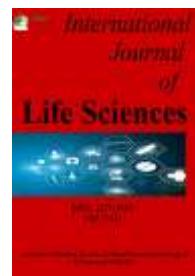


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Research Paper

Trace Element Chemistry of the Major Lakes in and around Nainital City, Kumaun Lesser Himalaya, Uttarakhand

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ABSTRACT

Lakes of Kumaun Lesser Himalaya, India are important water bodies for sustaining the life. These lakes are also the center of tourist's attraction. The lakes have a tectonic origin and are characterized by Dolomites, Limestones, Shales, Silicates and Volcanic Rocks and provide many ecosystem services. The present study was carried with the help of ICP-MS to determine the heavy metals (lithium, beryllium, sodium, magnesium, aluminium, potassium, calcium, titanium, vanadium, manganese, iron, cobalt, gallium, arsenic, selenium, rubidium, strontium, silver, cesium, barium, lutecium, gold, mercury, thallium, lead and uranium) pollution of the Nainital, Bhimtal and Naukuchiatal Lakes. The water chemistry indicates above permissible limit of Hg in all the three studied lakes as 5.825 ug/L, 2.03 ug/L and 2.44 ug/L respectively. The other heavy metals having high concentration levels are Be, Al, Ag and Se. The study suggests that these trace metals concentrations are attributed by anthropogenic as well as geologic factors. The elevated levels of heavy metals; specifically, mercury, beryllium, and selenium, identified in Nainital Lake represent a significant concern for both public health and environmental integrity. The presence of mercury poses substantial risks to human health, particularly through neurological complications and associated health hazards.

1. Introduction

The survival of life on earth depends on water. To support human's daily water needs, nature has provided a great variety of freshwater bodies, including rivers, lakes, and wetlands. Ninety percent of the world's surface freshwater is found in lakes (Mishra et al. 2011). Due to stagnant water, lakes lack the ability to purify themselves they are considerably more susceptible to water contamination as compared to the other water bodies (Khadka et al. 2012). Any artificial obstruction, such as change in nutrients dynamics have severe impacts on the physicochemical characteristics of water, which may negatively impact the variety of flora and fauna in and around the lake (Chakrapani, 2002; Kumar et al., 2019). Indian Himalayas has unique topography provoking the formation of several natural lakes. The lake in the Nainital district of Kumaun Lesser Himalaya, India includes- Nainital Lake, Bhimtal Lake, Naukuchiatal Lake, and Sattal Lake- which is the main sources of freshwater. These lakes constitute popular tourist destination as well (Purushothaman et al., 2012; Sah et al., 2024).

Water demands to meet the needs of the rapidly expanding population in the Nainital district (26.67% population decadal growth rate in 1991-2001 based on Census, 2001) and an increase in tourism-related waste have significantly exacerbated the water quality in the lakes (Sharma, 2014). These contaminants infiltrate the food chain and pose a serious threat to human health (Gautam et al., 2013). In this area, some studies have been undertaken to understand the ecological health of

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the lakes (Ali et al., 1999; Jain et al., 2007; Singh et al., 2008; Gupta et al., 2010). Lakes in this area have been investigated for tectonics and structure (Valdiya, 1980; Valdiya, 1988) accumulation of sediments (Das et al., 1995), water balancing (Kumar et al. 1988) and paleo-climatic circumstances (Chakrapani, 2002; Kotlia et al., 2000) However, no study has been conducted for a comparative assessment of the water quality in the major lakes of Nainital district in such a large number of trace element analyses.

Therefore, the present study was aimed to determine the eco-toxic profiles of heavy metal ions of three different lakes of Nainital district.

