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Influence of Nambul River on the quality of fresh water in Loktak lake

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The major and trace elements in the water samples of Loktak lake and Nambul river, the most polluted river draining into the lake were determined by using Energy Dispersive X-ray Fluorescence (EDXRF) technique. The physico-chemical parameters as well as the concentration of trace elements so far detected were compared with that of WHO limits for both cases and a comparative study were done to investigate the influence of the river to the quality of water of the lake. The co-efficient of correlation among the elements so far detected from both water samples were observed and it was found to be highest between copper (Cu) and manganese (Mn) was found followed by that of Cu and zinc (Zn) leading to the conclusion that if Cu concentration was higher, then there would be higher concentration of Mn and Zn. Though the polluted water of the Nambul river is drained into the lake, the concentration of different elements in the lake water were found to be within the safe limit prescribed by WHO except for iron (Fe).

Key words: EDXRF, trace element, Loktak lake, Nambul River, Eutrofication.

INTRODUCTION

Some elements present in drinking water at ppm or ppb levels, can improve or affect the function of the human physiology as deficit or excess of certain elements may lead to many diseases. Since drinking water is one of the most essential pathways to uptake harmful heavy metals by people, the quality control is particularly important in water supply. Some of the trace elements known to be essential are Cr, As, Co, Cu, F, I, Fe, Mn, Mo, Ni, Se, Si, Sn, V, Zn, and the other essential major elements are C, H, O, N, S, Ca, P, K, Na, Cl and Mg totaling twenty six essential elements (Madan Lal et al., 1991). Excess or deficit of such elements may lead to metabolic disorder to our body hence we have to keep them in proper level as far as possible. The elements present in the water are mainly dependent upon its source and the environment. Elements entering water bodies are derived from industrial effluents, weathering of rocks, leaching of metals from garbage and solid waste dumps, animal and human excretions, insecticides, fungicides and pesticides etc. Loktak lake is considered as the lifeline of Manipur, due to its importance in the socioeconomic and cultural life of the people. It is the largest natural fresh water lake in the north-eastern region of India with an area of 236.21 km^2 and plays an important role in the ecological and economic security of the region. It is an intermonte lake surrounded by tertiary hills. These tertiary hills, dominantly consisting of sedimentary sequences belonging to Dishang and Barails Surma and Tipam groups with little amount of igneous and metamorphics are the integral part of Indo-Burmese Range now known as Indo-Myanmar Range. There are a number of islands in the lake namely: Thanga, Karang, Ithing Sendra etc.

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The sewage and other waste products from industries in the Imphal town are drained into Nambul river and help directly to dump into the Loktak lake. The quality of water of this river is badly affected while it enters the city as the sewage, waste products from industries are dumped into it. Population of 0.28 million living within Nambul river catchments generates 31,207 m^3 of sewage daily. With rapid urbanization, industrialization and increasing population of the city the river gets polluted day by day leading to the increase of pollution levels of Loktak lake. The pollution of the lake is also being increased day by day due to the use of excessive amount of fertilizers, pesticides, insecticides and fungicides by the farmers, cultivators and people around the lake. Trace metals and their compounds are the non-degradable pollutants and they cannot be destroyed. Again, with the consumption of fishes and other edible plants collected from this lake (if it is severely polluted), the people may risk from many diseases due to food chain. So it is very necessary to analyse the quality of water of the lake. Adoption of suitable elemental analysis techniques for the treatment of polluted water and proper management of it has been a challenging interest in this modern world. Both the trace elements and major elements in the liquid samples can be analysed effectively by EDXRF, NAA and PIXE for their quick, highly sensitive multielemental analysis capability (Heiden et al., 2010; Joshi et al., 2006; Ekbatani et al., 2009; OH Jong-Seok et al., 1990).

