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WATER POLLUTION BY NATURAL INORGANIC CHEMICALS IN THE CENTRAL PART OF THE MAIN ETHIOPIAN RIFT

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ABSTRACT: The natural surface water and shallow groundwater quality in the Ethiopian Rift is influenced by excessive input of fluoride and some inorganic chemical constituents such as Li, Sr, Pb, Cu and Hg from the deep groundwater system. The surface water bodies are characterised by high fluoride, bicarbonate and chloride concentration far above the recommended consumption limit. The quality of surface water in the Ethiopian Rift is influenced by the complex geological activities, which increase the concentration of undesirable chemical constituents in surface waters by transfer from deep groundwater in the form of thermal springs, geysers and fumaroles. In fact, the concentration of some of the aforementioned chemical constituents highly exceeds the consumption limits giving rise to serious health problems to the local population.

Key words/phrases: Deep groundwater, inorganic chemical pollutants, Main Ethiopian Rift, teeth mottling, thermal springs

INTRODUCTION

The intense volcanic and tectonic activity has raised the geothermal gradient in the Main Ethiopian Rift, which has facilitated continuous discharge of deep thermal water into fresh surface water bodies. Therefore, continuous reduction of potable water resource has created difficulties on the water management policies of the region. The growing needs for drinking water require the protection of fresh surface water quality.

The Main Ethiopian Rift (MER), a sunken land feature mainly oriented in a NE-SW direction, is covered dominantly by recent peralkaline acidic volcanic rocks (lava flows, domes, pumice flows and ignimbrites) formed by central eruptions, and fissural basalts (Di Paola, 1972; Mohr, 1983; Zanettin, 1993; Peccerillo *et* *al.*, 1995). While the older volcanic units (the Trap Series, Oligo-Miocene) outcrop on the Rift margins, the recent volcanics (Aden Volcanic Series, Plio-Quaternary) cover the entire Rift floor (Kazmin *et al.*, 1980). The MER occupies very wide plain areas and is constituted by narrow belts of parallel faulting, sunken strips of land between a series of normal faults giving rise to characteristic graben-horst structures (Mohr, 1971; Di Paola, 1972). This typical morphology provides suitable place for the storage of large quantity of surface and sub-surface water fed by large number of big and small rivers that drain toward the Rift from the adjacent plateaus. There are also numerous perennial rivers, which are restricted to the Rift and form typical endorehic drainage systems.

In most cases fresh or saline lakes such as Abe, Beseka, Awassa, Abaya, Chamo, Ziway, Langano, Shalla and Abijata occupy the grabens and volcano-tectonic structures. The Rift is also characterised by patches of swampy areas, lacustrine deposits and great terraced alluvial terrains. In the MER, the surface and groundwater reservoirs which receive large amount of fresh water from highland rivers are characterised by low salinity and mineral content, while those which have direct contact with the deep hot water circulation, are saline, highly mineralised and are mostly alkaline (Berhanu Gizaw, 1996).

The purpose of this work is to locate the major provenance of inorganic chemical pollutants. With the help of major chemical and trace elements, this work also aims to reveal the contaminant role of deep groundwater and to show the main natural pollutants found in the surface water of the MER. The study area is characterized by the presence of numerous thermal springs with variable temperature (28–96° C).

HYDROGEOLOGICAL CONSIDERATION

The rock formations of the MER show wide local variation in porosity (primary and secondary) and permeability (primary and secondary). Basaltic lava flows and ignimbrites constitute the main aquifers of the whole area, due to their high fracture permeability (Tesfaye Chernet, 1982; Tamiru Alemayehu, 1993; Berhanu Gizaw, 1996; Tamiru Alemayehu and Vernier, 1997). Other phreatic and semi-confined aquifers also occur in weathered volcanic and pyroclastic rocks and alluvial sediments of high pore permeability, or along the main tectonic discontinuities. The intense tectonic and volcanic activity, which occurred since Miocene in the Ethiopian Rift, caused the geothermal gradient to rise by as much as 6 m/° C (Tamiru Alemayehu and Vernier, 1997). Consequently, even at shallower depths, a circulation of thermal groundwater occurs, as it is normally observed in the central part of the Rift. The whole Rift is also characterised by high thermal anomalies where large and deep hot water reservoirs are found in association with shallow silicic magma chambers. The hydrochemical and isotopic analyses indicate that in the Rift groundwater flow pattern is controlled by geologic structures mainly by faults (Tenalem Ayenew, 1998). Therefore, it is very common to find fumaroles and hot springs within the calderas and along main tectonic discontinuities. The main vertical conduits are generally represented by tectonic lineaments through which highly mineralised hot waters reach the surface in the form of springs, geysers and fumaroles, and recharge the surface water bodies.

