Analysis of Major and Trace Metal Levels in Kashar Lake, Artificial Lake of Tirana, Farka Lake, and Statistical Data Analysis

DAFINA KARAJ[1], DENISA KAÇORRI SALILLARI[2], ELONA SHAHU[3], ELMIRA MEHMETI[3], EDLIRA TAKO[1]

[1]Department of Chemistry,
Polytechnic University of Tirana, Faculty of Mathematical Engineering and Physics Engineering,
ALBANIA

[2]Department of Mathematical Engineering,
Polytechnic University of Tirana, Faculty of Mathematical Engineering and Physics Engineering
ALBANIA

[3]Department of Toxicology and Quality,
Food Safety and Veterinary Institute,
Tirana,
ALBANIA

Abstract: - This study aims to determine the presence and concentration level of major metals and trace elements in the three main artificial lakes of Tirana, namely Kashar Lake, Tirana Artificial Lake, and Farka Lake. The water samples were collected from three different stations on each lake during April 2019. The concentrations of the metals, Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Na, Mg, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, U, Zn, were determined using the ICP-MS method. These concentrations were then compared to EU standards. The results showed that metal concentrations in the water samples were lower than the maximum concentrations allowed by environmental quality standards. Using statistical methods, we estimate the relationships between the metal levels in samples collected from different stations in different lakes. Statistical analysis showed no significant differences in metal concentrations between the different stations and lakes.

Key-Words: - Major metals, trace elements, water, Artificial Lake of Tirana, Kashar Lake, Farka Lake, ICP-MS, Statistical analysis.

Received: March 6, 2024. Revised: August 8, 2024. Accepted: October 7, 2024. Available online: December 4, 2024.

1 Introduction

Water is one of the most essential constituents of the human environment, [1]. Lakes are vital and significant bodies in preserving fresh water and maintaining biodiversity and ecological processes, [2], [3]. Lakes are classified as natural lakes and artificial lakes, which are mainly built in streams in a location where the surrounding geology lends itself to a dam wall and with sufficient upstream catchments to capture run-off, [3]. That way, artificial lakes or reservoirs attract tourism and fisheries and promote aquaculture. On the other hand, if these artificial lakes are not properly designed and maintained, water quality degradation increases over time where accumulating pollutants and sediments can become grossly polluted, [3].

However, the benefits derived from artificial lakes are not without their challenges. Unlike natural lakes, which have evolved over millennia to achieve a delicate balance of ecological processes, artificial lakes are susceptible to human-induced disturbances and environmental degradation. Improper design, inadequate maintenance, and unchecked pollution can exacerbate water quality issues, leading to detrimental impacts on aquatic ecosystems, public health, and socio-economic well-being.

Among polluting substances, heavy metals are considered as dangerous for the aquatic environment, [4]. When heavy metals enter the waters,
they can be bioaccumulated by organisms living in the lakes enter the food chain, and harm predators and humans who consume marine biota, [5]. Heavy metals enter in Lake from two sources, natural and anthropogenic sources. The natural sources could be

natural geological weathering of rocks and soil, directly exposed to surface waters, climate changes inflicted on igneous and metamorphic rocks, etc. On the other hand, the main contributors to anthropogenic sources are the burning of fossil fuels, mining, industrial wastes, transport, the use of fertilizers, pesticides in agriculture, and atmospheric deposition, [6]. Toxic metals can be not eliminated through a biodegradable process and the impact of toxic metals could remain permanent, [7]. Even at low concentrations, heavy metals can damage human body organs and other internal organs of animal tissues easily, due to a lack of good mechanisms for their elimination from the body, [8]. Repeated long-term contact with low concentrations of some of these metals or their compounds may also cause cancer, [9], [10]. They find their way into the human body through various avenues like water, food, air, or even when they are absorbed through the skin upon contact, [11], [12].

As it is known, the content of major and trace elements in lake waters is an indicator not only of their origin and sources of nutrition but also of the ecological state of the catchments, [13], [14]. There are several artificial lakes near Tirana, the capital of Albania. In 2015, two studies were published about the concentration levels of heavy metals in Tirana's artificial lakes. One study focused on Tirana Artificial Lake, [15], while the other studied both Tirana Artificial Lake and Farka Lake, [16]. In this paper, our study focuses on estimating the presence and concentration level of major metals and trace elements in the three main artificial lakes of Tirana, namely Kashar Lake, Tirana Artificial Lake, and Farka Lake. The lakes' selections were due to their importance as regional primary water sources, and their vulnerability to anthropogenic impacts. Additionally, by analyzing the water samples collected from three different stations on each lake we will have a clear picture of the water quality status, identify any potential sources of water contamination, and assess the ecological and health impacts.