MATERIALS AND METHODS

The water samples were collected from 10 different stations in and around the lake in post-monsoon (November) including the heart of it that is, Karang (L7), the island of this lake (N 24°32', E 93°49'; 2516 ft). The map of Loktak lake along with various feeder streams is shown in Figure 1. The collection were done from north western (L1), south-western (L2, L3, L4, L5), southern (Ll0), eastern (L8), northern (L9) and it was done in this season to know the pollution level when there is no raining in Manipur. Similarly, the polluted water samples were collected from 10 different stations about 2 km apart of Nambul river and named as S1, S2 …. S10. The collection was made from upper to lower course of the river within Imphal city area in the same season. Five drops of concentrated HCl were added to each of the samples having 500 ml capacity as preservative and kept it with tight seal. The physico-chemical parameters like pH, turbidity, conductivity and DO were measured on the spot. 1000 ppm of $PdCl_2$ solution was made by dissolving 5 mg of it in 5 ml of distilled water. 200 μl of this solution was added to 50 ml of the water sample. After this the pH of it was maintained at 9 by treating with ammonia solution. 2.5 ml of saturated NaDDTC (sodium di ethyl di thio carbamate, $C_5H_{10}NaS_2.H_2O$) was added to precipitate the metals contents as their carbamates while $PdCl_2$ is added as a co-precipitant. Filtration was done to collect the precipitate on a nucleopore membrane having 2.5 cm diameter and pore size 0.2 μm by using a millipore vacuum filtration unit. The uniform thin layer of precipitate was used for irradiation. The blank target was also prepared by following the same procedure with the NIST standard water (SRM–1643e) as external standard. “Trace element in water”-SRM 1643e was used in different concentrations and calibration was done using them. Water standard of a different concentration was then checked which matched very well with the given value. The samples were analysed by the Jordan Valley Ex-3600 Energy dispersive X-ray fluorescence (EDXRF) spectrometer, which works with an oil-cooled system Rh anode X-ray tube having maximum voltage 50 kV and current of 1 mA. The measurements were carried out in vacuum chamber with a 0.05 mm thick Ti filter which was inserted in between the sample and source so as to find the optimum detection of elements in the sample at anode voltage 14 kV and current 300 mA. These parameters of 14 keV and 300 mA with Ti filter were used mainly for elements between Cr and Zn. One could use higher voltage with different filter and current-voltage settings to detect higher Z elements. The characteristic X-rays emitted from the sample due to the bombardment of primary X-ray from the Rh anode, were detected by the 12.5 mm^2 Si (Li) detector of resolution 143 eV at Mn K_α 5.9 keV, cooled at liquid nitrogen temperature (77K). The spectra were analysed by the inbuilt software called ExWIN integrated with the system (Raychaudhuri et al., 2008). The NIST water standard, (SRM-1643e) was used as external standard reference material.

RESULTS AND DISCUSSION

The various physico-chemical parameters so far measured of the lake along with the mean value of Nambul river are shown in Table 1. The pH of Loktak water was in the range 6.59 to 7.35 which were well within the permissible range of WHO limit (6.5 to 9.2). The turbidity was within the WHO permissible limit (25 NTU) except for water in Moirang site (31.1 NTU) of the lake. Similarly, the conductivity and DO for the lake were within the WHO permissible limits. The comparative mean values of pH, turbidity, conductivity and DO are shown as bar chart in Figure 2. As evident from the figure, the pollution level of Nambul river is far greater than that of the lake. The high value of turbidity signifies the decrease of penetration of light due to suspended particulates including disease causing pathogens, thereby affecting the habitats of many aquatic species living in deep water. These organisms can cause symptoms such as nausea, cramps, diarrhea, and associated headache. Similarly, conductivity was ranging from 78.9 to 152.0 μS/cm, leading to the conclusion that there were many dissolved inorganic materials in the lake which was enhanced by the Nambul river water. This is so because when concentration of salts dissolved increases the conductivity also increases.

The elements detected in the water samples collected from both the lake and river along with their concentrations and WHO limits (Sudarshan et al., 2000) are shown in Table 2. The elements namely: vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc were detected altogether. Further elements namely: Cr, Cu, Zn, Pb, Cd, Mn, Hg had been determined by using Atomic Absorption Spectroscopy (AAS) in the different sediment samples of the lake and their average concentration were found to be 0.38, 0.10, 1.02, 0.10, 1.15, 1.26, 3.53 mg/L (ppm) respectively (Devi et al., 2006). These elements can be derived from rocks namely: (a) Tipam groups consisting of mottled clay, mottled sandy-clay, sandy-shale, clayey shale and sandstone.