The tectonic discontinuities in the MER, while normally acting as horizontal conduits for cold water, often act as vertical pipelines for thermal water and steam (Tamiru Alemayehu, 1998). Some of these hot sources have high discharges as much as 1150 L/s Hippo pool springs, 780 L/s Sodere springs, (UN, 1973); 33 L/s Lake Shalla springs, (Tesfaye Chernet, 1982).

The waters of the MER show wide range of geochemical variation: bicarbonate, chloride and sulphate are the most common chemical components with predominance of alkali metals over alkali-earths (Fig. 1). The bicarbonate enrichment in the geothermal systems is attributed to the reaction of dissolved carbon dioxide with the rocks to produce mica or clay minerals and bicarbonate ions (Berhanu Gizaw, 1996 and references therein).

The MER provides suitable geochemical environment for sodium, chloride and fluoride dissolution in the water. The Rift waters have high residue at 180°C that varies between 600–7200 mg/L (see Table 1), which characterises them as mineral water. The high mineral content could be due to long residence time, high rate of water-rock interaction, less resistance of the host rocks to the weathering processes, high temperature of the water reservoirs which facilitate the removal of elements from the host rocks, and high rate of evaporation. It seems that these processes are active in the MER. The distribution and the concentration of chemical elements in the waters of the Rift is a function of the rock chemical composition. The successive ion exchange processes remove the elements from the rock and enrich thermal waters. Consequently, the input of mineralised thermal water deteriorates the quality of surface water.

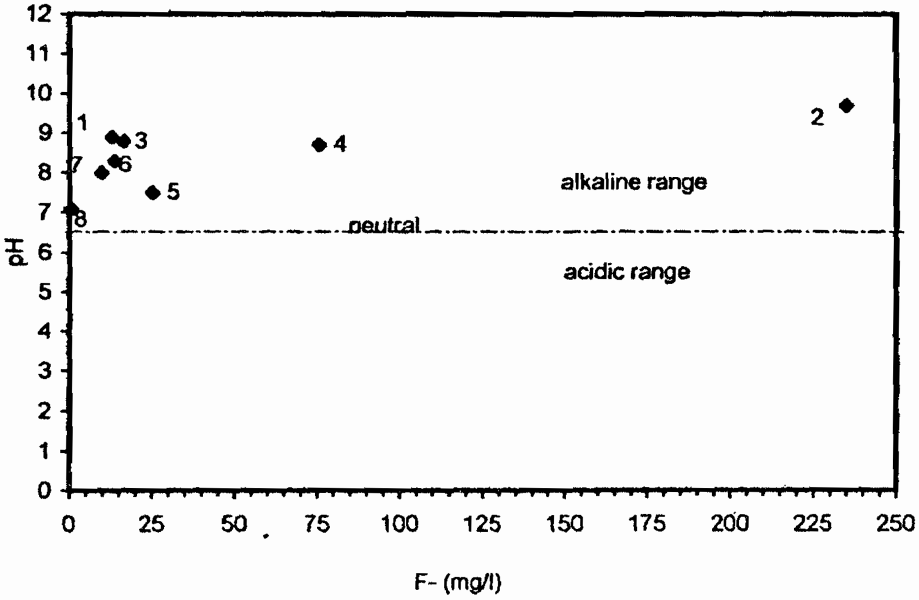

Fig. 1. **Water facies in the study area.** 1, Lake Langano; 2, Lake Shalla; 3, Edu Geysers; 4, East Shalla spring; 5, Oitu spring; 6, Gergedi spring; 7, Wonji Bulbula spring 8, Boku steam.

