part of the study area (Bwawani) (Figure 6). As with the first four clusters, distinctive characteristics also differentiate the last four clusters (clusters VI to IX). Cluster VI, comprising 22 sites, is the fluoride and heavy metal pollution cluster with 95% and 40% of the water sources having fluoride concentrations above the WHO and Tanzania standards, respectively. Similarly, the water sources sampled with high arsenic and lead, beyond the WHO standards, accounted for 30% and 30%, respectively. Spatially, these samples were found to dominate in the southern part of the study area (Mbuguni) and in the south-east side of Mt. Meru (Usa River and Maji ya Chai) (Figure 6). Cluster VII comprises 10 sites, which are generally scattered (although a high number of samples are in the northern side of the study area) and are characterized by a slightly low fluoride level (median= 2.5 mg/L) and TDS (median=2500 mg/L). Clusters VIII and IX are composed of streams and springs only. Cluster VIII, comprising 19 sites, is characterized by a low fluoride level (median=1.3 mg/L) and TDS (median=138 mg/L) and the samples were found to dominate at the southern lower slopes of Mt. Meru (Pori-Sing'isi-Nkoaranga-Usa River) (Figure 6). Cluster IX, comprising 12 sites, was dominated by springs, which were generally on the upper slopes of Mt. Meru (windward side) (Figure 6). They were characterized by the lowest fluoride level (median=1 mg/L) and TDS (median=80 mg/L). Twenty-five percent of the samples from this cluster were polluted by As and Pb.

DISCUSSION

DIFFERENCES AMONG WATER SOURCES

Physico-chemical properties: The high total dissolved solids in the lakes and dug wells, relative to the other water sources, had a TDS dominance pattern of alkaline lakes>dug wells>borehole>streams>springs. The TDS can be attributed to many factors such as excessive evaporation and the solubility of salt crusts in soils and rock surfaces. The dug wells with high TDS were located in the lowland where the rainfall is low and the temperatures are high. Under normal circumstances, the total dissolved solids in deep boreholes are supposed to have a high concentration of TDS relative to those in shallow dug wells owing to the prolonged water rock interaction in the deep borehole waters.[60] However, the deep percolation of rainwater to the readily dissolvable salt crusts, formed by a high rate of evaporation, may be hindered by the presence of alternating impermeable layers of basalts that represent several episodes of volcanism. The five year average temperature records at Kilimanjaro International Airport (lowland) and Tengeru (upper to mid slope) show differences in the mean temperatures of about 1ºC for the hottest months of January, February. and March (Figure 7). The dissolution of such salts and low rainfall could lead to the formation of water that has high TDS in shallow aquifers. A similar process could be invoked for the alkaline water with high dissolved ions in the small lakes of Momella (Small and Big Momella), and Mlolozi which are also characterized by a low surface input, low precipitation, high evaporation, high carbonates, and high bicarbonates, relative to the windward lakes.[4,12] High conductivity values, which are also a measure of TDS, have been reported in the East African rift valley lakes and have been attributed to excessive evaporation.[12]