2. Material and Methods

2.1 Study Area

Uttarakhand is largely a mountainous terrain region made up of thirteen districts with a predominance of hilly terrain at an altitude fluctuation of 200m to 7,800m ASL. In terms of significance for the environment and as a tourist destination, the three lakes in the district- Nainital, Bhimtal and Naukuchiatal are the most significant bodies of water. Their respective parameters are given in Table-1. District Nainital is located approximately between 80° 14' and 78° 80' East longitude and 29° 00' and 29° 05' North latitude. All lakes are small to medium in size with the Bhimtal Lake as the largest one, covering 72 ha area (Joshi et al., 2016). Lake Naukuchiatal is the deepest, with a maximum of 40.8 m depth. The proposed study area comprises the three virgin Himalayan lakes located in the Nainital District namely Nainital, Bhimtal and Naukuchiatal (Fig. 1). With an elevation of 2084m above mean sea level, the Nainital district is a popular hill area in the Kumaun region of the lesser Himalayas in the state of Uttarakhand.

2.2 Sample Collection and Processing

Water samples were collected from the surface of lakes located in Nainital districts namely Nainital, Bhimtal and Naukuchiatal shown in (Fig. 2). Collection of water samples were done during the month of October i.e., post monsoon and later on were transferred to a 15ml propylene tubes prior to the analysis. The samples were analyzed by Inductively Coupled Plasma Mass Spectrometry (Agilent technologies, 7700x series, ICP MS Mass Hunter, Version 4.1) to identify concentrations of elements in the sample. The samples were digested using the Microwave Reaction System (MWRS). The MWRS is effective and efficient in rapid sample preparation. The microwave was set with a minimum power of 700W and a maximum of 1200 W, the internal temperature was maintained at 200°C to 250°C. The microwave program ramping total time was 1 hour 33 minutes. The vessels were cooled to the room temperature, then the digestates were prepared in a fume hood and diluted up to 10mL and transferred in a 15mL centrifuge tube. The samples were centrifuged at 4000 rpm for 10 min and analyzed by ICP-MS. Multi element calibration standard was used for preparation of calibration standards. Metal free ultrapure grade water was used for preparation of calibration standards as well as dilution of the water samples.

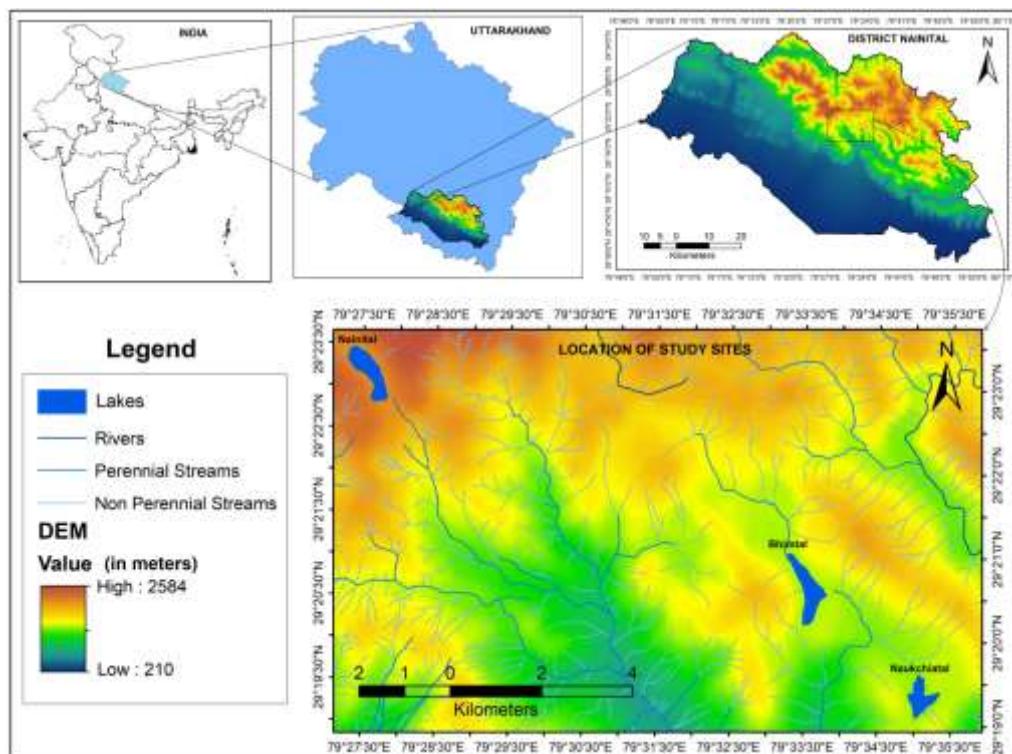
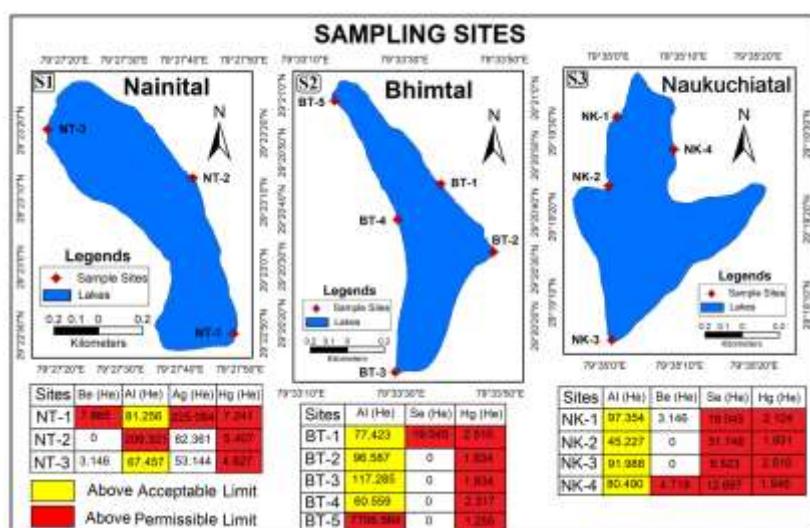