SAMPLING AND ANALYSIS

For the chemical analysis of the required ions (major and trace elements), six thermal springs, three lakes supplied by hot springs, twenty four samples from bore holes have been collected with plastic bottles and transported to the analytical laboratory with a mobile refrigerator to maintain the sample temperature at 4°C. The representative sampling points are shown in Figure 2. In-situ measurement of temperature, pH, and Electrical Conductivity (EC) of the samples has been carried with appropriate digital instruments. Major and trace elements have been determined by Atomic Absorption Spectrophotometer and major anions have been analysed by UV/VIS Spectrophotometer in the University of Cagliari, Italy. The analytical error varies between 4 to 7%. High error

error percentages may be induced due to sample transportation. The available chemical data have been critically evaluated with respect to major and trace inorganic chemical pollutants.

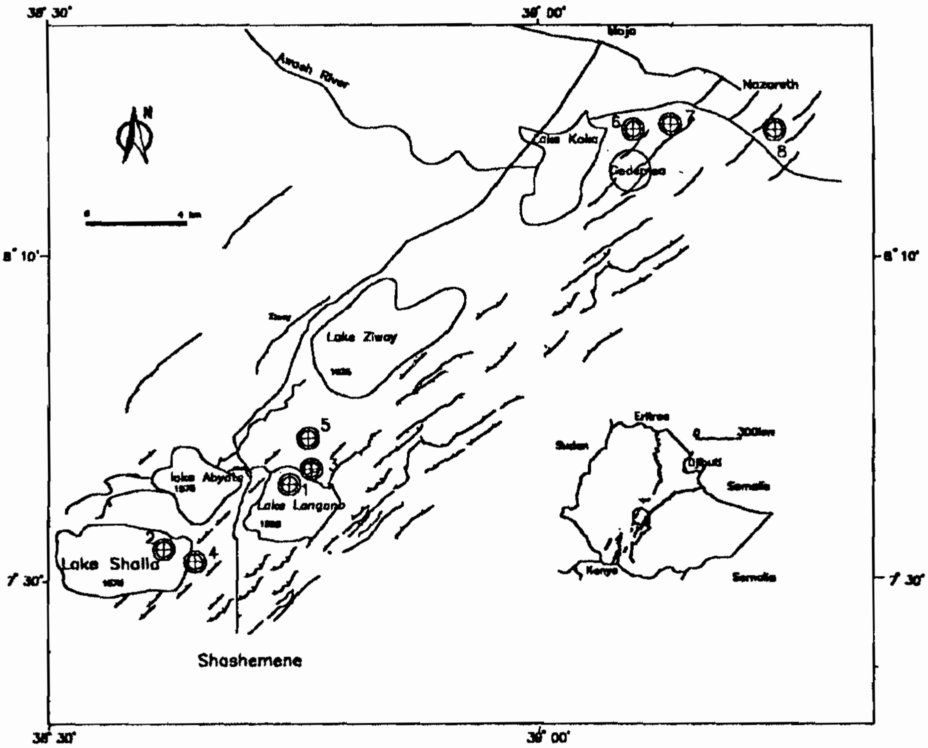

Fig. 2. Location of sample area (1, Lake Langano; 2, Lake Shalla; 3- Edu Geysers, 4- East Shalla spring 5-Oitu spring, 6- Gergedi spring, 7- Wonji Bulbula spring, 8- Boku steam).

ANALYTICAL RESULTS AND DISCUSSION

The analytical results of the various waters in the studied area are reported in Table 1. The concentration of major ions and trace elements is higher in the thermal springs than in the surface water bodies. However, some lakes show high concentration of fluoride, which can arise from calcium depletion in the water (Berhanu Gizaw, 1996), thus prohibiting calcium fluoride precipitation. Consequently fluoride ion will be concentrated in the surface water bodies (e.g. Lake Shalla).

Toxic chemical constituents such as Li, Sr, Pb, Cu and Hg are found in greater concentrations in thermal springs. Their continuous input from thermal springs into fresh surface water bodies is changing the overall chemical composition of fresh surface water bodies. Hence, lakes and rivers, which receive recharge from hot springs, are under their chemical influence.

Even the condensed Boku steam near Nazareth contains appreciable amount of chemical constituents where steam acts as a good transporting medium. As a result large number of thermal springs carry toxic metals and anions from deep groundwater to the surface. According to Kafri *et al.* (1989) at lower temperatures, up to 57°C, the fluoride concentration does not change. This indicates that high ground temperature favours easy removal of fluoride from rocks.

