The Fluoride and Trace Metals Contents in the Rift Valley Lake Eyasi Salt a Possible Threat to Human Health

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Abstract

The objective of the present investigation was to determine the actual concentrations of both fluoride and trace metals in Lake Eyasi salts and later to decide whether the salt is safe for human consumption. The importance of knowing optimum concentration of both fluoride and trace metals in human meals cannot be overemphasized, however, if it is left to exceed a minimum set by WHO may be detrimental to human health in both short and long term. This paper has revealed that lake brines and salt crusts contain fluoride concentration with mean values of 273 $mg.dm^{-3}F^{-}$ and 2.30 $g.Kg^{-1}F^{-}$, respectively of which are above the acceptable values. In addition, lead content in lake brines is up to 1.83 $mg.dm^{-3}$ Pb; Cd = 1.40 $mg.dm^{-3}$; Mn = 0.46 $mg.dm^{-3}$, and iron is up to 6.60 $mg.dm^{-3}$ Fe, thus exceeding WHO and Tanzanian limits which are 0.10 $mg.dm^{-3}$ Pb and 0.10 to 1.00 $mg.dm^{-3}$ Fe, respectively. In fact silicon is another contaminant noted in the salt crust which is up to 72.40 $g.Kg^{-1}$. It is imperative for Lake Eyasi salts to undergo a thorough purification to remove all contaminants found and stop population from using impure salts which might have long term health problems (ageing, fluorosis, thyroid gland, hypothyroidism, neurological complications, urinary stone deposition of iron oxide and inflammations).

Keywords: Fluoride, trace metals, lake brine, salt crust, fluorosis

Introduction

Fluoride is the world's 13th most abundant element and constitutes 0.08% of the earth crust. It has the highest electronegativity of all elements in a periodic table. Fluoride is highly reactive, participating in reactions almost with all organic and inorganic substances. At industrial level, fluorine and its compounds are used in various ways to produce plastics, ceramics, pesticides, and pharmaceuticals (Cady *et al*., 1974; Holleman e*t al*., 2001; Wong *et al*., 2003). Fluorochlorohydrocarbons are used in refrigeration and aerosol propellant applications (USEPA, 2000). The importance of fluoride on human teeth was first recognized in 1909 in Colorado USA, where researchers confirmed the link between mottled enamel and high water fluoride levels (NID, 2011). Furthermore the researchers found that water containing fluoride at a concentration of 1.0 parts per million (ppm) appeared to offer some protection while minimizing the extent of dental fluorosis (Dean *et al*., 1937). Indeed, it seems that there is no safe limit for fluoride ingestion in relation to dental fluorosis, but fluoridated level exceeding 0.30 ppm have associated with teeth mottling and discolouration (ECC, 2011).

Generally speaking fluoride chemical behavior and properties are different from other halogens. It is both beneficial oligoelement (needed for growth and bone tissue upholding teeth) and toxic (for adults the lethal does range between 0.20 to 0.35 g F^- per Kg body weight) (Tokalioglu *et al*., 2004). Higher fluoride ion concentration in human body can be resulted by living in a polluted environment and feeding with polluted food (salts, tea etc.). Higher fluoride consumption, above recommended levels (1.00 mg L^{-1}) leads to dental and skeletal fluorosis (Badet *et al*., 2004; Onyango *et al*., 2004). Skeletal fluorosis is a chronic metaboric bone disease caused by ingestion or inhalation of large amounts of fluoride. Vertebral osteosclerosis may result in spinal cord compression (Fisher, 1989). Serious fluoride intoxication can have neurological complications (Long *et al*., 2002), urinary stone formation (Singh *et al*., 2001) and hypocaemia (Pettifor *et al*., 1989) as consequences on endemic patients.

Fluoride is as well known as enzyme destructor. For example fluorides anticaries effect is derived in part from its ability to disturb the enzyme of cariogenic bacteria (Hamilton, 2004; Iwami *et al*., 1995). Fluoride interferes enzyme by attaching itself to metal ions located at an enzymes active site or by forming competing hydrogen bonds at the active site which is not exclusively just on the teeth (Czajka, 2012). Fluoride ingestion can affect almost sixty six (66) enzymes, (Barbier *et al*., 2010) which facilitate the formation of flexible enamel (Judd e*t al*., 1997). Indeed, due to high negativity of fluoride, it interacts with positive charged ions such as calcium and magnesium. Both calcium and magnesium play special role in optimal bone and teeth formation. The completion of calcium and magnesium in teeth and bone, fluoride deranges the delicate bone formation which intensify adverse effects on bone and teeth which amplify malnutrition, calcium and magnesium deficiency (Okazaki, 1987; Teotia *et al*., 1998).

Silicon is a breakthrough ingredient for bone health supplement and it directly impacts all aspect of bone care. In addition, it provides many benefits to bones, also promotes healthier skin, hair and nails (Chumlea, 2007). In fact bone will not form without adequate amounts of dietary silicon. For good bone health, 40 mg of dietary silicon a day is the amount associated with bone density (Nielsen *et al*., 1974). On the other hand excessive amount of silicon can decrease intestinal absorption of calcium and magnesium when very high amounts of silicon are taken in diet (Kayongo et *al.,* 2008). Heavy metals are metallic elements which have a high atomic weight and a density much greater (at least five times) than water. There are more than twenty (20) heavy metals, but four are of particular concern to human health: lead (Pb), cadmium (Cd), mercury (Hg), and inorganic arsenic (As). These heavy metals are four of the top six hazards present in toxic waste sites (Palacios, 2006; Son *et al*., 2007). They are highly toxic and can cause damaging effects even at low concentrations. They tend to accumulate in the food chain and in the body and can be stored in soft (e.g. kidney) and hard tissues (e.g.

bone) (Luis *et al*., 2012). Also these being metals, they often exist in a positively-charged form and can bind on to negatively-charged organic molecules to form complexes. Most of the known metals and metalloids are very toxic to both organism and even those considered as essential, can be toxic if are present in excess (Singh *et al*., 2011). Concentration of several toxic metals and metalloids have been increased as a result of human activities, however this is not a serious case for the targeted Lake Eyasi salts of which was the focus of this research. Toxic metals can disturb biochemical processes constituting an important threat for the health of plants and animals (Jadia et *al*., 2009; Nagajyoti et *al*., 2010; Raskin *et al*., 2000).