2 Materials and Methods

2.1 Area Selected and Samples Collected

The study area encompassed three prominent artificial lakes located near Tirana, Albania presented in Figure 1: Kashar Lake (coordinates: 41.35634°N, 19.726989°E), Tirana Artificial Lake (coordinates: 41.306626°N, 19.82072°E), and Farka Lake (coordinates: 41.308517°N, 19.862312°E). These lakes were chosen based on their significance as primary water sources for the region and their susceptibility to anthropogenic influences.

Water sampling was carried out during April 2019 to capture seasonal variations and ensure representative sampling.

Fig. 1: Map of the lakes taken in the study

A total of three sampling stations were designated within each lake, strategically positioned to capture spatial heterogeneity and potential sources of contamination.

At each station, water samples were collected from approximately 20 cm below the water surface using horizontal PVC sample collectors to minimize surface disturbance and ensure sample integrity.

To prevent contamination and maintain sample quality, we used acid-washed polyethylene bottles for sample collection. Additionally, to stabilize dissolved elements and prevent precipitation during storage, we added 0.5 mL of pure nitric acid to each sample bottle before refrigeration.

The elements were determined according to the International Water Quality Standard, [17], [18].

2.2 Metal Analysis in Water Samples by ICP-MS

The concentrations of major and trace elements in the water samples were determined using inductively coupled plasma mass spectrometry (ICP-MS), a highly sensitive and precise analytical technique capable of quantifying a wide range of elements at low detection limits.

An Agilent 7900 series ICP-MS instrument equipped with a reaction system developed for complex matrix analysis was employed for metal analysis.

Instrumental parameters, including plasma mode, radiofrequency (RF) power, RF matching, sample depth, nebulizer pump rate, nebulizer gas flow, auxiliary gas flow, and plasma gas flow, were optimized for maximum sensitivity and accuracy (Table 1).

The elements were determined according to the International Standard of Water Quality, [17], [18]. A standard solution (Environmental calibration standard, Agilent 5183-4688) containing 5 macros elements (Ca, Fe, K, Mg, and Na) in concentrations of 1000 m g/l and 20 microelements, mentioned above at a concentration of 10 mg/l was applied for the instrumental calibration.

Table 1. Instrumental characteristics and setting for ICP-MS

Plasma Mode	Low Matrix
RF Power	1550 W
RF Matching	1.8 V
Sample Depth	8.0 mm
Nebulizer pump	0.10 rps
Nebulizer Gas	1.07 L/min
Auxiliary Gas	0.90 L/min
Plasma Gas	15.0 L/min
Internal Standard mix	Bi, Ge, In, Sc, Tb, Y

The concentrations of calibration curves of 0, 0.5, 2, 5, 10, and 200 µg/L were used for quantification of element concentration. To ensure the reliability and reproducibility of analytical results, quality control measures, including the analysis of control materials at regular intervals, were implemented throughout the study.

Statistical analyses of data are realized using R studio software, with descriptive statistics and ANOVA employed to compare metal concentrations among lakes and stations. Applying Ward's agglomerative clustering method, we classify elements observed in each lake by concentration levels.

3 Results and Discussion

The results of mean concentration values of major and trace elements investigation in the water samples taken from Kashar Lake, Artificial Lake of Tirana, and Farka Lake, are presented in Appendix in Table 2. These results provide insight into the overall chemical composition of these artificial lakes and can help to determine their environmental quality. The most abundant element among the major elements in all three lakes is sodium (Na), with levels of concentration between 23.25 to 27 mg/L. It is followed by magnesium (Mg) and calcium (Ca), with different concentrations depending on the lake. The highest concentrations of the main elements were observed in the water of the Artificial Lake of Tirana, probably influenced by the local geology.

Regarding trace elements, the presence of mercury was not detected in all three lakes. Thorium (Th) was detected only in Kashar Lake, while beryllium (Be) and thallium (Tl) were not detected or below the detection limit. The results suggest that the contamination levels of trace elements are relatively low. We can also observe that in water samples taken from the Artificial Lake of Tirana, the levels of metals such as chromium (Cr), cadmium (Cd), and silver (Ag) are below the detection limit.