Inorganic constituents

Since obsidians and pumices contain relatively greater amount of fluoride (Gezahegn Yirgu *et al.*, 1999), weathering and hydrothermal activities can release large amount of fluoride into groundwater. The sharp increase in fluoride from mafic to acidic rocks has been explained by fractional crystallisation processes, which concentrate incompatible elements in the residual melt (Peccerillo *et al.*, 1995). This concept has also been supported by Gezahegn Yirgu *et al.* (1999), who demonstrate that fractional crystallisation from basaltic magma or partial melting of a basaltic lower crust are responsible for the enrichment of fluoride and chloride in acidic volcanic rocks. In line with above observation groundwater in basaltic aquifers are known to have low concentration of fluoride as it has been found, for example, in the Debre Zeit area 0.3-1.8 mg/L (Tamiru Alemayehu, 1992). It is, therefore,- possible to hypothesise that, even in the other parts of the Rift, groundwater in the basaltic aquifers would have low fluoride content.

Table 1. **Newly acquired analytical results on chemical constituents of water in the Rift.** [Lake Langano (1); Lake Shalla (2); Edu Geyser (3); East Shalla spring (4); Oitu spring (Langano) (5); Gergedi spring (6); Wonji Bulbula spring (7); Boku Steam (Nazareth) (8)].

Parameters	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Temp. at source (°C)	31	28	95	93	63	43	35	-
pH at source	8.9	9.7	8.8	8.7	7.5	8.3	8	7.1
EC (µS/cm)	3250	41200	5850	16180	6410	1710	1690	100
Resi. at 180°C (mg/L)	1273	7200	2080	5890	2320	653	617	34
Turb. (mg/L SiO_2)	31	0.15	0.45	0.7	0.4	0.09	0.11	0.22
Ca^{2+} (mg/L)	11.4	6.2	4.5	3.8	10.2	8.1	8.7	4.4
Mg^{2+} (mg/L)	2.3	0.71	0.064	0.38	2.3	0.65	1.1	0.07
Na^+ (mg/L)	400	6900	750	2225	800	207.5	205	10
K^+ (mg/L)	22.8	230	27.2	22.4	60	12.8	13.6	0.6
Al^{3+} (mg/L)	5.8	0.15	0.26	1.7	0.06	0.02	0.06	0.05
HCO_3^- (mg/L)	612	<1	720	3038	85.4	500	505	18
CO_3^{2-} (mg/L)	9.12	5563.7	-	-	541.6	-	-	-
SO_4^{2-} (mg/L)	10.8	178	360	26	12	11.2	14.5	0.57
Cl^- (mg/L)	192	3550	570	1635	568	32	35	10

Table 1. (Contd.)

Parameters	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
NH_4^+ (mg/L)	1.1	0.11	0.37	0.7	0.46	<0.05	13.6	<0.05
NO_2^- (mg/L)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
NO_3^- (mg/L)	28	83	3.4	17	2.4	1.2	1.7	0.7
PO_4^{3-} (mg/L)	0.08	2.1	0.27	0.2	0.16	0.07	0.12	0.09
F^- (mg/L)	12.8	235	16.5	75.5	25	13.7	9.8	0.38
Fe tot. (mg/L)	4.2	0.063	0.09	1.3	0.14	0.04	0.02	0.05
Mn^{2+} (mg/L)	0.14	<0.01	<0.01	0.07	0.16	<0.01	<0.01	0.01
Cu^{2+} (mg/L)	<0.01	<0.01	0.03	<0.01	<0.01	0.01	<0.01	<0.01
Pb^{2+} (mg/L)	0.03	<0.01	0.09	0.01	0.02	0.03	0.02	<0.01
Hg^+ (mg/L)	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Sr^{2+} (mg/L)	0.04	0.05	0.27	0.19	0.06	0.3	0.03	<0.01
Li^+ (mg/L)	<0.02	0.1	0.35	0.5	0.58	0.04	<0.02	<0.02

pH represents negative logarithm of hydrogen ion concentration, **EC** represents Electrical Conductivity, **Resi.** represents the solute Residue found at 180° C, **Turb.** represents Turbidity of water.

The major thermal aquifers in the Rift are found in the acidic rocks mainly constituted by pyroclastic deposits such as ash flows, unwelded tuffs etc. (Tesfaye Chernet, 1982; Berhanu Gizaw, 1993; Darling *et al.*, 1996; Tamiru Alemayehu and Vernier, 1997). It seems from these aquifers that after long residence time and strong chemical reactions thermal waters rich in fluoride and toxic metals come out to replenish surface water bodies in the Rift.