Plants and animals often absorb these elements from soils, sediments, and water by contact with their external surfaces through ingestion and also from inhalation of air bone particles and vaporized metals (Mudgal *et al*., 2010; Madaan *et al*., 2009). The required metal ingestion from heavy metals such as Fe and Cu ions to maintain normal body functions such as synthesis of metallo-protein is well established (Gamakaranage *et al*., 2011; Kaosar *et al*., 2004). It is generally known that trace elements such as iron, iodine, fluoride, copper, zinc, chromium, selenium and molybdenum are vital for maintaining health. These trace elements are part of enzymes, hormones, and cells in the body. Insufficient intake of trace minerals can cause symptom of nutritional deficiency (Seaborn, 2002). However, cases of excess intake of trace minerals (metal ions) are credited with pathological events such as the deposition of iron oxides in Parkinson's disease (Candelaria *et al*., 2006). In addition, to aiding neurological depositions (e.g. Alzheimer and amyotrophic lateral sclerosis), (Querfurth, 2010; Peterson, 2011) these redox active metals ions enhance oxidative damage, a key component of chronic inflammatory disease, (Umanzor, 2006) and a suggested initiator of cancer (Elot *et al*., 2007). It is well known that inflammation is a characteristic feature of a wide range of diseases, further potential pathological roles for metal ions are emerging an exemplified by premature ageing (Gonzalez-Cortijo *et al*., 2008). It should be noted that both Cu(I)/(II) and Fe(II)/(III) are redox active metal ions which have been implicated in the free radical theory of ageing as they enhance oxidative stress (Sunilson *et al*. 2009). Nonetheless, beyond radicals, metal ions can disrupt normal cell tissue function through multiple pathways including interactions with proteins and other biomolecules and disruption of membrane potentials.

Regarding lead as one of trace metals can enter the human body in various ways. It can be inhaled from lead paints or waste gases from leaded gasoline. Lead being, toxic most people receive a large portion via food (Tandon *et al*., 2001). Individuals will always absorb more lead in their food if their diets are deficient in calcium, iron or zinc (Siddiqui, 2002; Mahaffey, 1990). Chronic Pb intoxication in adults can result in anemia, some type of cancer; reproductive harm in males while in young children hormonal imbalance of metabolite of vitamin D (Tandon *et al*., 2001; Siddiqui, 2002). Lead can as well alter hematological system by inhibiting the activities of several enzymes; it is distributed particularly to the liver, kidney, as well as it affects the immune system (ADSDR, 2005).

Cadmium is a nonessential heavy metal however; it is considered as one of the most toxic water contaminants and could cause toxicity at any level in organisms, from populations and communities to cell elements (Rashed, 2001). Chromium exists primarily in Cr(III) and Cr(VI) oxidation states, the latter hexavalent species is considered as more toxic in the environment due to its higher solubility and mobility. The species are known to be associated with a spectrum of DNA lesions occurring during Cr(VI) exposure (Reynolds *et al*., 2004). The body of adult has about 15-20 mg of manganese stored in his or her body (Palacios, 2006; Son *et al*., 2007). This nutrient is found from various foods we are eating. Manganese is associated with bone formation due to its role in keeping mineral like Ca in place (Gunter *et al*., 2013). Manganese is required for skin health, it helps to protect skin against damage from ultraviolet (UV) light. Manganase helps in conversion of amino acids or organic acid into sugar, thus some enzymes require manganese to function properly. It can also provide protection against free radical damage, because being a cofactor enzyme called manganese superoxide dismutase (MnDOD), which is a potent antioxidant associated with protection against free radical damage. Such damages are happening to cells, and tissues, skin, and result in asthma (Zheg *et al*., 2011; Pattel *et al*., 2006). On the other hand excess intake of manganese may result in psychiatric illnesses, mental confusion, impaired memory, loss of appetite and neurological problems (Collipp, 1983).

While World Health Organization still believe that 1.00 ppm of fluoride is effective for oral health intervention. Other countries have stopped fluoridating their water supplies due to concern about safety and effectiveness (Pizzo, 2007; NHMRC, 2007). The existing controversy has acted as a driving force in the determination of fluoride concentration of Lake Eyasi salt. This was done in line with establishment of metalloids and trace metals concentrations in the salts of which were as well not known. Because of such conflicting views particularly on the actual fluoride concentration one can ingest per day despite the fact that of the existing WHO standards it was wise for this research to establish the actual fluoride and trace metals concentrations in the targeted salt lake (Lake Eyasi), which is located in northern part of Tanzania in former Arusha region as it can be seen in Figure 1.

Figure 1: The Geographical Boundaries of Tanzania and the Location Lake Eyasi.

Materials and Methods

The samples were collected from Lake Eyasi which is located 3° 30 between 4° 30 south of Equator and 34° 10 to 36° 15 west of Greenwich meridian as it can be seen in Figure 1 and Figure 3 which shows sampling sites.

Determination of Fluoride

The fluoride ion-activity electrode is a specific ion sensor. The electrode is designed to be used with a standard colomel reference electrode and any pH meter having an expanded millivolt scale. The fluoride ion activity electrode can be used to measure activity or concentration of fluoride in aqueous sample by use of an appropriate calibration curve. For both, a Total Ionic Strength Adjustment Buffer

(TISAB) is added to standards and samples to bring them to approximately the same ionic strength; in this way concentration rather than the activity of fluoride ion is determined (Skoog *et al*., 2006). The pH of the buffer is about 5, a level at which the fluoride ion is predominant fluoride-containing species. The buffer also contains an amino carboxylic acid complexing agent, cyclohexylene-dinitrilotetra acetic acid (CDA), which forms strong complexes with heavy metal ions such as iron(II), iron(III), silicon(IV), and aluminum(III), thus freeing the fluoride ion from its complexes with these cations, (Skoog e*t al*., 2006; Frant *et al*., 1966; Lingane, 1967). A good working chemical condition should not be too acidic because hydrogen will form complexes with fluoride, but this tendency is negligible if pH is adjusted to above pH = 5. In alkaline solution the hydroxide interferes with the electrode response to fluoride ion, however, at pH = 8 and below virtually no interference occurs with any measurable fluoride concentration.

Preparation of TISAB Solution

A volume of 57 mL glacial acetic acid was pipetted into a 1000 mL beaker containing about 500 mL distilled water. To the same beaker 58.0 g of sodium chloride and 1.00 g of (CDTA) were added and stirred vigorously. The contents in the beaker were cooled in ice-water for five minutes, and the 5.0 M sodium hydroxide solution was slowly added to the mixture until the solution attained a pH of 5.0 to 5.5. This was diluted to one litre and stored in a stoppered plastic bottle.

Preparation of Standard Fluoride Solution

Exactly 0.221 g of an hydrous sodium fluoride (analytical reagent grade, dried at 120 ^{o}C) was dissolved in distilled water and diluted to the mark in a 1 litre volumetric flask. The stock solution was stored in a stoppered plastic bottle.