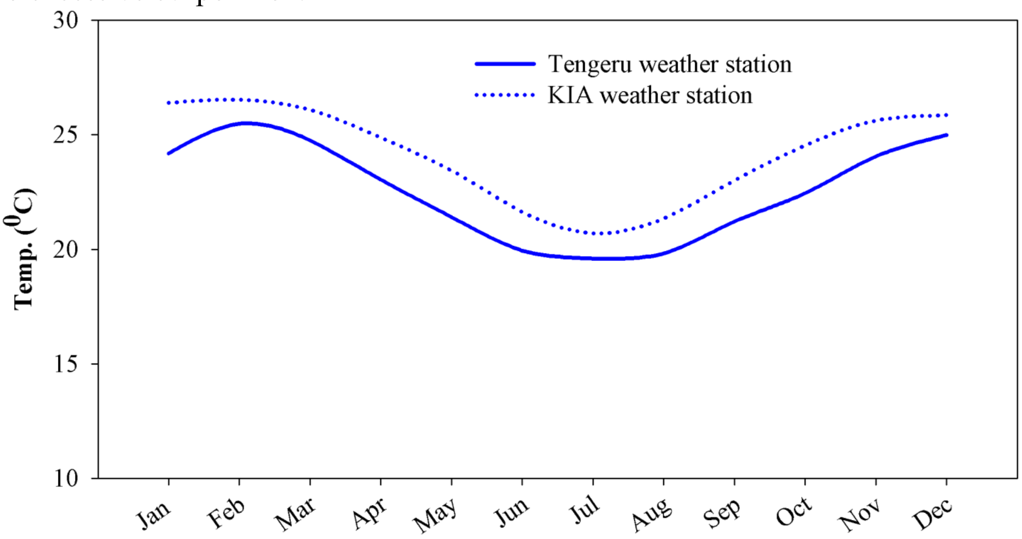

Figure 7. Mean monthly temperature variation from 2002–2006 for the Tengeru and Kilimanjaro International Airport stations.

The low pH for the springs, relative to the other water sources, can be attributed to the short water-rock interaction time owing to the fact that most of the springs were observed to be located in an area studded with nephelinitic and phonolitic formations which are generally fractured (Figure 8). The low pH of the spring water (6.5–7.0) on the windward side of the mountain, which is close to that of rainwater (6.5), could also be a result of a high hydraulic gradient over the slopes of Mt. Meru. Mt. Meru is considered to be the main recharge zone.[12] This observation is in agreement with the work of Ghiglieri et al.[4] who inferred a short residence time for groundwater in western Mount Meru using ^{3}H results.

Most of the shallow lakes along the eastern arm of the East Africa rift valley are characterized by excessive evaporation, high carbonates, and high bicarbonates.[12,61,62] The high pH in the Momella series lakes is a result of high carbonates, high bicarbonates,[12] and excessive evaporation. Such high pH values in Lake Momella were reported by Hecky[63] and Nanyaro.[12]

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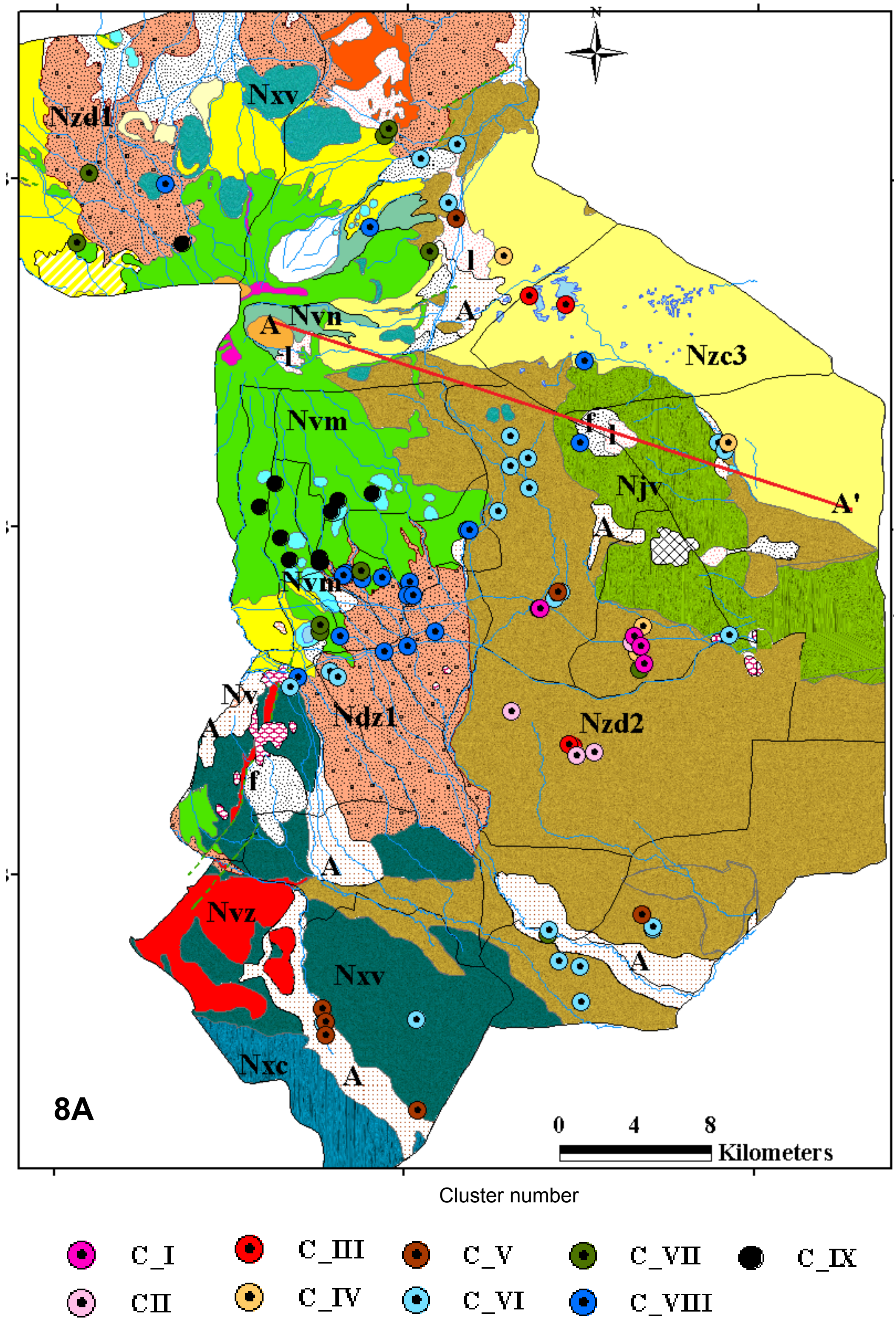