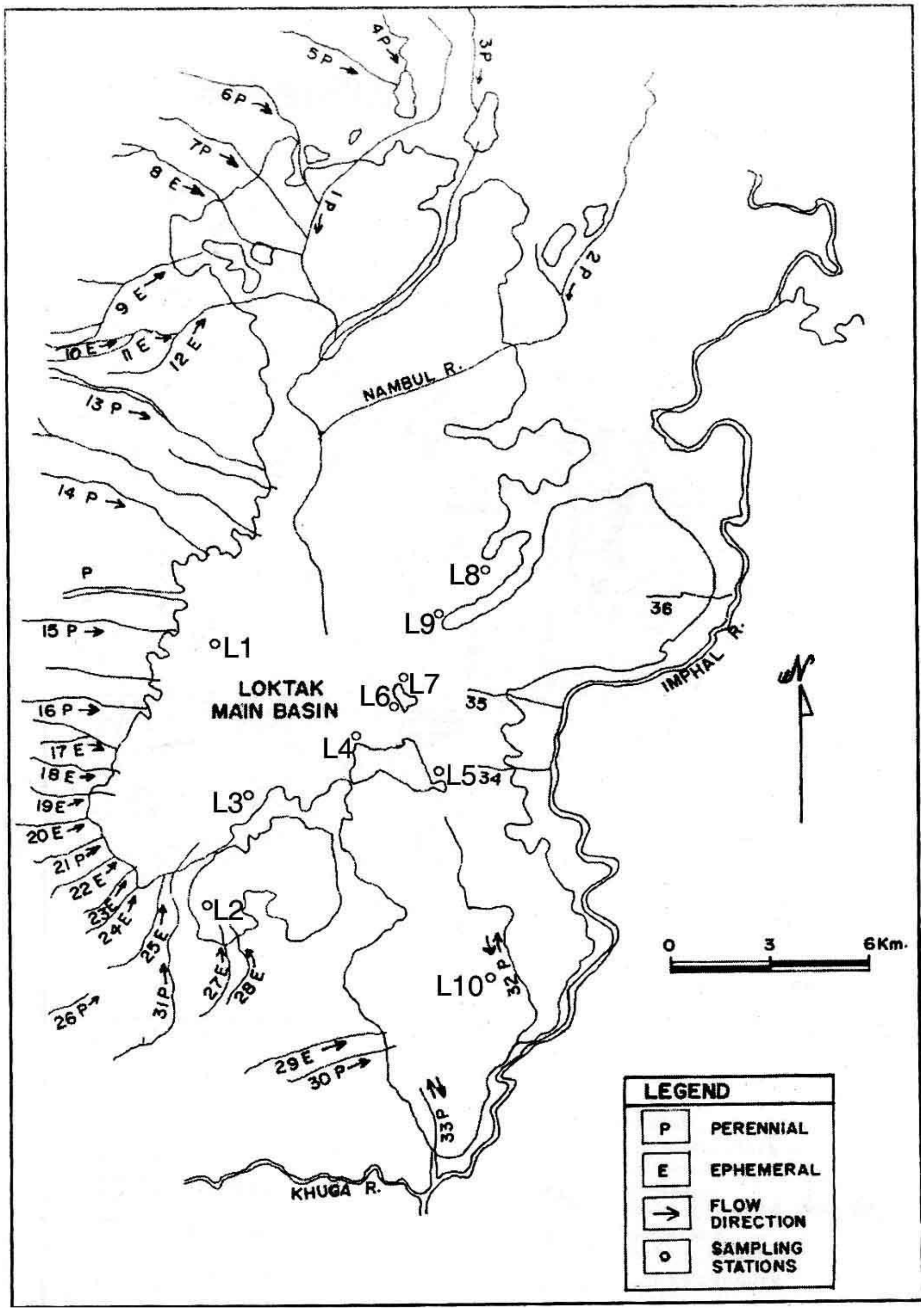

Figure 1. The map of Loktak lake along with its various feeder streams.

Greenish to blue, moderate to course ferruginous sanstone with sady shale, clay often brown to orange due to weathering molasses type of deposits; (b) Disang group consisting of Areneceous rocks, dark gray splintery shale interbedded sandy-shale and siltstone in upper part. Argillaceous gray shale interbedded with mudstone mudstone and minor amount of silt in lower part; (c) Barail group consisting of massive sandstone, alternation of shale and sandstone, and bedded structure, Flysch sediments of turbidite character; (d) Surma group

Table 1. Physico-chemical parameters of Loktak lake and Nambul river (mean value): temperature 25°C.