Calibration and Analyses

The pH meter with fluoride electrode and reference electrode was switched on, allowed to warm up and stabilize for at least 30 minutes. From prepared fluoride standards solution containing 0.5. 1.0, 2.0, 4.0, 5.0, and 10.0 ppm, volumes of 20 mL were pipette into 100 mL plastic beakers. To each plastic beaker 20 mL of TISAB solution was added by using a pipette. The stirring magnet was inserted into the solution and the electrodes i.e., reference and fluoride electrodes were immersed, the magnetic stirrer was switched on and 15 minutes allowed before recording the mV value. The same procedure was repeated for all standards. The measured potential values were then plotted against the logarithm concentration of the standard fluoride solution.

For solid samples about 1.00 g of each sample was dissolved into 500 mL volumetric flask and topped up to the mark with distilled water. A 20 mL portion of the solution was transferred into 100 mL plastic beaker and mixed with the same volume of TISAB solution. The same procedure was used as described above to obtain potential for each sample. The dilution of the brine was necessary depending on their concentrations. A 20 mL of this liquid was mixed with 20 mL of TISAB solution into 100 mL plastic beaker. Same procedure was used to get the potentials for unknown brine concentrations. The potentials recorded in both solid and liquid samples were substituted into the calibration curve equation and corresponding concentration to each potential was recorded.

Experimental Procedure for Analysis of Metals

Atomic Absorption Spectrophotometry (AAS) instrument was used in the analysis of metal ions. Atomic absorption is the process that occurs when a ground state atom absorbs energy in form of light of a specific wavelength and is elevated to an excited state. The amount of energy absorbed at this wavelength will increase as the number of atoms of a selected element in the light path increases (IM 2380 AAS, 1984). Through measuring the amount of light absorbed, a quantitative determination of the amount of analyte can be made.

***Solid Samples*:**

About 1.00 g of a dry solid sample was weighed and transferred into 500 mL volumetric flask, about 100 mL of distilled water was added to dissolve the solid. Then the volume was made up to the mark with distilled water.

Liquid Samples:

An appropriate volume of 1, 2, to 10 mL (depending on concentration of test sample) was pipette from original sample and transferred into 100 mL volumetric flask and topped to the mark with distilled water. Appropriate dilution factors for both solid and liquid samples were used in the calculation of the final concentrations.

Preparation of AAS Standards

Magnesium: 1000 mg dm^{-3}

A weight of 1.00 mg of magnesium ribbon was transferred in a 50 mL of 5.0 M hydrochloric acid. After dissolution of the metal, the solution was transferred to a 1 dm^3 volumetric flask. The volume was made to the mark with distilled water.

Interferences:

The presence of aluminum, silicon, titanium and phosphorus depresses the magnesium signal. The effects were controlled by addition of 0.10% potassium chloride to the samples and standards. Similar procedure for preparation for AAS standard of each analyzed element was used except for zinc metal where no interferences were indicated. All standard procedure for running AAS, instrument calibration, and analysis were followed in the analyses of all samples indicated in the table of results in next chapter.

Results and Discussion

Fluoride content in both liquid and solid samples were obtained as described under material and methods. The typical linear curve in Figure 2 was used to obtain the values of abscissa (concentration) when given the ordinate (potential). Indeed, fluoride contents in both aqueous and solid samples at different sites (Figure 3.0 Lake Eyasi sketch) were established as can be seen in Table 1.0 and 2.0. This suggests that lake brines, hot springs and the salt crust contain significant amounts of fluoride. Up to a maximum of 654 $mg.dm^{-3}$ of fluoride concentration was recorded in Lake Eyasi brine while associated hot springs have fluoride concentration values ranging from 81 and 140 $mg.dm^{-3}$ F^-.