Figure 8A. Spatial distribution of the clusters.

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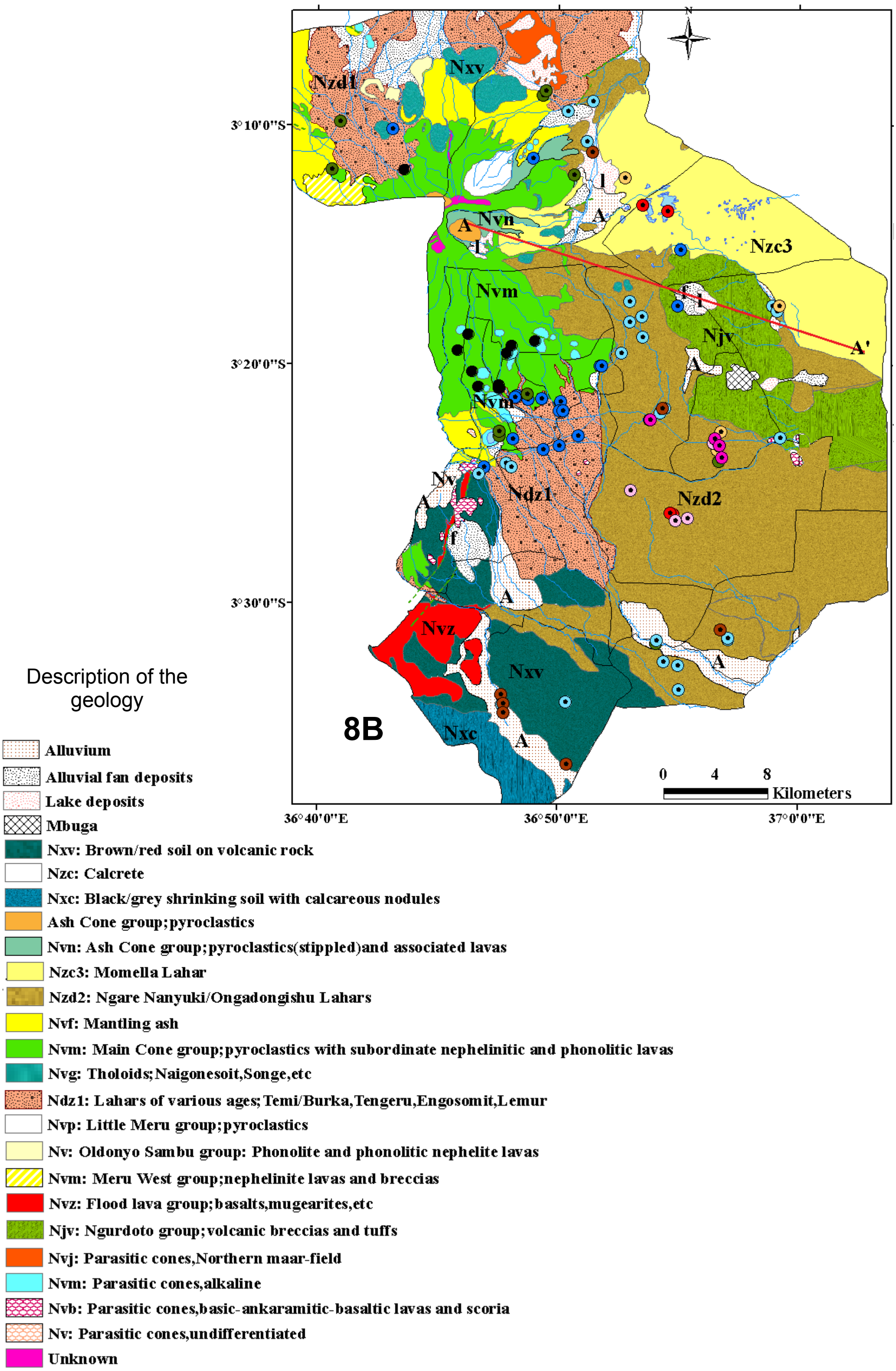