Sample	pH (1)	Turbidity (NTU) (2)	Conductivity (µS/cm) (3)	DO (mg/l) (3)
L1 (Ningthoukhong)	6.59	1.73	100.5	10.4
L2 (Moirang)	7.10	31.1	81.2	10.45
L3 (Sendra)	7.35	0.77	78.9	10.40
L4 (Thanga Machin)	7.06	0.90	114.0	10.41
L5 (Thanga Maton)	6.99	0.82	105.0	10.39
L6 (Karang Machin)	6.91	0.83	115.9	10.36
L7 (Karang Maton)	6.86	1.50	116.6	10.33
L8 (Mayang Imphal A)	6.73	0.58	115.3	10.01
L9 (Mayang Imphal B)	6.80	1.44	134.8	9.61
L10 (Keibul Lamjao)	6.67	0.62	152.0	7.9
Mean	6.90 ± 0.22	4.02 ± 9.52	111.42 ± 22.09	10.03 ± 0.79
Nambul river mean value	6.73 ± 0.10	19.58 ± 4.15	281.08 ± 123.04	8.54 ± 0.094
WHO Limits	6.5 - 9.2	25 NTU	300 mS/cm	4 - 6 mg/L

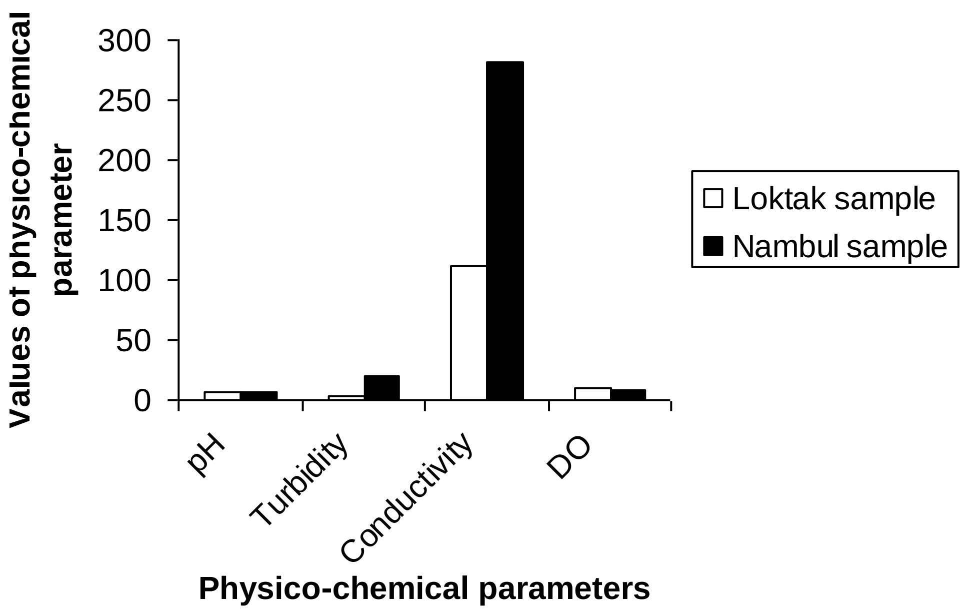

Figure 2. Bar chart of different mean values of physico-chemical parameters of Loktak lake and Nambul river.

consisting of Shale, sandyshale, siltstone, ferruginous sandstone, massive to false bedded ferruginous sandstone, alternation of sandstone and shale with more horizons in the middle and minor conglomerate, transitional characters from flysch to molasses sediments; (e) Metamorphic complex consisting of low to medium grade metamorphic rocks of various composition, phyllitic schist, quartzite, micaceous quartzite, quartz-chlorite-mica achiest, marble etc. Chromium salts impart colour to water. The salts of trivalent chromium are physiologically not harmful but hexavalent chromium salts are known carcinogen and it causes corrosive effects in the intestinal tract and to nephritis when large doses are used. This hexavalent chromium is mutagenic in nature and is highly mobile in soil and aquatic system and also a strong oxidant capable of adsorbed by the skin (Singh et al., 2002). Hexavalent chromium readily crosses cell membranes and is reduced to trivalent chromium in the cellular environment. It is thought that the biological effects of chromium are related to its reduction to trivalent from hexavalent state and formation of complexes with macromolecules present in the biological system. Trace amounts of trivalent chromium are essential in

Table 2. Elemental concentration of Loktak lake water and Nambul river water.