Fig. 1 Location map of the Study Sites, i.e. Nainital, Bhimtal and Naukuchiatal Lake, Kumaun Division, Uttarakhand (based on DEM, field surveying by using GPS).

Table-1: Parameters of the three lakes of the study area (Sharma et al., 1982; Gupta et al., 1989; Khana et al., 1985).

SNo	Parameters	Nainital Lake	Bhimtal Lake	Naukuchiyatal Lake
1	Altitude(m)	1937	1331	1320
2	Longitude	79°28'E	79°32'E	79°35'E
3	Latitude	29°24'N	29°20'N	29°19'N
4	Length(m)	1432	1974	1050
5	Width(m)	423	457	675
6	Max deepness(m)	27.3	25.8	42.25
7	Mean deepness(m)	16.2	11.5	21.89
8	Surface area(km ²)	0.48	0.85	0.375
9	Catchment Area(m)	3.96	11.4	3.25
10	Shoreline	3630	4023	3600
11	Annual rainfall(mm)	2300	1711	NA
12	Max air temp(°C)	24.6	33	NA
13	Min air temp (°C)	0.5	1.5	NA
14	Max water temp (°C)	25	28	NA
15	Min water temp(°C)	10	14	NA
16	Volume of water(m ³)	5907500	4245700	7055000

**Fig. 2** Sample locations on study sites (based on field surveying by using GPS).

2.3 Heavy Metal Testing and Analysis

This research paper presents the findings of a trace metal analysis conducted on 12 water samples collected from three lakes using the ICPMS-7700 series instrument manufactured by Agilent Technologies, USA shown in (Fig. 3). The lakes samples were selected strategically as they represent convergence points for all drainages, allowing for comprehensive analysis of potential contamination sources. The study aims to assess the levels of trace metals present in these water bodies, thereby providing valuable insights into the environmental quality and potential risks associated with contamination. The instrument was operated in helium mode and argon gas was used as plasma gas and carrier gas. The metals were studied while Rhodium metal was used as an internal standard. The composite water samples were taken in airtight acid-washed plastic containers to prevent unpredictably changing characteristics of water. All samples were kept in sampling kits with a 4°C temperature (APHA, 1992). The water samples were then taken to the lab for an experimental investigation. The standard permissible and acceptable limit of water is given in Table-2.