Figure 8B. Spatial distribution of the geology, modified from Wilkinson 1983.[66]

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The high pH in the dug wells, mostly located in lowland areas, may be attributed to a combination of several factors including (i) evaporation-crystallization and precipitation processes which lead to the formation and dissolution of salts near the surface; (ii) increased water-rock interaction time which is favored by a low hydraulic gradient, particularly at the foot of the mountain; and (iii) the dominance of ash and lahar materials which could dissolve more easily leading to an increase in alkalinity. The restricted range of pH between 8.0–8.5 for most of the dug wells is basically the result of the common geological materials (lahars) in the shallow parts where alkalinity is gained through the dissolution process (Figure 9).

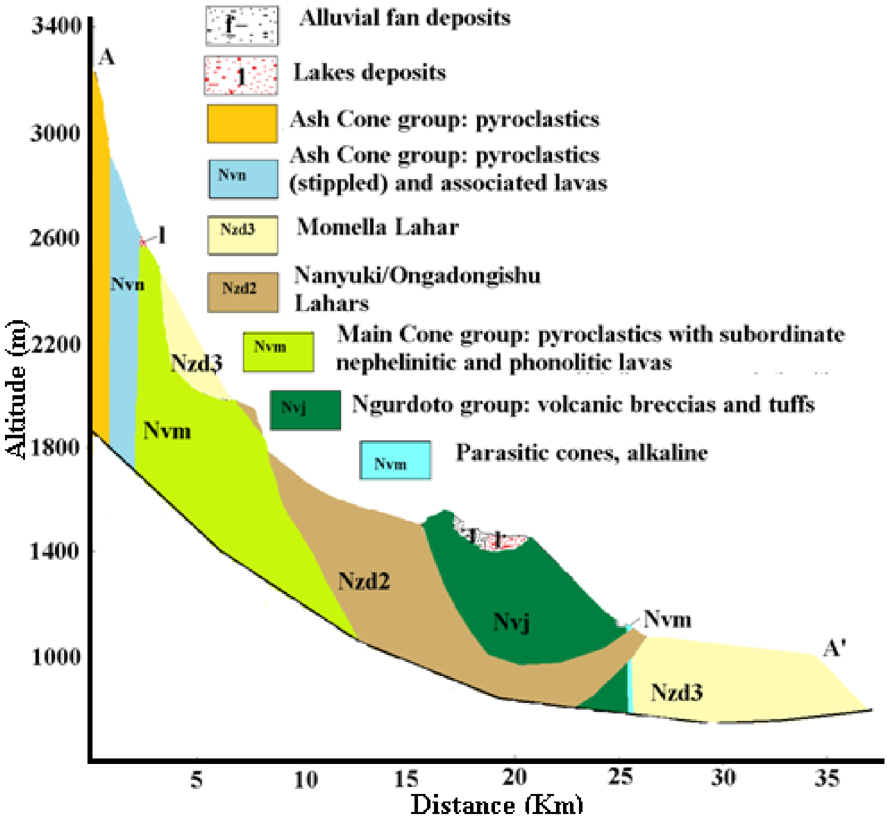

Figure 9. Cross section A-A', from Figures 8A and 8B, hypothesizing that some laharatic materials are floating on other volcanic materials as a result of different volcanic episodes.