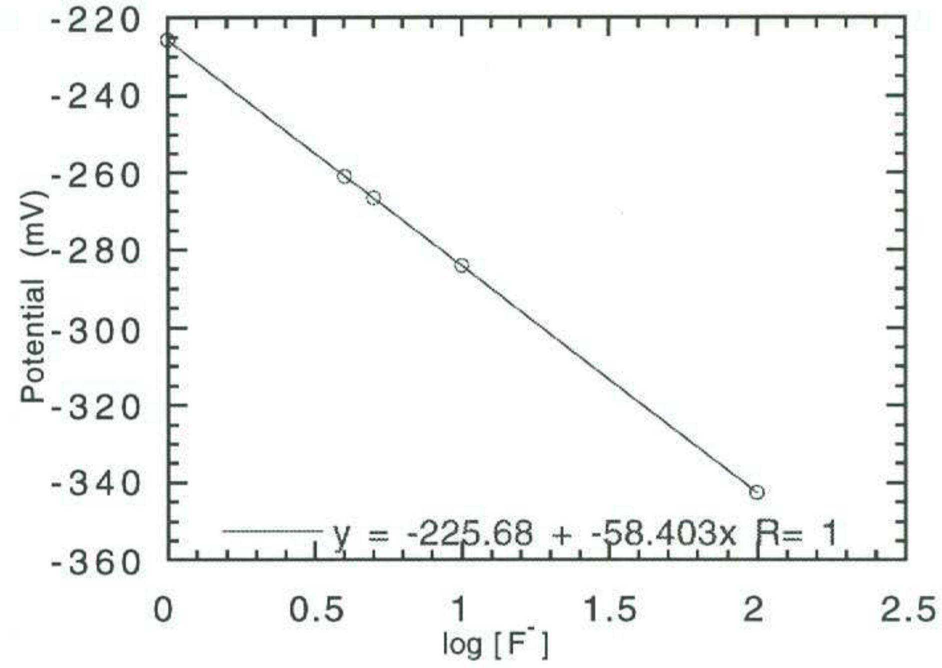

Figure 2: The Calibration Curve for Fluoride Electrode for Collected Samples

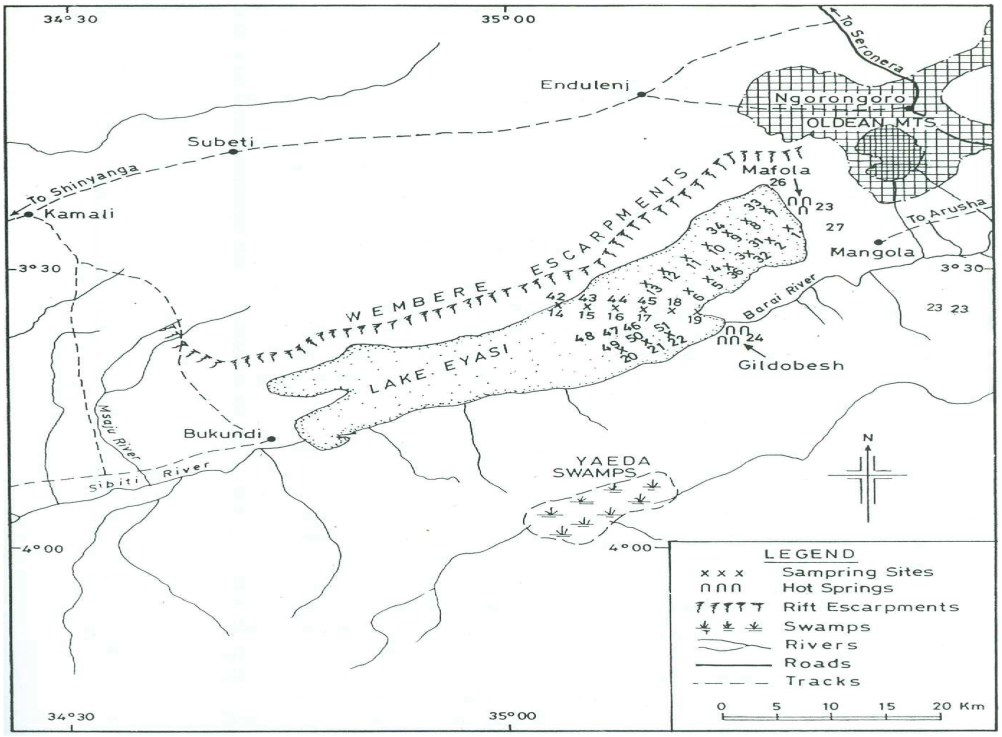

Figure 3: Lake Eyasi Sampling Sites and Hot Springs

This has revealed that these hot springs around the target lake are among the major sources of fluoride in lake brines. The lake brines and salt crusts contain fluoride concentration with mean values of 273 mg.dm^{-3} F^{-} and 2.30 g.Kg^{-1} F^{-}, respectively. The rivers around the target lake contain low levels of fluoride ranging from 1.00 to 8.00 mg.dm^{-3} F^{-}. These values fall well below the limit acceptable for Tanzania standards for drinking water i.e., 8.00 mg.dm^{-3}F^{-} (Table 3) (DWSCOL, 1980). There were no obvious fluoride related health problems (fluorisis) were evident in local populations around the lake as a result of using such drinking water sources. Though teeth discolouration was observed among the people I met with, but this was not enough evidence because there are several reasons which can contribute to teeth discolouration. Tooth discolouration may be a result of extrinsic or intrinsic stains. While extrinsic may be due to coffee, tea, soda, wine, smoking and bad oral habits, intrinsic can be caused by drugs e.g., tetracycline, dental fluorosis i,e., too much fluoride, trauma, dental fillings as well as genetics and ageing. However, one would expect some fluoride related health problems for those who are consuming the lake salts, since it possesses high concentration fluoride. In fact, a low concentration (0.50 to 1.00 ppm) of fluoride is recommended by World Health Organization (WHO) for healthy teeth and bones (APHASM, 1971). It is apparent that, concentration above 10.00 ppm is considered excessive and detrimental to both teeth and bones (Evans, et al., 1995).

Table 1: Fluoride Content in Aqueous Samples

	Sample numbe	$g.dm^{-3}$	$Mole.dm^{-3} x 10^{-3}$	$w/w\ x\ 10^{-5}$
Lake brines	1	0.022	1.158	2.191
	2	0.050	2.632	4.995
	3	0.068	3.580	6.773
	4	0.074	3.895	7.370
	5	0.080	4.210	7.960
	6	0.083	4.368	8.275
	7	0.039	2.053	3.888
	8	0.024	1.263	2.388
	9	0.024	1.263	2.395
	10	0.024	1.263	2.395
	11	0.023	1.210	2.279
	12	0.023	1.210	2.291
	13	0.026	1.368	2.590
	14	0.419	0.022	0.325
	15	0.578	0.030	0.459
	16	0.415	0.022	0.326
	17	0.441	0.023	0.346
	18	0.468	0.025	0.386
	19	0.654	0.034	0.527
	20	0.560	0.029	0.452
	21	0.548	0.030	0.453
	22	0.617	0.033	0.493
Hot spring				

	23	0.140	0.007	0.138
	24	0.081	0.004	0.080
Rivers				
	25	0.008	0.0004	0.008
	26	0.001	0.0001	0.001
	27	0.001	0.0001	0.001
Marine/ Ocear				
	28	0.001	0.0001	0.001
Tape water				
	29	0.0001	0.00001	0.0001

Table 2: Fluoride Content in Salt Crust Samples

Lake brine.mple number	$g.Kg^{-1}$	$Mole.g^{-1}$	% w/w
30	4.250	0.224	0.252
31	1.250	0.066	0.070
32	6.050	0.318	0.344
33	2.088	0.220	0.110
34	4.574	0.241	0.231
35	2.352	0.124	0.121
36	5.158	0.272	0.289
37	2.865	0.151	0.161
38	0.837	0.044	0.411
39	0.837	0.042	0.040
40	0.482	0.025	0.030
41	0.398	0.021	0.023
42	8.928	0.470	0.431
43	0.431	0.023	0.021
44	1.441	0.076	0.089
45	0.226	0.012	0.011
46	0.194	0.010	0.014
47	0.674	0.036	0.050
48	1.989	0.105	0.126
49	0.420	0.022	0.023
50	5.366	0.282	0.267
51	1.014	0.053	0.077

Table 3: WHO and Tanzanian Standards for Drinking Water. $mg.dm^{-3}$

Substance	WHO highest Desirable Levels	WHO Maximum Permissible Levels	Tanzania Standards
Cadmium	-	0.05	0.05
Lead	-	0.10	0.10
Calcium	75.0	200.00	-
Copper	0.05	1.50	3.00
Iron	0.10	1.00	1.00
Magnesium	30.00	50.00	-
Zinc	5.00	15.00	15.00
Chloride	200.00	600.00	800.00
Fluoride	-	0.80	8.00
Nitrate	-	45.00	100.00
Sulphate	200.00	600.0	800.00
TDS	500.00	1500.0	2000.00
Total hardness $Mg.dm^{-3}$	100.00	500.00	100.00
pH	7.0-8.0	6.5-9.2	6.5-9.2

Fluoride is enriched in the target lake brines to an extraordinary degree since villiaumate (NaF) which has high solubility remains the dominant compound after evaporation compared to fluorite (CaF_2) which is relatively less soluble. This has been revealed by percentage composition of salt crust samples with mean value of 1.10% NaF while CaF_2 is below the detection limit (see Table 4). Fluoride concentration in Lake Eyasi seemed to be so high, probably due to unusual inflow sources (hot springs) which possess high fluoride concentrations. In addition, weathering processes which probably have been the primary determinant of surface water fluoride concentration through the geological time scale might have contributed to high fluoride content of this rift valley lake.