**Fig. 3** ICPMS-7700 Series, Agilent Technology, USA.

Table-2: Bureau of Indian Standard (BIS, 2012) guidelines for trace elements in water.

S. N.	Element (mg/l)	AL (ug/l)	PL (ug/l)	Sample Sites											
				NT- 1	NT- 2	NT-3	BT-1	BT-2	BT-4	BT-5	BT-6	NK-1	NK-2	NK- 3	NK- 4
1	Li	NA	NA	29.23 9	23.38 8	11.694	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	Be	4	NA	7.865	ND	3.146	ND	ND	ND	1.573	1.573	3.146	ND	ND	4.719
3	Na	2000 00	NA	1041 9.37	1374 0.92	17011. 59	4616. 995	4889. 643	4910. 169	4727. 949	8720. 445	4537. 99	5824. 56	419	4149. 8.68 26
4	Mg	3000 00	1000	4542 5.23	4423 1.47	59776. 88	7742. 562	7774. 581	8139. 855	8167. 254	8494. 639	8154. 62	6688. 05	689 8.05 45	6917.
5	Al	30	200	81.25 6	209.3 21	67.457 3	77.42 7	96.58 85	117.2 9	60.55 564	7706. 4	97.35 7	45.22 88	91.9	80.49
6	K	1000 00	5000	485.2 62	701.2 31	3362.6 61	ND	ND	ND	ND	277.8 02	ND	ND	ND	ND
7	Ca	7500 00	2000	5848. 924	6360. 732	7225.9 91	2583. 202	2741. 62	2778. 185	2985. 328	3034. 089	2875. 68	2363. 9	288 7.87 76	3143.
8	Ti	0.1	0.1	ND	ND	ND	ND	ND	1025	3517	4539	ND	ND	ND	ND
9	V	21	21	0.636	0.091	ND	2.633	2.542	1.513	2.33	4.902	0.908	1.453	0.69 6	0.938
10	Mn	100	300	ND	62.42 9	ND	ND	ND	ND						
11	Fe	300	NR	32.25 1	36.90 2	38.472	45.46	47.18	45.52	47.00	266.1	57.66	46.32	52.0	45.46
12	Co	NA	NA	0.377	0.04	ND	0.04	ND	0.377	0.148	8.773	0.606	0.067	0.44 5	0.121
13	Ga	NA	NA	0.294	0.391	0.785	0.589	0.294	0.491	0.294	2.158	0.392	0.098	0.09 8	0.785
14	As	10	50	3.159	2.218	1.613	0.672	0.269	0.403	0.538	3.294	1.412	1.143	ND	1.21
15	Se	10	NR	6.348	9.523	3.174	19.04	ND	ND	ND	ND	19.04	31.74	9.52	12.69
16	Rb	NA	NA	5.192	3.166	7.788	ND	ND	ND	ND	11.27 1	ND	0.507	ND	ND
17	Sr	NA	NA	433.6 33	439.7 73	684.59 4	81.86 2	85.02 1	83.29 8	79.80 3	96.51 3	78.31 8	51.98 6	55.3 85	59.31 1
18	Rh	NA	NA	1103 48	1066 19	10954 5	1044 41	1067 64	9546 3	9596 6	9609 7	1060 02	1021 39	105 977	10276 6
19	Ag	100	NR	225.0 84	82.36 1	53.144	2.473	2.815	2.302	1.67	2.275	5.445	5.471	3.88	2.683
20	Cs	NA	NA	1.991	1.645	2.38	0.433	0.108	0.173	ND	0.628	0.454	0.216	0.23 8	0.173
21	Ba	700	NR	176.3 55	186.1 4	161.85 3	149.5 9	167.6 31	156.7 82	127.8 97	218.9 16	170.4 57	199.1 1	197. 696	157.1 35
22	Lu	NA	NA	0.061	0.114	0.045	0.174	0.144	0.189	0.151	0.212	0.159	0.106	0.16	0.151 7
23	Au	NA	NA	342.8 82	196.5 14	149.67 2	13.32 2	12.92 6	10.94 4	11.42 8	10.01 7	15.41 7	13.76 03	13.9 03	13.27 7
24	Hg	1	NR	7.241	5.407	4.827	2.51	1.834	1.834	2.317	1.255	2.124	1.931	2.51	1.545
25	Tl	0.00 2	0.00 5	7.214	4.719	3.401	0.627	0.572	0.53	0.565	0.634	0.718	0.572	0.63 4	0.425
26	Pb	10	NR	6.783	4.57	3.725	2.686	2.871	2.559	2.564	8.419	2.86	2.839	2.90 3	2.729
27	U	NA	NA	0.181	ND	ND	ND	ND	ND						