The observed differences in the DO in all the water sources are mainly attributed to variations in aeration, surface input, particularly with organic matter (OM), and algal growth as a result of a high concentration of nutrients. The nutrients concentration and the coliform bacteria counts in the shallow wells and boreholes have been reported to be high along the slopes of Mt. Meru, particularly during wet season.[64,65] Such nutrients could support the growth of algae, which could be the source of high OM. Moreover, most of these dug wells were locally constructed in high density residential areas with poor well completion (not well protected from surface inflow leading to an increase in the surface input, particularly from human settlements/ activities).[64] Most of the dug wells lacked aeration, because of their not being used due to uncertainties in water quality (particularly at the foot of Mt. Meru), and hence had a low DO relative to the boreholes (Cluster V, Figure 6). Furthermore, the anoxic condition for some of the fresh water lakes (e.g., Ngurudoto Crater Lake) can be attributed to the colonization of the lakes by swampy vegetation. The springs and streams had a high DO relative to other sources because of their intensive aeration.

TRENDS FOR FLUORIDE, BORON, LEAD, AND ARSENIC AMONG THE WATER SOURCES

Fluoride: The distribution of fluoride in the surface and groundwater has been reported on by several workers for the areas around Mt. Meru,[3,4,12,22,23,63] for other parts of Tanzania,[18,23,24] and for East Africa in general.[13,14,17,19,61] All these studies have generally not provided trends for the concentrations of fluoride in the various water sources/types. The present study has noted that the fluoride dominance pattern is alkaline lakes>dug wells>boreholes>streams>fresh water lakes>springs. Such a distribution pattern is likely to be controlled by the geology and differences in the rates of precipitation and evaporation. As noted, the study area is studded with volcanic materials that were deposited during several episodes of volcanic eruption. Some of the volcanic rocks such as basalts, lahars, ashes, calcareous tuff, pyroclastic rocks, and rhyolite are considered to have a high concentration of fluoride.[4,12,14,34,61] Such rocks are widespread in the study area[66,67] and could contribute to the observed trend.

The Momella lakes (Big and Small Momella), which were formed as a result of the collapse of the eastern part of Mt. Meru[61,68,69] have the highest fluoride concentration with values as high as 1410 mg/L. Such high fluoride values in Lake Momella were reported by Hecky[63] and Nanyaro.[12] However, the reported values have been increasing with time. The fluoride concentration value reported in 1973 was 382 mg/L while that reported in 1984 was 690 mg/L. Such high concentrations, with an increasing trend, are likely to have been a result of a high pH which enhances the release of fluoride from rocks,[70] the solubility of fluorine-bearing minerals in lahar, and the year to year increase in the rate of evaporation owing an increase in the air temperature, as exemplified by the temperature record at the Kilimanjaro International Airport (Figure 7).

Many dug wells showed a high fluoride concentration relative to the deep boreholes. A similar heightened fluoride concentration in the shallow wells relative the deep boreholes was reported by Apambire et al.[71] and Gupta et al.[72] The origin of the high fluoride concentrations in these two reported cases were excessive evaporation and granitic rocks. Although such explanations can be invoked in the present study, it is likely that in addition to evaporative enrichment, the observed high fluoride concentration in the shallow dug wells could be related to the interaction of fluoride-bearing volcanic materials, such as lahar (Figure 9), with water and the dissolution of the trona rich crystals that are frequently formed during the evaporation-crystallization process. Trona crystals, which are highly soluble, have been observed to contain appreciable amount of fluoride.[21,73-75] Thus, the surface runoff at the beginning of the rainy season is likely to contribute a significant amount of salt and fluoride to the unprotected dug wells, streams, and lakes.

The springs had the lowest fluoride level because of their short water-rock interaction time, relative to other sources, which is strongly attributed to a high hydraulic gradient on the slope of Mt. Meru, where most of the springs are located. Furthermore, unlike the streams and other water sources, the springs are free from runoff and the interflow resulting from the evaporation-crystallization process that could carry fluoride and other ions.