Table 4: The Percentage Composition of Lake Eyasi Salt Crusts from the Northern Area

Sample number	30	31	32	33	34	35	36	37	38
NaCl	b.d	50.10	2.70	19.56	37.76	78.80	38.76	16.29	23.21
NaF	1.40	1.92	3.20	0.35	1.46	1.00	2.74	1.65	0.48
Na_2SO_4	63.03	8.16	11.76	1.82	33.36	5.60	44.14	19.38	1.58
Na_2CO_3	14.18	12.72	71.17	53.02	13.13	10.41	8.64	48.67	11.28
$NaHCO_3$	24.15	3.44	4.87	9.63	1.57	2.95	11.66	28.94	12.59
Na_3PO_4	8.23	0.55	1.69	0.52	0.64	2.42	1.00	n.d	n.d
SiO_2	b.d	1.50	3.48	1.76	2.27	0.06	0.77	0.42	29.71
KCl	b.d	0.56	2,52	15.43	1.33	0.08	0.57	0.40	4.43
$MgSO_4$	0.06	0.08	0.04	2.30	0.02	0.01	0.04	0.09	0.31
$CaSO_4$	0.07	0.26	0.03	0.33	0.38	0.08	0.40	1.44	n.d
Total	100.00	100.00	100.00	100.00	99.99	100.00	100.00	100.00	100.00

n.d stands for not determined

Similarly different elements in both liquid and salt crust samples were obtained after running AAS and their respective concentrations can be seen in Table 5.0 and 6.0. The analyses of cations have shown that sodium (Na^+) is the most abundant ion of Lake Eyasi brines, accounting for an average of up to 99% of all cations. It retains its abundance in the salt crust too. The analysis of Indian Ocean brine at Kawe Dar es salaam coast Tanzania by author revealed that sodium constitutes 93%. Lake Eyasi brines are dominated by chloride and sodium as it has been observed in the Great Salt Lake (Western United State) (Nissenbaum, 1980). Both hot springs and the salt crust possess high sodium concentrations as can be seen in Tables 5.0 and 6.0.

Table 5: Concentration of Cations in Aqueous Samples (g.dm^{-3})

Lake brines	Sample No.	Na	Ka	Mg x 10^{-4}	Ca x 10^{-4}	Fe x 10^{-4}	Mn x 10^{-4}	Cd x 10^{-4}	Pb x 10^{-4}	Si x 10^{-1}
	1	0.51	0.03	0.414	0.44	5.86	0.21	0.60	b.d	0.17
	2	0.57	0.04	32.90	1.08	0.80	0.33	14.0	b.d	0.16
	3	0.63	0.05	1.39	0.38	20.00	0.16	12.0	b.d	0.13
	4	0.49	0.09	3.46	1.31	12.10	0.39	0.10	b.d	0.23
	5	0.99	0.04	1.13	0.36	17.10	0.25	b.d	b.d	0.16
	6	0.47	0.09	0.40	0.38	17.00	2.75	b.d	b.d	0.44
	7	0.46	0.10	1.24	0.32	b.d	0.22	b.d	b.d	0.28
	8	0.46	0.10	1.07	0.30	15.71	0.21	b.d	b.d	0.18
	9	0.37	0.09	0.34	0.40	6.34	0.40	b.d	b.d	0.20
	10	0.28	0.10	1.30	0.47	2.56	0.16	b.d	b.d	0.20
	11	0.28	0.10	1.30	0.31	18.00	0.18	b.d	0.10	0.31
	12	0.28	0.10	1.30	0.44	2.05	0.25	b.d	b.d	0.25
	13	0.28	0.09	1.00	0.44	6.74	0.25	b.d	b.d	0.21
	14	145.0	0.58	220	b.d	28.00	2.80	b.d	10.3	0.16
	15	43.01	0.37	650	400	41.00	3.51	b.d	17.3	0.18
	16	98.23	0.32	120	b.d	0.03	2.67	b.d	12.5	0.22
	17	95.62	0.53	760	1290	0.01	1.94	b.d	11.1	0.10
	18	43.70	0.40	215	b.d	34.00	2.61	b.d	12.9	0.18
	19	16.27	0.35	310	b.d	0.04	3.22	b.d	18.3	0.14
	20	81.70	0.37	680	2180	31.00	3.42	0.60	15.0	0.14
	21	60.61	0.33	910	670	66.00	2.55	14.0	14.6	0.14
	22	32.70	0.44	2150	1690	0.45	4.61	12.0	13.0	0.25
Hot spring	23	1.14	b.d	b.d	b.d	b.d	b.d	0.10	b.d	0.21
	24	4.28	0.09	680	180	b.d	b.d	b.d	b.d	0.04
Rivers	25	0.05	b.d	5.70	11.6	b.d	b.d	b.d	b.d	0.08
	26	0.15	b.d	1130	483	b.d	b.d	b.d	b.d	0.27
	27	0.01	b.d	790	442	b.d	b.d	b.d	0.40	0.27
Ocean	28	0.12		498	343	b.d	b.d	b.d	b.d	0.02
Tape water	29	0.01	b.d	346	487	b.d	b.d	b.d	b.d	0.07

Table 6: Concentration of Cations in Aqueous Samples (g.Kg^{-1})

Lake Salt crust	Sample No.	Na x 10^1	Ka	Mg	Ca	Fe	Mn	Cd	Zn	Si
	30	16.80	0.43	0.05	0.13	b.d	0.01	0.01	b.d	b.d
	31	25.30	2.06	0.13	0.53	1.02	0.02	b.d	b.d	4.84
	32	15.71	5.50	0.03	0.23	0.07	0.01	b.d	b.d	6.78
	33	39.52	9.76	5.54	1.17	b.d	0.01	b.d	b.d	9.93
	34	24.35	4.85	0.03	0.79	b.d	0.02	b.d	b.d	7.37
	35	18.40	0.22	0.01	0.13	b.d	b.d	b.d	b.d	0.15
	36	15.85	1.24	0.03	0.49	0.15	b.d	b.d	b.d	1.49
	37	14.50	0.80	0.07	1.63	b.d	b.d	b.d	b.d	0.74
	38	8.74	9.03	0.24	b.d	9.37	0.06	b.d	b.d	53.34
	39	3.13	17.00	0.24	0.17	7.98	0.06	b.d	0.03	46.62
	40	2.89	12.70	0.23	b.d	13.10	0.07	0.02	0.07	72.40
	41	3.80	10.01	0.18	b.d	8.43	0.05	b.d	0.04	72.35
	42	29.12	0.34	0.08	0.24	b.d	b.d	0.20	b.d	b.d
	43	24.22	0.77	0.10	0.52	b.d	b.d	0.16	b.d	b.d
	44	30.72	0.27	0.06	1.84	b.d	b.d	0.04	b.d	b.d
	45	30.61	0.13	0.06	2.18	0.01	b.d	b.d	b.d	b.d
	46	26.44	0.22	0.11	0.73	0.02	b.d	b.d	b.d	b.d
	47	25.71	0.29	0.24	0.93	0.06	b.d	0.04	b.d	b.d
	48	20.88	0.48	0.21	0.99	b.d	b.d	0.04	b.d	b.d
	49	36.80	0.29	0.14	0.54	b.d	b.d	0.06	b.d	b.d
	50	11.10	0.33	0.40	1.38	b.d	b.d	0.05	b.d	b.d
	51	35.61	0.24	1.63	4.75	b.d	b.d	0.03	b.d	b.d