NT- Nainital Lake, BT- Bhimtal Lake, NK- Naukuchiatal Lake AL- Acceptable Limit, PL- Permissible Limit, NA- Not Applicable, NR- No Relaxation, ND- Not Detected,

2.4 Data analysis

Variations in the heavy metal concentration among the lakes were assessed by Analysis of Variance (ANOVA) using IBM SPSS version 23. Means and pair wise comparisons of significance were recorded for significant factors.

3. Results

The mean of the heavy metal analysis and ANOVA results (F and P value) of selected lakes is presented in Table-3:

3.1 Non-Carcinogenic Elements

Beryllium: Be is reported from all the lake sites having a concentration range from 0 to 7.865 ug/L. The trace element is found to cross the permissible limit of 4 ug/L in the following lake sites named as NT-1 (7.865 ug/L) and NK-4 (4.719 ug/L) stated in Table-1.

Aluminium: This trace element is reported from every studied lake site and has a concentration range from 45.227 ug/L to 7706 ug/L. It is clearly seen that Al concentration has crossed its acceptable limit of 30 ug/L in every sample site and has reported to exceed its permissible limit in the sites named as NT-2 and BT-6, in Table-1 i.e. in the lakes of Nainital and Bhimtal respectively.

Rubidium: The maximum concentration is found to be 7.788 ug/L from the Nainital Lake.

Silver: Ag is reported to cross its acceptable and its permissible limit from the site of Nainital lake namely NT-1 having a concentration of 225.084 ug/L.

Table-3: The mean of the heavy metal analysis and ANOVA results of Nainital, Bhimtal and Naukuchiatal Lake.