The determination of the concentration level of traces and main metals in Kashar Lake and Farka Lake is realized for the first time in this study. Previous studies related to some of the heavy metals in the lakes of Tirana were published in 2015. The determination of some metals (Cu, Pb, Fe, Mn, Cr, Zn, Cd) in the Artificial Lake of Tirana are defined in [15], and of the heavy metals (Cd, Cr, Cu, and Pb) in Farka Lake are defined in [16]. In [15], [16], the concentration level values of the mentioned metals were low so, according to European EEC standards and WHO for surface water quality, the Artificial Lake of Tirana and Farka Lake were considered with clean water. Among these metals, the concentration of Fe determined in the Artificial Lake of Tirana has increased from 29.30 ug/L to 40.71 ug/L. Also, Mn resulted in increased concentration from 5.97 ug/L to 41.12 ug/L. While the concentration of other metals has decreased, where Cd and Cr are below the limit of detection. On the other hand, for Farka Lake, the concentration of Cu has increased, while the average values of other metals vary closely with the values obtained from this study.

Although at low levels, Farka Lake contains the highest concentration of Ca, Fe, Cu, Al, Mo, Sb, Ba, and Pb, compared to the other two lakes. In the area of Farka Lake, the development of agriculture is high compared to other areas. The development of agricultural activities in the area causes an increase in the application of fertilizers, pesticides, etc., which often leads to an increase in the concentration of these metals in lake waters. For Kashar Lake the metals with the highest concentration are: Cr, V, Zn, As, Ba, and Cd, this may be related to the industrial development of the area.

To provide a visual representation of elements by mean concentration values in each lake we applied Ward's agglomerative clustering method in Euclidean distance function.

We determined five main clusters of major and trace elements according to mean concentrate levels for each lake presented by the dendrograms as they are shown in Appendix in Figure 2, Figure 3 and Figure 4. These dendrograms provide visual representations of similarities and differences in metal concentrations between sampling stations within each lake. ANOVA analyses were performed to assess differences in metal concentrations among the three lakes as it is shown in Table 3 (Appendix).

The results indicated no significant differences in metal concentrations, as evidenced by P-values higher than 0.05, suggesting that the chemical composition of the water samples from Kashar Lake, Artificial Lake of Tirana, and Farka Lake were comparable.

The different concentrations of metals determined among the lakes can come from natural sources like rock and soil weathering, or human activity like industrial discharges and the use of fertilizers, pesticides, etc.

In general, the results of this study provide valuable basic data on the chemical composition of artificial lakes in Tirana and underline the importance of continuous monitoring to preserve the quality of the environment, due to urban and industrial development around these areas.

4 Conclusion

In this paper, for the first time, we explored the concentration levels of 26 metals, including major and trace elements, in the three main artificial lakes of the city of Tirana.

All metals, major and trace, are below the standard set by the European Union for surface water.

The concentration of heavy metals (Cu, Ni, Zn, Mn, As, and Fe) in the lakes can be explained by anthropogenic sources, including the development of agriculture in these areas, especially in Kashar and Farka Lake and the industrial area in Kashar Lake. Further urban development around these artificial lakes makes it necessary to monitor the quality of surface water.

Statistical processing was performed to see the similarity of the chemical composition of the waters of the three lakes.

Declaration of Generative AI and AI-assisted Technologies in the Writing Process

During the preparation of this work the authors used Grammarly for language editing. After using this service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

References:

[1] Gramowska H, Krzyzaniak I, Baralkiewicz D, Goldyn R. (2010). Environmental applications of ICP-MS for simultaneous determination of trace elements and statistical data analysis. *Environmental Monitoring and Assessment*, 160(1-4), 479-490. https://doi.org/10.1007/s10661-008-0712-9.

[2] Wardhani E, Roosmini D, Notodarmojo S (2017). Status of heavy metal in sediment of Saguling Lake, West Java. *IOP Conf. Series: Earth and Environmental Science*, 60, 012035. DOI: 10.1088/1755-1315/60/1/012035.

[3] Hodaj A, Shehu A, Baraj B (2015). Evaluation of the environmental state and WQI variations in water of Tirana Artificial Lake. *Albanian Journal of Agricultural Sciences*. 14(3) 267-277, [Online]. https://www.proquest.com/docview/1731537780?sourcetype=Scholarly%20Journals (Accessed Date: October 2, 2024).

[4] Hounkpe J.B, Kelome N. C, Adechina R, Lawani, R.N (2017). Assessment of heavy metals contamination in sediments at the lake of Aheme in southern of Benin (West Africa). *Journal of Materials and Environmental Sciences*, Vol 8 (12), 4369-4377. https://doi.org/10.26872/JMES.2017.8.12.460.