The fluoride concentration in the groundwater of the MER has been found to vary between 0.5 mg/L to 253 mg/L (Table 2). High fluoride concentration of up to 180 mg/L is also a characteristic feature of the Kenyan Rift thermal waters (Clarke *et al.*, 1990). The highest natural level reported is 2800 mg/L (World Health Organization, 1970). Since the thermal aquifers of the Rift are made of acidic rocks, which have low calcium, there could be low degree of CaF_2 precipitation. The high fluoride values in the Rift lakes are attributed also to the complete removal of calcium by carbonate precipitation (Berhanu Gizaw, 1996) or calcium undersaturation in the case of Shalla Lake (see Table 1). High fluoride content of the groundwater in the Rift is also found to be related to the high salinity and alkaline environment (Fig. 3), which may favour high concentration of fluoride in the water. In fact, the substitution of fluoride by hydroxyl ions takes place effectively in high pH waters (Hem, 1971) and the activity of fluoride seems to be higher in high temperature medium where high temperature springs are found to contain high fluoride than the low temperature ones. Generally, high ambient temperature, alkaline medium and low calcium concentration favour the abundance of fluoride in waters.

The thermal waters of the MER are also characterised by high sodium, bicarbonate, chloride and fluoride concentrations. Even water from the lakes reflects more or less similar chemical composition as that of the recharging thermal springs, because the lakes act as major destination point for deep mineralised thermal water.

Table 2. **Fluoride concentration (mg/L) in the central part of the Rift and the nearby escarpments** (taken from Tesfaye Chernet, 1982*; Berhanu Gizaw, 1996[ε]; Tamiru Alemayehu, 1993[ξ], 1998[δ], Aynalem Ali, 1999[ϑ], Present work[α], Unpublished personal data[β]).

Locality	F (mg/L)
Assella	0.3 [β]
Ambo	0.35 [β]
Woliso	0.4 [β]
Alem Gena	0.5 [β]
Sebeta	0.55 [β]
Jimma	3.0 [β]
Tulu Bolo	9.8 [β]
Gergedi spring	13.7 [α]
Boku steam	0.38 [δ]
Akaki	0.2-0.7 [ϑ]
Debre Zeit	0.3-1.75 [ξ]
Arsi Negele	1.0 [ξ]
Metehara	1.2 - 4.75 [ξ]
Ziway	1.1-5 *, [ξ]
Nazareth	2.9-5.75 [ξ]
Bulbula Sp.	9.8 [α]
Lake Langano	12.8 [α], 13.7[ε]
Bulbula	14.75 [ξ]
Edu Geysers (Langano)	15-16.5[α]
Oitu spring (Langano)	25[α]
Koka	29.5 [ξ]
Lake Beseka	33 [ξ]
East Shalla Spring	75.5 [α]
Lake Shalla	227 [ε], 235 [α]

The presence of high fluoride in the groundwater corresponds to high fluoride content of the acidic rocks. Shallow wells and cold springs contain low fluoride concentration than the deep groundwater system. The principal contaminant of the fresh surface and shallow groundwater is generated mainly from deep thermal water, which appears on surface in the form of thermal spring and steam (Table 3). The fluoride concentration of 0.38 mg/L, which has been obtained from the Boku condensed water (Nazareth), indicates that there is high degree of steam-rock interaction. In many parts of the Rift, high yield cold springs contain small amount (up to 0.6 mg/L) of fluoride. Therefore, areas, which are relatively devoid of thermal springs, contain small amount of fluoride in the water. The fluoride concentration seems to increase from escarpments toward the Rift centre (discharging zone). For example, taking into consideration Awash River, near Addis Ababa-Ambo road where its major feeding spring is located, the fluoride value is 0.3 mg/L, while near Wonji (axial part of the Rift) its value reaches 1.3 mg/L, a quadruplicate increment in the range of 200 km, which may be attributable to the inflow of thermal water. In some cases, high concentration of chemical compounds change the natural colour of surface waters, as the case of Tikur Wuha River near Awassa town, southern Ethiopia. According to Pitwell (1972), the black colour of Tikur Wuha River, which drains from Lake Shalla, is due to the precipitation of iron as a black lime from organicferrate III when the organic acid content changes.