b.d stands for below detection

The next abundant cation is potassium (K^+), which suggests that may be there is a greater depletion of potassium compare with sodium. Potassium seemed to increase for vertically collected samples from top to bottom 0.80 to 10.01 g Kg^{-1}K^+ (Table 6). This trend may be due to the strong chemical bonding between potassium and silicates which makes it to precipitate to the bottom layers as potassium rich silicates. The concentration of Ca^{2+} and Mg^{2+} in the salt crust are relatively low because most of them have been already lost as precipitates during evaporation concentration and settled to the bottom sediments.

Trace metal constituents in the salt lake brines are important to be examined because heavy metals in high concentrations are known to be toxic particularly when they exceed permissible range for WHO and Tanzania standards. Heavy metal concentration levels upstream are below the WHO standards for drinking water Table 3. All trace elements noted in the lake brines are within permissible range with the exception of lead, iron, cadmium and manganese. The lead content in lake brine is up to 1.80 $mg.dm^{-3}$ and iron is up to 6.60 $mg.dm^{-3}$ thus exceeding WHO and Tanzanian limits which are 0.10 $mg.dm^{-3}$ Pb and 0.10-1.00 $mg.dm^{-3}$ Fe, respectively. The content of iron in the target lake is higher than some of those recorded in other rift valley lakes e.g. Lake Manyara (1.83 $mg.dm^{-3}$) (Quilwi, 1995), Dead Sea (0.02 $mg.dm^{-3}$) (Baker *et al*., 1983) and Ethiopia Rift Valley lakes (4.97 $mg.dm^{-3}$) (Zinabu, et al., 2003). On the other hand, Fe on the target lake is less than that of Lake Shalla (13 $mg.dm^{-3}$) (Wood e*t al*., 1988), and Lake Langano (9.4 $mg.dm^{-3}$) (Wood, et al., 1988).

Also upstream sources have revealed both heavy metals cadmium and manganese have significant concentrations of 1.40 $mg.dm^{-3}$ Cd and 0.46 $mg.dm^{-3}$ Mn, respectively. Indeed, the latter heavy metals Cd is higher than that of Ethiopian rift valley lakes 9 $\mu g.dm^{-3}$ Cd while Mn of the target lake is slightly less than that Ethiopian rift valley which is 0.52 $mg.dm^{-3}$ Mn (Zinabu e*t al*., 2003). The rest of the heavy metals are below detection limit in the crust because most of heavy metal salts possess extremely low solubility hence they precipitate first and accumulate to the bottom sediments. It is true that heavy metals in the lake, along with clays, organics and carbonates are precipitating to the bottom sediments. This was revealed by examination of the vertical layer samples, which were found to possess high Fe contents in the sediments (Table 6). This good characteristic makes the lake to avoid the accumulation of heavy metals in brines and it is self cleansing. During this study there was no obvious human or industrial activities (wheat, barley and coffee estate) upstream, which were going on, therefore some of, Pb, Fe, Cd, and Mn noted in the salt crust should most likely be from geological sources.

Upstream sources also possess significant amounts of silicon of up to 27.00 $mg.dm^{-3}$ Si (Table 5). This reveals that silicon in the target lake was derived mainly from the silicates and the geochemistry of the surrounding terrain. It has been noted that silicon content in the lake brine decreases with raise in salinity and pH of the brine. For the samples with pH ranges from 8.25 to 8.80 and 9.75 to 10.32 their silicon contents are up 44.00 $mg.dm^{-3}$ and 24.90 $mg.dm^{-3}$, respectively. Indeed, salt crust has also revealed the presence of high amount of silicon up to 72.40 $g.Kg^{-1}$ Si (Table 6). In fact, silicon content in the salt crust was variable depending on the position and depth that is why in the northern area solid samples contain significant amounts of silicon while the central part possesses only trace amount. Upstream sources may be another major factor contributing to silicon content in the northern area of the lake. Again Lake Eyasi is situated in an area with active volcanic peaks (Baker *et al*., 1983; Saemundsson, 2010).

Conclusions

The study findings indicate that the Lake Eyasi salt fluoride, metalloids and some trace metals concentrations are above the optimal range set by both WHO and Tanzanian standards. Thus, lake brines have been identified as a major source of fluoride in the salt crust. The salt sodium chloride has been identified as the most abundant compound whereas Na accounting for an average of up to 99 % of all cations in salt brines. The salt contains some elements: Si = 72.40 $g.Kg^{-1}$; Fe = 6.60 $g.dm^{-3}$; Cd = 1.40 $mg.dm^{-3}$; Pb = 1.83 $mg.dm^{-3}$ and Mn = 0.46 $mg.dm^{-3}$, which are relatively above the optimal ranges set by WHO and the majority of all these are likely contributed by geological sources. Indeed, a thorough purification of Lake Eyasi salt is inevitable before the salt is used as normal table salt by people around the lake. Due to relatively large excess concentrations of fluoride, metalloids and trace metals in the target lake salt, this may be accompanied with various health drawbacks, because health impact which goes with such excess covers a wide spectrum of health problems (thyroid gland, hypothyroidism, fluorosis, neurological complications, ageing, mental confusion, impaired memory, loss of appetite, urinary stone deposition of iron oxide and inflammations).

Thus future research plan should specifically focus on the improvement of salt quality as well as allowing health experts to look at the possible health problems among the people who are consuming Lake Eyasi salt particularly those people who are living around the lake. This can be followed by salt harvest because during the dry season the lake contains plenty of salt crust. The limitation of this two years research was that there was no chance to discuss with local people if they were experiencing some health problems which may be the results of consuming this salt.

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References

American Public Health Association Standard Method for the Examination of Water and Wastewater 3rd ed. (1971). Washington.