The insignificant variations in fluoride levels in the surface flow from the head points to the foot of the mountain, as observed in the Malala, Tengeru, and Maji ya Chai rivers, is due to the high hydraulic gradient which is likely significantly lower the base flow contribution to the streams (Equation).

$$i = \frac{dh}{dl} \quad \text{.............................. Equation}$$

Where

i	=	the hydraulic gradient (dimensionless)
dh	=	the difference between the two hydraulic heads (length, usually in m or feet)
dl	=	the flow path length between the two piezometers (length, usually in m or feet)

The high hydraulic gradient lowers the period of water-rock interaction leading to an insignificant release of fluoride even with the presence of fluoride-bearing materials. The insignificant fluoride variation is further attributed to the higher precipitation on the windward side of the mountain which enhances the dilution effect.

Arsenic and lead: The samples with arsenic and lead levels above the recommended standards were the same, indicating that they have the same concentration profile. While these heavy metals were absent in the lakes and only weakly present in the dug wells, they dominated in the stream and spring samples indicating that they are largely controlled by the geology. Despite the fact that these heavy metals are commonly associated with hydrothermal deposits,[36]volcanic materials are known to be a source of these metals in water systema.[34,61, 76, 7] For instance, high Pb values (as high as 90.5 ppm), which are likely to cause groundwater contamination, were reported from flood basalt in the Harrat Hutaymah, in one of the largest alkali basalt volcanic provinces of the world in western Saudi Arabia.[78] Such a province is geologically related to the study area with an abundance of flood basalts and tuff-ring craters with xenoliths.[66] Similarly, along the East Africa rift valley, high arsenic values, as high as 0.4 mg/L in lake water and 0.3 mg/L in geothermal wells, were found to result from rhyolitic rocks along the rift system in Ethiopia.[34]

Contrary to above information on the volcanic materials hosting As and Pb, within the study area they are likely to be more associated with pyroclastics with nephelinitic and phonolitic lava on the slope of Mt. Meru (Figures 8A and 8B) where the springs dominate compared to the lahars which host most of the dug wells and lakes. The occurrence of As and Pb in spring samples, where the water-rock interaction time is short as discussed previously, suggests that part of the As and Pb is still locked in these formations. However, in the study area, they enter the streams as base flow after being dissolved from the source rocks. The occurrence of these metals in one borehole could be related to the geology at that particular area.

Boron: Volcanic materials, such as basalt, tuff, volcanic ashes, and associated weathering products and evaporates have been pointed out as some of the major sources of boron in groundwater systems.[79-81] Clay-rich sediments derived from the

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weathering of volcanic ash deposits have been known to contain significant amounts of boron. Uppin and Karro[81] reported 57–1,124 mg/kg boron in volcanic ashes in Estonia. Also, high values of boron ranging from 2.1 to 33 mg/L were reported in evaporitic fresh aquifers in Greece.[80] Similar to the presence of fluoride in significant amount in salts (trona), the light element boron can also be incorporated in such salts and the evaporation crystallization process can lead to a high boron concentration in the water system. Therefore, despite the poor record of boron levels in the study area, the high boron concentration, particularly in the dug wells and leeward lakes (Momella and Mlolozi), can be attributed to volcanic ash, lahar material, and the evaporation-crystallization process near the earth surface. The high boron concentration in one borehole, with a depth of 85 m, in the lowland can be attributed to basalt.

SPATIAL DISTRIBUTION OF PHYSICO-CHEMICAL PROPERTIES, FLUORIDE, ARSENIC, LEAD AND BORON

Windward and leeward differences in physical-chemical properties: As noted previously, the streams and springs on the leeward side of Mt. Meru were more alkaline relative to those found on the windward side of the mountain with a pH>8.5. This can be attributed to differences in evaporation and precipitation. The high precipitation on the windward side has a diluting effect and tends to maintain the pH at a nearly neutral level whereas the excessive evaporation on the leeward side leads to an enrichment of carbonates and bicarbonates which raises the pH.[61,62] A similar mechanism explains the high dissolved ions in the leeward streams relative to those on the windward side. The low precipitation on the leeward side also limits the number of springs and lowers the possibility of the occurrence of a spring on the upper slope of the mountain. As a result, springs occur in a few specific locations controlled by the morphology/landscape. To some extent, this causes the rain water on the leeward side to have a reasonable amount of time for water-rock interaction leading to a slightly elevated TDS relative to the windward springs. Furthermore, the precipitation and crystallization-evaporation cycles dominate on the leeward side leading to the dissolution of salt at the beginning of the rainy season which eventually flows to the streams through runoff and interflow and raises the TDS. It is likely that the dissolved ions in such leeward streams is a function of the season and is high at the beginning of the rainy season.