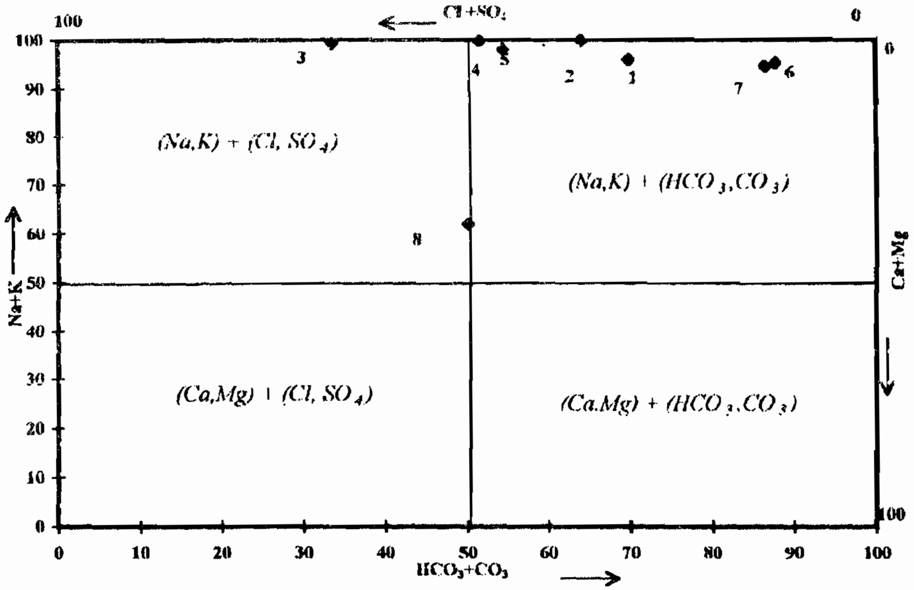

Fig. 3. Variation of fluoride with pH (1, Lake Langano; 2, Lake Shalla; 3, Edu Geysers; 4, East Shalla spring; 5, Oitu spring; 6, Gergedi spring; 7, Wonji Bulbula spring; 8, Boku steam).

Inorganic constituents such as lithium, strontium, lead, copper, mercury and fluoride are carried from deep thermal reservoir by thermal springs and get mixed with the nearby surface waters (rivers and lakes). It is observed that the Wonji Bulbula and Gergedi springs flow towards the Awash River. North and East Shalla springs flow towards Lake Shalla. Edu Geysers and Oitu springs flow towards Lake Langano. The surface water bodies contain relatively small amounts of toxic elements as compared to the recharging thermal springs (Table 3) and therefore, the flow of thermal springs and geysers into the surface waters can be considered as the main determining factor for the chemical composition of the lakes and other surface water bodies considering the chemical parameters Li, Sr, Pb, Cu, Hg and F.

Table 3. Concentrations of hazardous constituents in surface water and deep groundwater.

Source water point			Receiver water point
Edu Geyser	Oitu Spring		Lake Langano
Li 0.35 mg/L	0.58 mg/L		0.02 mg/L
Sr 0.27 mg/L	0.06 mg/L		0.04 mg/L
Pb 0.09 mg/L	0.06 mg/L	⟶	0.03 mg/L
Cu 0.03 mg/L	0.02 mg/L		0.01 mg/L
Hg <0.0005 mg/L	<0.0005 mg/L		<0.0005 mg/L
F 16.5 mg/L			12.8 mg/L
Eastern Shall spring			Lake Shalla
Li 0.58 mg/L			0.1 mg/L
Sr 0.06 mg/L			0.05 mg/L
Pb 0.02 mg/L		⟶	0.01 mg/L
Cu 0.01 mg/L			0.01 mg/L
Hg <0.0005 mg/L			<0.0005 mg/L
F 75.5 mg/L			235 mg/L
Wonji Bulbula spring	Gergedi spring		Awash River (at Wonji)
Li <0.02 mg/L	0.04 mg/L		<0.01 mg/L
Sr 0.03 mg/L	0.03 mg/L		<0.01 mg/L
Pb 0.02 mg/L	0.03 mg/L	⟶	<0.01 mg/L
Cu <0.01 mg/L	0.01 mg/L		<0.01 mg/L
Hg <0.0005 mg/L	<0.0005 mg/L		<0.0005 mg/L
F 9.8 mg/L	13.7 mg/L		3.5 mg/L

Low Cl/F ratio in the thermal springs such as Gergedi and Wonji Bulbula indicates interaction with cold and shallow groundwater. These springs have also low temperature at source. Thermal springs (or boiling springs) such as Edu Geysers, East Shalla springs and Oitu springs, have high Cl/F ratio. Berhanu Gizaw (1996) also made similar observation for Edu Geysers. Lakes, which receive recharge from boiling springs, show relatively high Cl/F ratio.