Sample	Element (ppb)								
	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Hg
L1	0.00	1.37	101.96	105.70	0.00	0.21	1.29	16.44	0.00
L2	5.20	1.96	151.96	421.93	2.49	1.39	2.28	38.94	0.00
L3	0.00	1.19	42.43	53.41	0.15	0.26	1.38	34.69	0.00
L4	1.73	1.80	226.50	153.85	0.16	0.29	1.17	18.83	0.80
L5	1.59	2.71	121.41	339.83	0.36	0.18	1.47	44.95	0.30
L6	1.01	1.60	245.30	194.60	0.60	0.16	1.18	8.27	0.00
L7	0.29	2.49	331.33	360.69	0.40	0.00	1.72	36.35	0.20
L8	0.00	2.51	147.78	168.73	0.75	0.06	1.52	13.78	0.00
L9	1.73	3.73	214.62	646.17	2.68	0.01	1.25	13.73	0.00
L10	2.89	3.58	468.41	615.23	2.73	0.00	2.25	22.93	0.20
Mean	1.44	2.29	205.17	306.01	1.03	0.25	1.55	24.89	0.15
S1	8.39	2.64	1290.88	330.32	0.48	0.98	2.53	244.84	0.80
S2	17.36	0.78	778.08	939.21	1.07	0.32	1.92	48.77	0.00
S3	4.48	3.65	1039.70	1143.04	0.55	1.99	2.16	25.91	0.00
S4	4.63	0.93	1707.86	1486.51	1.72	0.00	2.38	69.53	1.00
S5	4.05	1.78	985.78	558.89	0.66	0.23	1.59	23.55	0.50
S6	2.31	2.76	907.97	169.62	0.29	1.10	1.84	19.80	0.50
S7	6.50	5.46	1713.47	563.04	0.00	0.23	1.94	24.93	0.00
S8	0.00	2.85	1550.41	113.99	0.24	1.21	2.38	43.18	2.90
S9	0.00	3.25	1900.68	290.34	0.78	1.07	2.22	61.81	0.80
S10	2.60	1.05	1966.47	301.81	0.80	0.24	1.72	87.68	0.80
Mean	5.03	2.51	1384.13	589.67	0.65	0.73	2.06	65.00	0.73
WHO limits			500	100		20	2000	5000	
Indian limits			50	300			50	5000	

* Hg concentration was determined from AAS.

carbohydrate metabolism in mammals while this element is a co-factor for the action of insulin. The detection of this element is attributed to the washing of chromite rock from surrounding hills and dumping of industrial wastes like ceramic items in the river stream draining into this lake. The concentration of it was found in the range 1.19 to 3.73 ppb which is well below 10 ppb WHO limit. Chromium is essential functioning as a glucose tolerance factor. It is also used for insulin signaling for biological role and thus to sugar metabolism and diabetes (Chen et al., 1993). The relatively insoluble compounds in the soil containing essential iron, manganese, copper and zinc are solubilized by chelating agents as the citrate anion. For manganese the microorganism is bacteria to dissolve the compounds of it in the soil and rocks by the anaerobic action. Its concentration ranged 42.43 to 468.41 ppb within the permissible WHO limit (500 ppb). In most soils, several of these effective chelating agents are produced naturally from soil organic matter by soil microorganisms (Mack, 1964). Highest concentration was observed in the sample (L10) collected from Keibul Lamjao, the only home of Sangai (*Cervus eldi eldi*). This may be due to the coverage of the entire fresh water by the thick floating weeds (40 km^2) leading to the anaerobic action of the bacteria with the soil at the bottom of water. It is essential for the nutrition of both plants and animals, but it is undesirable in domestic water supplies as it causes unpleasant tastes, deposits on food during cooking, stains and discolours laundry and plumbing fixtures.

Iron in natural water usually exists in ferrous; however it is readily oxidized to ferric form and ferric salts are precipitated as rust colour deposits. It imparts a bitter sweet astringent taste to water. Both iron and manganese tend to precipitate as hydroxide. The iron content is attributed to the solubilization of different compounds in the rocks draining of such water in addition to the industrial effluents of different rivers into the lake. The concentration of this element is slightly higher than the WHO limit (100 ppb). So, proper treatment is required for this element. Metal plating waters when discharged into water courses contribute nickel. Increased used of stainless steel and other nickel containing alloys in water