Fluoride: Many researchers have reported high fluoride concentrations along the East Africa rift system,[2,3,12-16,18-23,30] in the sub arid to arid areas in India, and in South America.[72,82] The higher fluoride values in the surface and groundwater in these areas have been attributed to volcanic materials particularly volcanic ash in Northern Tanzania[12] and rhyolitic rocks in the main Ethiopia rift system.[34] In the study area, the cluster analysis clearly delineated zones that have high fluoride concentrations (Figure 6 and Table 3). Very high fluoride levels (as high as 260 and 1410mg/L in the leeward lakes) and generally levels of fluoride>25 mg/L were found at Maji ya Chai-Kikatiti and Maroroni and in the leeward lakes as shown in Clusters I to IV (Figure 6). The high fluoride level around Maji ya Chai Kikatiti-Maroroni is likely to be a result of the interaction of water with fluoride-bearing rock materials (Figures 8 and 9), whereas the interaction of water with fluoride-bearing rock in conjunction with excessive evaporation accounts for the very high fluoride levels in the leeward alkaline lakes. Despite of the lack of a specific cluster, most of the northern parts (Ngarenanyuki-Oldonyosambu) are dominated by high fluoride levels, generally between 4 and 33 mg/L, and this can be attributed to an abundance of fluoride source materials and the increased evaporation in this side. The southern parts of Makiba- Bwawani-Mbuguni are dominated by intermediate fluoride levels (Clusters V to VI) (Figure 6). This can be attributed to a decrease in the fluoride source materials and a low hydraulic gradient which is likely to limit/lower the flow from the foot of the mountain to the lowland area. However, this could also be a result of the presence of basaltic/volcanic rocks that act as conduit for the recently recharged water. The area, which is generally a flood plain, is likely to be a recharge zone and thus dilute the effect of the dissolution of trona crystals.

The intermediate fluoride level area, generally between 2 and 3.5 mg/L, mostly covers the lower to upper slopes of the windward side of Mt. Meru (Maji ya Chai-Leguruki-Pori-Sing'is-Nkoaranga-Akheri-Usa River) as shown in Clusters V1 to VII (Figure 6). As this zone is composed of different volcanic materials (Figures 8A and 8B), such values reflect a short water-rock interaction time caused by the high hydraulic gradient relative to the values at the foot of the mountain. The lowest fluoride zone is the windward zone dominated by the spring on the upper slopes of Mt. Meru in Cluster IX (Figure 6) indicating a short water-rock interaction time relative to all the other sources.

Based on the above findings, field observations, and the documented information, the areas which are seriously lacking water for domestic purposes are the ones with high fluoride levels in the few available water sources (e.g., Maroroni, Kikatiti, Ngarenanyuki, and OldoinyoSambu). The adverse health effects of fluoride, such as dental and skeletal fluorosis, are pronounced in these areas.[3,4,15,18,21-23] Moreover, the use of water with a high fluoride level (e.g., F_{water}= 30mg/L in the Ngarenanyuki river) in agricultural activities, such as growing tomatoes, and in livestock feeding is a common practice in the study area. It has been established that fluoride can bioaccumulate in plants[83] and strongly inhibits photosynthesis and other processes leading to a reduction in crop yield, with greater effects being observed when in combination with arsenic.[84,85] The accumulation of fluoride occurs when the concentration in pore water is above 25 mg/L.[85] Therefore, this research calls for an urgent need/program that will govern the proper distribution of water with an acceptable fluoride level for domestic purposes. Also, the effects related to the consumption of foods, such as tomatoes and vegetables, need to be studied as the community may continue to suffer from fluoride if only the consumption of fluoride from drinking water is considered.

Arsenic and lead: The principal component analysis (PC_2) showed a strong positive loading on arsenic and lead which explained 28.4% of the total variance and indicated a dominance by these metals. Spatially, arsenic and lead dominate on the windward side of the lower to upper slopes of Mt. Meru and the lowland area (Mbuguni-Bwawani) as shown in cluster VI (Figure 6). The occurrence of As and Pb on the lower to upper slopes is related to natural sources, specifically pyroclastics with nephelinitic to phonolitic lava (Figures 8A and 8B). A study by Rango et al.[34] in the main Ethiopian rift system (the same rift system as in the study area) revealed that

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arsenic is more reflected in the sediments than in the dominant rhyolitic and basaltic rocks. Therefore, the high arsenic and lead levels in the groundwater in the lowland areas in the southern part of the study area (Figure 6) indicates that it has been transported there from the upland areas. The occurrence of arsenic in one spring, located in Arusha National Park in the upland area, which has been free from human activities for many years showed that arsenic is a natural contaminant.