According to Mazor (1997) mixing of cold and warm water is indicated when sodium and Total Dissolved Solids (TDS) are linearly correlated against chloride ion. As shown in Figure 4, linear relationship exists (correlation coefficient (r)= 0.9524 and 0.9876) between sodium and (TDS) and chloride for the studied waters indicating that cold water is mixed with ascending warm water. The correlation coefficient values are close to 1, which indicate strong correlation between the data points. The sample levelled number 2 deviates from the correlation line indicating mineral enrichment due to other factors such as evaporation in addition to input from thermal springs.

Effect of pollution

Fluoride exists from major to trace amount in drinking water, in air and in foodstuffs. Fluoride taken with water gets distributed rapidly throughout the body and is retained mainly in the skeleton and teeth (World Health Organization, 1984). Proper dose reduces the solubility of enamel under acidic condition thereby providing protection against dental caries. Long-term consumption of water containing fluoride with 1 mg/L leads to such mottling in patients with long standing renal disease (National Research Council, 1977). Even though 1.5 mg/L of fluoride is recommended in potable water supply, in high temperature regions, 0.8 mg/L is sufficient for consumption (Hem, 1971), which could be safely applied for the region such as the MER. This implies that the ambient air temperature usually is the deciding factor for the consumption of fluoride. The studied samples contain very high fluoride concentration that varies between 9.8 mg/L and 235 mg/L and fall above the permitted limit for drinking purpose. Consumption of high dose is acutely toxic to man. Pathological changes include haemorrhagic gastro-enteritis, toxic nephritis and various degrees of injury to liver and heart muscles (World Health Organization, 1984).