ATSDR, Draft Toxicological Profile for Lead, US Department of Health and Human Services. (2005). Atlanta, Georgia, USA.

Badet, C. and Richard, Y. (2004). *EMC-Dent*. 1 (1), 40-48.

Baker, B. H., Mohr, P. A. and Williams, L. A. J. (1983). Geology of the Eastern Rift System of Africa. *Geol. Soc. Amer. Special Paper*, 136, 1-67.

Barier, O., Arreola-Mendoza, L. and Dal Rozo, L. (2010). "Molecular Mechanisms of Fluoride Toxicocity" *Chemical Biological Interactions,* 188 (2), 319-333.

Cady, G. H. and Misra, S. (1974). Hydrolysis of Sulfurly Fluoride, *Inorganic Chemistry*, 13 (4), 837-841.

Chimlea, C. M. W. (2007). "Silica a Mineral of Unknown but Emerging Health Importance," *Journal of Nutrition Health and Aging*, 11 (2), 93-110.

Collip, P. J., Chen, S.T., Maitinsky, S. (1983). Manganese in Infant Formulas and Learning Disability," *Ann. Nutr. Metab*. 27 (6), 488-494.

Condelaria, M., Garcis-Arias, A., Cetian, L. and Duenas-Gonzalez, A. (2006). Radio Sensitizers in Cervical Cancer: Cisplatin and Beyond," *Radiat Oncol.,* 1 (1), 15-32.

Czajka, M. (2012). "Systemic Effects of Fluoridation," *Journal of Orthomolecular Medicine*, 27 (3), 123-130.

Dar es salaam Water Supply Corporation-Water Quality Laboratory, (1989). Annual Report.

Deboral, S. Lake Manyara National Park, (1980). Elsevier Scientific Publishing Co. Amsterdam.

Dean, E. and Elvove, E. (1937). Further Studies on the Minimum Threshold of Chronic Endemic Dental Fluorosis, *Public Health Reports*, 52, 1249-1264.

Elot, P., Ahaulcour, F. and Tjalma, W. (2007). Management of Recurrent Cervical cancer, Eur. *J. Gynaecol. Concol.*, 28 (5), 435-441.

European Commission Critical, "Review of Any New Evidence on the Hazards Profile, Heath Effects and Human Exposure to Fluoride and Fluoridating Agents of Drinking water," (2011). Scientific Committee on Health and Environmental Risks (SCHER).

Evans, J. D., Rugg-Gunn, J. A. and Tabari, D, E. (1995). "The Effects of 25 years of Water Fluoridation in Newcastle Assessed in Four Surveys of 5-Year-old Children Overan18-Years Period, *Br. Dent. J.*, 178 (2), 60-64.

Fisher, L. R., Medcalf, W. T. and Henderson, C. M. (1989). "Endemic Fluorosis with Spinal Cord Compression. A Case Report and Review" *Archives of Internal Medicine*, 149 (3), 697-700.

Frant, M. S. and Ross, J. W. *Jr.* (1966). Electrode for Sensing Fluoride Ion Activity in Solution. *Science*, 154 (3756), 1553-1555.

Gamakaranage, C., Rodrigo, C., Wearasinghe, S. Gnanathasan, V. P. and Fernando, H.(2011). Complications and Management of Acute Copper Sulphate Poisoning; A Case Discussion, *J. Occup. Med. Toxicol*., 6 (1), 34-38.

Gonzalez-Cortijo, L. and Corballo, N. (2008). Novel Chemotherapy Approaches in Chemoradiation Protocal. *Gyneco. Onco*l., 110 (3), 45-48.

Gunter, T. E., Gerstner, B. and Gunter, K. K. et al. (2013). "Manganese Transport Via the Transferring Mechanism," *Neurotoxicology*, 34 (1), 118-127.

Hamilton, R. I. Biochemical Effects of Fluoride on Oral Bacteria, (2004). *Journal of Dental Research*, 69 (5), 660-667.

Hollemen, A. F. and Wiberg, E. (2001). "Inorganic Chemistry" Academic Press: San Diego.

Instruction Model 2380 Atomic Absorption Spectrophotometer, (1984). The Perkin–Elmer
New York.

Iwami, R. I., Hata, S., Schachtele, F. C. and Yamada, Y. (1995). "Simultaneous Monitoring of Intracellular pH and Proton Excretion During Glycolysis by Steptococcus Mutants and Streptococcus Sanguis: Effect of Low pH and Fluoride" *Oral Microbiology and Immunology*, 10 (6), 355-359.

Jadia, D. C. and Fulebar, H. M. (2009). Phytoremediation of Heavy Metals: Recent Techniques,"*Africa Journal of Biotechnology*, 8 (6), 921-928.

Judd, F. G. (1997). *Good Teeth: Birth to Death-Prescription for Perfect Teeth*, Research Publications. Co., Glendale, Calif. USA.

Kaosar, A., Kazuki, S., Sotashi, I. and Hiroshi, H. (2004). Reducing Effect of Ingesting Tannic Acid on the Absorption of Iron, But not of Zinc, Copper, and Manganese by Rats, *Bioscience Biotechnology and Biochemistry and Agrochemistry*, 68 (3), 584-592.

Kayngo, H. and Julson, L. J. (2008). Effects of High Levels of Dietary Silicon on Bone Development of Growing Rats and Turkeys, Fed semi-purified Diet," *Biological Trace Element Research*, 123 (3), 191-201.

Lingane, J. J. (1967). "A Study of the Lanthanum Fluoride Membrane Electrode for End Point Detection in Titration of Fluoride with Thorium, Lanthanum, and Calcium," *J. Anal. Chem.* 39 (1), 881-889.

Long, Y. G., Wang, Y. N., Chen, J., Jiang, S. F. Nordberg, A. and Guan, Z. Z. (2002). Chronic Fluoride Toxicity Decreases the Number of Nicotinic Acetylcholine Receptor in Rat Brain," *Neurotoxicol. Teratol.*, 24 (6), 751-757.

Luis, A., May-Ix, J., Abriel, R., Martha, M., Arturo, F., Castellanos, R., Chel, G., Madaan, N. and Mudgal, V. (2009). "Differential Tolerance Behaviour of Safflower Accessions to Some Heavy Metals," *Int. J. Apply. Environ. Sci.*, 4 (4), 413-420.

Mahaffey, K. R. (1990). "Environmental Lead Toxicity Nutrition as a Component of Intervention," *Enviro. Heath Perspect*, 89, 75-78.

Mudgal, U., Madaan, N., and Mudgal, A. (2010). "Heavy Metals in Plant: Phytoremediation: Plant Used to Remediate Heavy Metal Pollution," *Agric. Biol., J.*, 1 (2), 40-46.