Metal	Nainital Lake Mean \pm SD	Bhimtal Lake Mean \pm SD	Naukuchiatal Lake Mean \pm SD	F	P
Li	20.952603 \pm 7.35873396	Not detected	Not detected	37.417	0.000
Be	2.752704494 \pm 3.716792546	0.62919 \pm 0.861553	1.966217 \pm 2.359461	.855	.454
Na	13793.5809 \pm 2694.89056	5573.04 \pm 1763.575	4677.621 \pm 783.9048	28.759	0.000
Mg	50785.70131 \pm 7327.596405	8063.778 \pm 311.8298	7164.539 \pm 668.1732	158.194	0.000
Al	113.080276 \pm 65.088915	1611.684 \pm 23.43913	78.76485 \pm 23.43913	.761	.492
K	1411.284978 \pm 1325.264271	55.56035 \pm 124.2367	Not detected	4.956	0.032
Ca	6494.8004 \pm 569.253	2824.485 \pm 185.0893	2817.802 \pm 326.8715	130.674	0.000
Ti	0.000 \pm 0.000	18164.85 \pm 20935.81	0.000 \pm 0.000	2.895	.102
V	0.1815659 \pm 0.3056412	2.784082 \pm 1.263952	0.998646 \pm 0.321202	11.565	0.003
Mn	4.4848796 \pm 8.9697591	12.48587 \pm 27.91926	0.000 \pm 0.000	.540	.599
Fe	36.15375 \pm 2.6995677	90.27034 \pm 98.34303	50.3799 \pm 5.675277	.928	.427
Co	0.104424 \pm 0.182911	1.867844 \pm 3.863039	0.309925 \pm 0.25851	.714	.513
Ga	0.367913 \pm 0.292965	0.765259 \pm 0.789162	0.343386 \pm 0.325395	.844	.458
As	2.453702 \pm 0.682342	1.035203 \pm 1.271577	0.941098 \pm 0.637713	3.260	.081
Se	4.761366 \pm 4.097931	3.809093 \pm 8.51739	18.2527 \pm 9.827947	4.334	0.044
Rb	4.432416 \pm 2.680939	2.254208 \pm 5.040563	0.000 \pm 0.000	1.503	.269
Sr	525.2998 \pm 117.4914	85.29942 \pm 6.554972	61.25 \pm 11.76593	67.116	0.000
Rh	107738.5 \pm 2719.695	99746.3 \pm 5413.748	104220.8 \pm 2058.221	4.742	0.036
Ag	97.57339 \pm 87.69376	2.306891 \pm 0.415771	4.369881 \pm 1.348464	5.343	.026
Cs	1.839342 \pm 0.447671	0.268327 \pm 0.25632	0.270506 \pm 0.125545	37.481	.000
Ba	161.2047 \pm 28.93057	164.163 \pm 33.88223	181.0996 \pm 20.71521	.561	.587
Lu	0.0549 \pm 0.0468834	0.174165 \pm 0.027826	0.14577 \pm 0.027826	13.842	.001
Au	197.9382 \pm 103.9452	11.72579 \pm 1.379622	14.08946 \pm 0.924859	14.643	.001
Hg	5.527255 \pm 1.188686	1.950167 \pm 0.489461	2.027389 \pm 0.401975	30.597	.000
Tl	4.424376 \pm 2.0959053	0.585459 \pm 0.044356	0.587196 \pm 0.123559	80.150	.000
Pb	4.635552 \pm 1.507084	3.819696 \pm 2.574238	2.832693 \pm 0.074119	.979	.409
U	0.045128 \pm 0.090257	Not detected	Not detected	1.154	.354

• Indicates the level of significance is 0.05

3.2 Carcinogenic Elements

Gallium, Arsenic and Strontium: The following trace elements namely Ga, As and Sr has been reported from the lake sample sites and has a maximum concentration of 2.158 ug/L from the Bhimtal Lake, 3.294 ug/L from the Bhimtal Lake, and 684.494 ug/L from the Nainital Lake respectively.

Selenium: Se concentration is found to be awfully close to its acceptable limit from the sites named as NT-4 and NK-3. However, Naukuchiatal Lake has Se above its acceptable limit (10 ug/L) and in a state of no relaxation as per BIS regulation 2012 having a mean concentration of 18.25 ug/L. There is also a site named as BT-1 from the Bhimtal Lake having Se concentration of 19.045 ug/L and reported to be above its acceptable limit.

Cesium, Lutecium and Lead: Cs, Lu and Pb are all to be present in trace amounts in the lake sites. However, none have exceeded their acceptable and permissible limit in the study area.

Mercury: The level of Hg has been seen to cross the acceptable limit (1 ug/L) and there is no relaxation above it in the three lakes of the study area situated in the Nainital district. The mean concentration of Hg ranges from 1.42 to 5.52 ug/L. Nainital Lake has shown the max concentration of 7.241 ug/L.

Uranium: U concentration is reported from the Nainital lake site namely NT-1 having 0.181 ug/L.