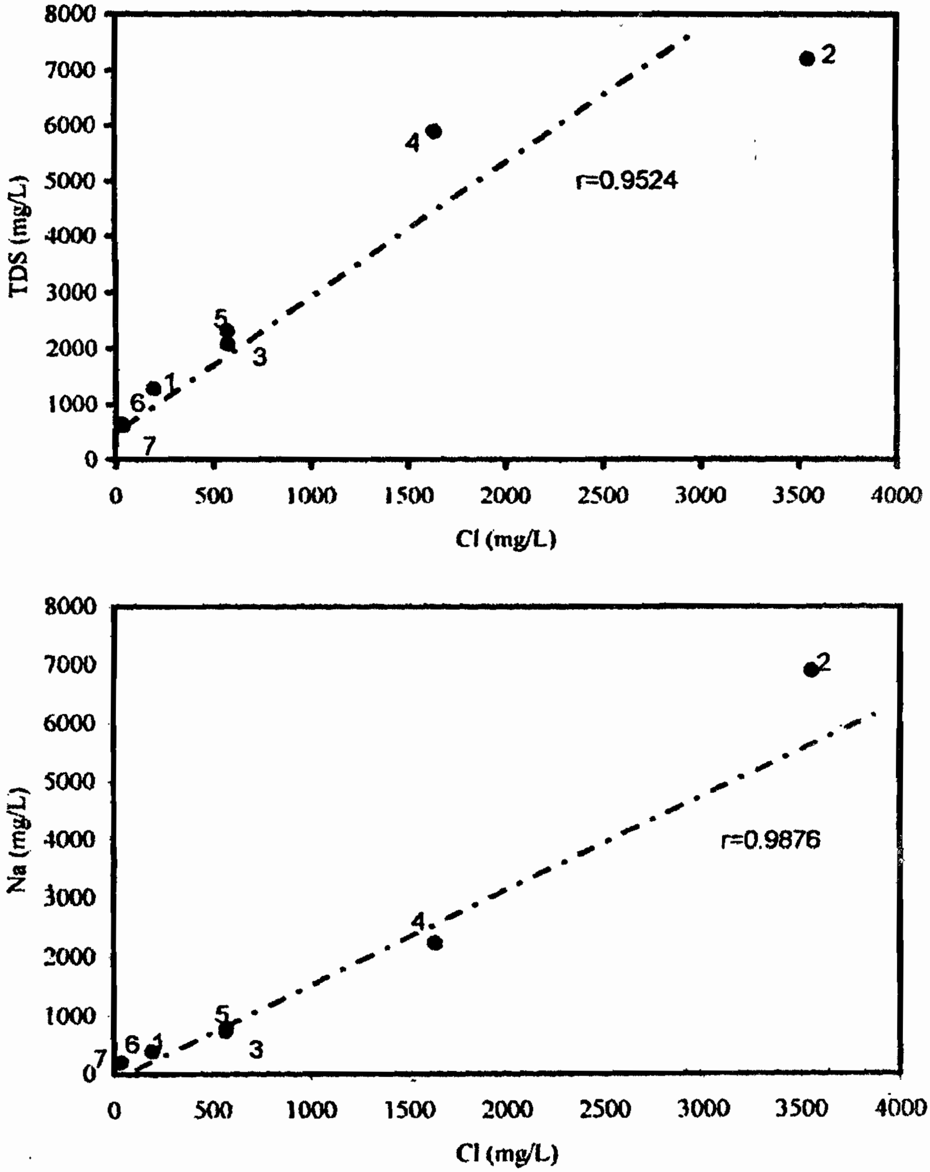

Fig. 4. Cold water and thermal water mixing pattern in the Rift (1, Lake Langano; 2, Lake Shalla; 3, Edu Geysers; 4, East Shalla spring; 5, Oitu spring; 6, Gergedi spring; 7, Wonji Bulbula spring).

In many areas of the central MER, nine out of ten children have mottled teeth where the enamel is totally destroyed by long-term consumption of fluoride-rich high temperature waters. Adding this fact to the lack of proper tooth care, the adults remain with small fragments of incisor in such areas. In the MER, teeth mottling is a wide spread fluoride effect in the local population.

Lead contamination occurs during its processing and from use of products made from it. Lead is distributed in the earth crust at low concentration, sometimes replacing potassium in silicates particularly in feldspars and in phosphates. Generally, it has low geochemical mobility and its compounds have low solubility (Mathess, 1982). According to World Health Organization (1984) the natural lead content of surface water is about 0.001–0.01 mg/L. In the studied area its concentration is high in boiling springs (about 0.09 mg/L) than in cold surface waters (about 0.03 mg/L). The major lead input comes from man-made source, which is rare in the type area.

The natural source of mercury is from degassing of earth's crust (World Health Organization, 1984). Industrial activities related to mercury production contribute significant amounts of this element to the water environment. Because of its mobility, mercury may be transported more readily in hot than in cold water (Hem, 1971). Hence, high temperature springs of the area provide suitable condition for the mercury transportation.

According to World Health Organization (1984) the maximum permissible limit for fluoride is 1.5 mg/L, for lead 0.05 mg/L and for mercury 0.001 mg/L. These constituents are not essential for proper functioning of biological systems and high dose causes acute poisoning (World Health Organization, 1984). They are considered as inorganic chemical constituents of health significance.

It is important to note that lithium, strontium and copper are not strictly related to human health but with his activities. Generally, the present concentration of natural inorganic constituents is not so elevated and these constituents are also restricted in lake and river waters.

CONCLUSIONS

The impact of volcanic and tectonic activity on surface water chemistry is evident from the presence of anomalously high concentration of natural inorganic chemical constituents such as F, Li, Sr, Cu, Pb and Hg. The surface waters, under normal conditions, cannot be highly affected by runoff, recharge etc. by these elements. Based on the presented data, the major source of these contaminants, in the case of the Ethiopian Rift, come from deep groundwater systems through deep running tectonic fractures. Groundwater in deeper volcanogenic aquifers has higher fluoride, lithium, strontium, lead, mercury and copper than surface and shallow groundwater. Since the studied area is characterised by high thermal anomaly, it is possible to conclude that high ground temperature favours the removal of the toxic constituents from volcanic rocks. The continuous discharge of these natural contaminants through non-gravity springs can deteriorate the quality of surface water bodies of the MER.

Further investigation is needed on the genesis and concentration of inorganic chemical constituents in the thermal springs of the Ethiopian Rift.

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