Table 3. Correlation among the elements

Element	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Hg
V	1	- 0.011	0.211	0.526	0.159	0.096	0.359	0.343	- 0.177
Cr		1	0.181	0.026	0.052	0.225	0.226	- 0.089	- 0.044
Mn			1	0.315	- 0.127	0.279	0.618	0.413	0.530
Fe				1	0.436	0.047	0.416	0.041	- 0.124
Co					1	- 0.097	0.252	- 0.066	- 0.182
Ni						1	0.541	0.206	0.259
Cu							1	0.529	0.422
Zn								1	0.266
Hg									1

system also contribute nickel (Manivasakam, 1996). Water soluble nickel salts, such as the chloride are quite toxic to higher plants. They are more active against some fugal parasites, particularly wheat rust. Copper is attributable to the corrosive action of the water on copper and brass tubing compounds to industrial effluents or frequently to the use of copper compounds to control plant diseases. But its concentration is much less than the WHO limit (2000 ppb). So it will not lead to any health hazard with this element for the time being. Further copper can be deposited in metallic form in the distribution pipes with the dissolution of iron. Most of the heavy metals are highly toxic, especially to micro organisms. One of the most commonly used metal is copper in inorganic form. Bordeaux mixture is prepared by mixing a slurry of lime in water into a solution of copper sulphate in water (fungicide). Zinc is commonly found in small quantities in domestic water supplies and industrial water due to corrosion of galvanized iron and brass in condensing and distributing systems. The presence of zinc in the water of this lake may be due to effluents of industrial effluents and solubilization of zinc containing soils by the microorganism or zinc compounds used for plant diseases. The concentration of it ranged 8.27 to 44.95 ppb which is in permissible levels of potable water as WHO limit is 15000 ppb. The highest concentration was observed in the samples collected from Moirang (L5). The presence of zinc and manganese may be also because of the constant use of the fungicides like Dhanuka M-45, Dithaine M-45, ABIC M-45, commonly known as Mancozeb, consisting of zinc ion and manganese ethylene. Vanadium occurs in greatest amount in shales and intermediate igneous rock and cobalt is rich in the soils carrying healthy stocks. The detection of these elements may be due to dissolution of their compounds. The toxic element, like Hg was also detected from the river and the lake but in specific locations. However, this will not make any harmful effect as its concentration is less than 2 ppm of USEPA. The availability of it may be due to draining of industrial effluents into the river, dumping of unused compact fluorescence lamp in surrounding water and use of insecticides, pesticides, mercurials fungicides such as Ceresan dry Phennyl Mercuratare-dust 1%, Agrosan G.N., Hexason (Phenylmercuric accutate plus ethyl mercury-dust %), Agallol Tillex (Mercury chloride 36%) by the farmers living at the periphery of the lake. Another factor may be partly due to the inorganic and arylmercury compounds generated by the action of micro organisms in the sediments of the water body. Summarily, the observed elemental concentrations of the river were greater than that of the lake. The detection of elements like Cr, Mn, Fe, Co, Cu and Zn in the river water were also reported by earlier workers (John et al., 1999). The elemental concentrations of Fe and Mn of the river were too high for drinking purpose. Again, the concentration of phosphate ranges from 0.153 to 1.686 mg/L and that of nitrate ranges from 0.013 to 0.585 mg/l for Nambul river (Sharat et al., 2010). So the water in the lower course of the river from Imphal city can be used for the irrigation purpose if the physico-chemical characteristics of the soils are maintained properly such that it may help to provide the micronutrients for the paddy plants leading to the increase of yield.

The correlation among the detected elements in the two series of water samples are shown in Table 3. As evident from the table, the correlation co-efficient between Cu and Mn was found to be highest followed by that of Cu and Zn leading to the conclusion that if Cu concentration was higher, then there would be higher concentration of Mn and Zn. Similarly, for the toxic element viz. Hg, it was found to be highly correlated to Cu but highly correlated negatively to V and Fe. Again, since the correlation between V and Fe was high, the vanadium present might be attributed from iron containing vanadates. Lastly, the element like S and Ca were also detected in the samples, but their concentrations were unable to be calculated as we used certain energy range only.

Conclusion

The trace elements in water samples of Loktak lake and Nambul River were determined by using EDXRF technique as it is one of the quickest, reliable multi-elemental analytical tool. The physico- chemical parameters and trace element concentrations of Nambul river were almost greater than that of the lake leading the conclusion that it might take some significant role for pollution and eutrofication of the lake. However, the pollution in terms of physico-chemical parameters and trace elements were in the permissible range except for iron. This is due to the dilution of fresh water from different rivers (namely: Thonjaorok River, Imphal River, Moirang River, Khuga River) draining into the lake. Further, pretreatment of iron is required before the water is distributed for public use.

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