4. Discussion

ANOVA table reveal that the value of Li, Na, Mg, K, Ca, V, Se, Sr, Rh, Ag, Cs, Lu, Au, Hg and Ti are significantly different among the three lakes. The geological map of the area (Fig. 4) shows that the Nainital Lake is surrounded by the Krol group of rocks comprising dolomites associated with limestone and shale (Awasthi, 1970).



Fig. 4 Geological map of the study area (Valdiya, 1980; Valdiya, 1988; Awasthi, 1970).

On the other hand, Bhimtal and Naukuchiatal Lake lies in the Naghat formation which consists of thickly bedded quartz arenite associated with the penecontemporaneous mafic lava flows (Pant et al, 1999). The source of aluminum in the lake waters is due to the weathering of rocks containing feldspar and aluminum containing rocks. Selenium has its major occurrence in the mafic igneous rocks (Malisa et al., 2001). Volcanic igneous rocks surround the Bhimtal and Naukuchiatal region (Chakrapani, 2002). Therefore, it is assumed that the main cause of selenium contamination in the area is the leaching from the basic volcanic rocks. Low grade uranium mineralization is associated with phosphatic sediments and carbonaceous shale around the Krol-Tal contact in the region of inner Krol belt (Sinha et al., 2016). Mercury is emitted by natural sources and as well as from the volcanoes, geothermal springs, geologic deposit and the oceans. Human related sources primarily include coal combustion, waste incineration, industrial uses and mining (USGS, 2018). Mercury in the Nainital region may be mostly due to the anthropogenic sources through the sewage waste water. But in Naukuchiatal and Bhimtal region, mercury deposits appear related with the geological and anthropogenic sources. The source of silver in Nainital which is found above the impermissible limit might be related with the limestone rock of Krol-Tal formation.

5. Conclusion

Therefore, from the analysis of trace element concentration sites NT-1 and NK-4 are prone to high concentration of beryllium. Silver is found to be above permissible limit in lake site namely NT-1 and selenium have higher concentration above permissible limit in the entire Naukuchiatal lake. Mercury is found to be present in all the entire lakes of the study area with values crossing their permissible limit in every sample sites. Data comparisons with WHO drinking water criteria reveal that the majority of lake water sites are unfit for human consumption. In conclusion, the elevated levels of heavy metals, specifically mercury, beryllium, and selenium, identified in Nainital Lake represent a significant concern for both public health and environmental integrity. The presence of mercury poses substantial risks to human health, particularly through neurological complications and associated health hazards. This finding is particularly alarming given that all three lakes under study serve as primary sources of drinking water, indicating a direct threat to the well-being of local communities.

Furthermore, from an ecological standpoint, the heightened concentration of beryllium in the lake water has the potential to detrimentally impact aquatic ecosystems. Beryllium contamination may lead to a reduction in biodiversity within the lake, thus disrupting the delicate balance of the aquatic food chain. Such ecological disturbances can have far-reaching consequences, ultimately affecting the overall health and sustainability of the aquatic environment. In light of these findings, urgent action is warranted to address the sources of heavy metal contamination in Nainital Lake and mitigate the associated risks to both human health and ecological stability. Implementing effective pollution control measures, enhancing water treatment protocols, and raising awareness about the dangers of heavy metal exposure are crucial steps in safeguarding the health of both communities and ecosystems reliant on these vital water resources. Additionally, ongoing monitoring and research efforts are essential for assessing the efficacy of remediation strategies and ensuring the long-term resilience of Nainital Lake and its surrounding environment. For both residents and visitors, the lake is of the utmost importance and value, making its preservation essential. It has become polluted and is on the verge of losing its original traits as a result of growing urbanisation. Therefore, careful water management and ongoing monitoring of the lake's water are necessary.

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Declarations

Conflict of Interest: The author(s) declares no conflict of interest.

Ethics Approval Statement: There is no any experimental work done on human and animals.

Data Availability Statement: The datasets analyzed during the current study are available from the corresponding author on reasonable request.

Author Agreement: All authors approve the submission of the manuscript.

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