Nagajyoti, C. P. and Lee, D. K. (2010). Heavy Metals Occurrence and Toxicity for Plants: A Review. *Environmental Chemistry Letters*, 8 (3), 199-216.

National Health and Medical Research Council Public Statement: The Efficacy of Fluoridation, (2007). NHMRC, Canberra.

National Institute for Dental and Craniofacial Research, (2011). *The*

Story of Fluoridation, NIDCR Bethesda, Md, USA.

Nielssen, H. F. and Sandstead, H. H. (1974). Are Nickel, Vanadium, Silicon, Fluoride and Tin, Essential for Man? A Review" *Journal of Clinical Nutrition*, 27 (5), 515-520.

Nissenbaum, A. (1980). Hypersaline Brines and Evaporitic Environments; Elsevier Scientific Publishing Co., New York.

Okazaki, K. (1987). "$Mg^{2+}F^{-}$ Interactions During Hydroxyapatite Formation," *Magnesium*, 6 (6), 296-301.

Onyango, S. M., Kojima, Y., Aoyi, O., Bernardo, E. C. and Matsuda, H. (2004). Adsorption Equilibrium and Solution Chemistry Dependence of Fluoride Removal From Water by Trivalent-Cation Exchanged Zeolete F-9. *J. Colloidal Interface Sci.*, 279 (2), 341-350.

Palacios, C. (2006). The Role of Nutrients in Bones Heath from A to Z. *Crit. Rev. Food Sci. Nutr.*, 46 (8), 621-628.

Pattel, B. D., Welch, A. A. and Wareham, N. J. (2006). "Dietary Antioxidants and Asthma in Adults," *Thorax*, 61 (5), 388-393.

Peteson, R. C. (2011). "Clinical Practice Mild Cognitive Impairment. N," *Engl. J. Med.*, 364 (23), 2227-2234.

Pettifor, M. T., Schnitzler, M. C., Ross, P. F. and Moodley, G. G. (1989). "Endemic Skeletal Fluorosis in Children: Hypocalcemia and the Presence of Prenatal Resistance of Parathyroid Hormone," *Bone Miner.*, 7, 275-288.

Pizzo, G., Piscopo, M. R., Pizzo, I. and Giuliana, G. (2007). "Community Water Fluoridation and Caries Prevention: A Critical Review," *Clinical Oral Investigations*, 11 (3), 189-193.

Querfurth, H. W. and Laferla, F. M. (2010). "Alzheimers Disease," N. *Engl. J. Med.*, 362 (4), 329-344.

Qulwi, Q. (1995). A Study of Hydrochemistry of Brines and Associated Inflows of Lake Manyara Tanzania. Thesis, University of Dar es Salaam.

Raskin, I. and Ensley, D. B. (2000). "Phytoremediation of Toxic Metals: Using Plants to Clean up the Environment," John Wiley & Sons, New York, NY, USA.

Reynolds, M. Peterson, E., Quierryn, G., Zhitkovich, A. (2004). "Human Nucleotide Excision Repair Efficiently Removes

Chromium-DNA Phosphate Adducts and Protects Cells Against Chromate Toxicity," *J. Biol. Chem*., 279 (29), 30419-30424.

Saemundsson, K. (2010). East Africa Rift System an Overview. Presented at Short Course
V on Exploration for Geothermal Resources Organized by UNU-GTP, GTP and KenGen, at Lake Bogoria and Lake Naivasha, Kenya.

Seabrn, D. C. and Nielsen, H. F. (2002). Dietary Silicon and Arginene Effect Mineral Element Composition of Rat Femur and Vertebra," *Biological Trace Element Research,* 89 (3), 239-250.

Singh, P. P. Barjatiya, M. K. Dhing, S., Bhatnagar, R., Kothari, S. and Dhar, V. (2001). Evidence Suggesting that High Intake of Fluoride Provokes Nephrolithiasis in Tribal Populations," *Urol Res*., 29 (4), 238-244.

Singh, R., Gautam, N., Mishra, A. and Gupta, R. (2011). Heavy Metals and Living Systems: An Overview, *India J. Pharmacol*., 43 (3), 246-253.

Skoog, D. A. and West, D. M. (2006). Fundamentals of Analytical Chemistry, 6th ed., Holt-Sounders International Editions Japan.

Son, E. W., Lee, S. R., Koo, H. J. et al. (2007). Effects of Supplementation with Higher Levels of Manganese on Immune Function. *Arch. Pharmo. Res*., 92 (2), 123-129.

Sunilson, J. A. J., Rejitha, G. and Anandarajagopal, K. et al. (2009). "Cytotoxic Effect of Caytatia Carnosa Leaves on Human Breast Cancer Cell Lines," *Int. J. Cancer Res*., 5, 1-7.

Tandon, S. K., Chatterjee, M., Bhargava, A, Shukla, V. and Bihari, V. (2001). "Lead Poisoning in India Silver Refineries," *Sci. Total Environ*., 281 (1-3), 177-182.

Teotia, M., Teotia, S. P. S. and Singh, P. K. (1998). "Endemic Chronic Fluoride Toxicity and Dietary Calcium Deficiency Interaction Syndromes of Metabolic Bone Disease and Deformities in India," *India Journal of Pediatrics*, 65 (3), 371-381.

Tokalioglu, S., Kartal, S., Sahin, U. and Turk, J. (2004). *Turk J. Chem*., 28 (2), 203-211.

Umanzor, J. and Aguiluz, M. (2006). Cisplatin/Gemcitabine Chemotherapy Along with Radiorherapy in Locally Advanced Cervical Carcinoma: A Phase II Trial. *Gynecol. Oncol.*, 100 (1), 70-75.

United State Environmental Protection Agency, Fluoride Report to Congress Section 112 (n) (16), (2000). Clean Air Act, Washington, DC, USA.

Wong, M. H., Fung, F. K. and Carr, P. H. (2003). " Aluminium and Fluoride Contents of Tea, with Emphasis on Brick Tea and their Health Implications Review" *Toxicology Letters*, 137 (12), 111-120.

Wood, R. B. and Talling, J. F. (1988). "Chemical and Algal Relationships in a Salinity Series of Ethiopian Inland Waters," *Hydrobiol.*, 158 (1), 29-67.

Zinabu, M. G. and Pears, N. J. G. (2003). "Concentration of Heavy Metals and Related Trace Elements in Some Ethiopian Rift-valley Lakes and Their In-flows," *Hydrobiologia*, 492 (1), 171-178.

Zheng, W., Fus, X. and Dydak, K. et al. (2011). "Biomarkers of Manganese Intoxication. *Neurotoxicology*, 32 (1), 1-8.