Boron: Boron showed a strong positive loading in the principal component analysis (PC_1) which explained 44.4% of the total variance and is concentrated in clusters I to IV around Kikatiti and Maroroni (Figure 6) and in the leeward lakes (Mlolozi and Small and Big Momella). Similar to the situation for fluoride, the occurrence of boron in this zone indicates that it is strongly associated with pyroclastics, ashes, and lahar materials (Figures 8A and 8B).

CONCLUSIONS

The integration of the physico-chemical parameters (pH, TDS, and DO) with the chemical parameters (F, As, Pb, and B) led to a proper determination of the levels and spatial distribution of these elements in the study area. The principal component analysis indicated that there are three major factors controlling water chemistry which account for 86.9% of the total variance. Factor 1 was influenced by fluoride, TDS, and boron; Factor 2 was influenced by arsenic and lead; and Factor 3 was influenced by pH. The cluster analysis grouped the samples into 9 significant clusters based on the water quality parameters. Clusters I to IV were generally alkaline water characterized by high TDS and fluoride levels and were dominated by dug wells and the leeward alkaline lakes. Cluster V was the intermediate cluster in terms of TDS and fluoride while clusters VI to IX, were dominated by streams and springs and were generally characterized by high DO, low fluoride, and low TDS. The study has revealed that fluoride is a natural pollutant and it significantly lowers the water quality for domestic purposes (mean=27 mg/L). Its abundance pattern, which is similar to the TDS pattern was alkaline lakes>dug wells>boreholes>streams>fresh water lakes>springs. The high level of the TDS, as well as fluoride, in the leeward alkaline lakes (pH=9.2) and dug wells was attributed to the abundance of the readily weathered volcanic materials and the evaporation-crystallization process. Materials such as lahars, ashes, and pyroclastic materials dominate the shallow parts of the earth’s surface where the evaporation-crystallization process leads to the formation of salts which eventually dissolve to generate more ions and fluoride. The springs were characterized by low TDS and fluoride which is attributed to the geology and the short water-rock interaction time relative to the other sources. A short water-rock interaction time is favored by a high hydraulic gradient in the fractured pyroclastic phonolitic to nephelinitic formation. However, the leeward springs had more elevated TDS (median= 396 mg/L) and fluoride (median=10 mg/L) relative to the windward springs where the median TDS and fluoride levels were 135 mg/L and 1 mg/L, respectively, reflecting the low precipitation and high evaporation in the leeward side relative to the windward side of Mt. Meru. Some fresh water lakes and dug wells were found to have low DO, sometimes up to an anoxic condition, and this was attributed to high OM inputs and poor aeration. The present study revealed that F, As, Pb, and B are highly associated with natural sources and their distribution is strongly controlled by the geology, the water-rock interaction time, and the climatic conditions. Fluoride and boron were high in the areas dominated by lahars, ash, and pyroclastic materials whereas arsenic and lead, which were found to have a similar concentration profile, were high in the springs that are located in a specific zone dominated by nephelinitic to phonolitic lava. However, the boron level was high and above the recommended standard in only one sample (1.65 mg/L in Lake Big Momella). The presence of high arsenic and lead, particularly in some of the springs with a low fluoride level, continued to lower the availability of water for domestic purposes. Therefore, it is recommended that a detailed study should be made on the movement and distribution of fluoride among the commonly grown plants/crops within the study area as well as in livestock, particularly cattle. Also, detailed studies on the sources, release mechanisms, and distribution of elements such as arsenic, boron, and lead should be carried out. Furthermore, the springs with acceptable levels of F, As, B, and Pb should be properly utilized. Finally, water sources with these elements at levels above the recommended standards should be treated to lower the pollution to a safe level or abandoned as water sources.

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DISCLOSURE STATEMENT

No potential conflict of interest was reported by the authors.

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