[5] Ramadhan Tosepu, Parman Parman, Nasaruddin Nasaruddin. Heavy Metal Pollution in the Waters of South Konawe Regency, Southeast Sulawesi Province, Indonesia. *WSEAS Transactions on Environment and Development*, vol.19, pp.820-825, 2023. https://doi.org/10.37394/232015.2023.19.77.

[6] Chen M, Li F, Tao M, Hu L, Shi Y, Liu Y (2019). Distribution and ecological risks of heavy metals in river sediments and overlying water in typical mining areas of China. *Marine Pollution Bulletin*, 146, 893-899. https://doi.org/10.1016/j.marpolbul.2019.07.029.

[7] Said K, Shuhaimi-Othman M, Ahmad A.K (2012). The evaluation of water quality and metal concentrations of Titiwanga Lake, Selangor, Peninsular Malaysia. Pakistan *Journal of Biological Sciences*, 15(10), 459-468. https://doi.org/10.3923/pjbs.2012.459.468.

[8] Wasike P. W, Nawiri M.P, Wanyonyi A.A (2019). Levels of heavy metals (Pb, Mn, Cu and Cd) in water from river Kuywa and the Adjacent Wells. *Environment and Ecology Research*, 7(3), 135-138. DOI: 10.13189/eer.2019.070303.

[9] WHO (2008). Guidelines for drinking-water quality: incorporating 1st and 2nd addenda, Vol. 1, Recommendation. - 3rd edition. Geneva, Word Health Organization, 2008. Chap. 1, p.6, [Online]. https://www.who.int/publications/i/item/9789241547611 (Accessed Date: September 20, 2024).

[10] WHO (2017). Guidelines for drinking-water quality: fourth edition incorporating the first addendum. Geneva, Word Health Organization, 2017. Chap. 12, p 307-340, [Online]. https://www.who.int/publications/i/item/9789241549950 (Accessed Date: September 20, 2024).

[11] Linnik, P.M., (2000). Zinc Lead and Cadmium Speciation in Dnieper Water Bodies. Department of Ecotoxicology and Hydrochemistry, Institute of Hydrobiology and Academy of science, Ukraine. *Reservoirs Research and Management*, vol. 4, pp.261-270. https://doi.org/10.1046/j.1440-1770.2000.00126.x.

[12] Calkins, M., (2009). *Materials for Sustainable sites: A complete Guide to the Evaluation*. Hoboken, New Jersey: John Wiley and sons. p341-342.

[13] Kakareka, S., Kukharchyk, T., Kurman, P., (2019). Major and trace elements content in freshwater lakes of Vecherny Oasis, Enderby Land, East Antarctica. *Environmental Pollution,* 255, 113126. DOI: 10.1016/j.envpol.2019.113126.

[14] Karolina Koś, Eugeniusz Zawisza. Heavy Metals Contamination of Sediments from Chosen Dam Reservoirs in Terms of their Usage in Earthworks. *WSEAS Transactions on Environment and Development*, vol. 11, pp.136-142, 2015.

[15] Hodaj, A., *Assessment and monitoring of the degree of pollution of the artificial lake of Tirana*. (2015). (PhD Thesis in Chemistry, Faculty of Natural Science, University of Tirana, Albania), [Online]. https://api.fshn.edu.al/uploads/Doktorata_Arvjola_Hodaj_Kimi_143c36db10.pdf (Accessed Date: September 23, 2024).

[16] M., Alushllari., S., Mico. (2015). Analyses of heavy metals in the superfical water of lakes. *Zastita Materijala*, 56(4):492-495. DOI: 10.5937/ZasMat1504492A.

[17] EN ISO 17294-1: 2004, Water quality. Application of inductively coupled plasma mass spectrometry (ICP-MS). Part 1: General guidelines, [Online]. https://dps.gov.al/sq/project/show/iso:proj:32957 (Accessed Date: September 23, 2024).

[18] EN ISO 17294-2: 2016. W ater quality - Application of inductively coupled plasma mass spectrometry (ICP - MS). Part 2: Determination of selected elements including uranium isotopes, [Online]. https://dps.gov.al/en/project/show/iso:proj:62962 (Accessed Date: September 23, 2024).

Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

Dafina Karaj: Conceptualization, Writing-Original draft preparation, Methodology, Investigation. Denisa Salillari: Software Data curation, Software, Validation. Writing-Reviewing and Editing. Elona Shahu: Methodology, Investigation. Elmira Mehmeti: Writing-Reviewing and Editing, Edlira Tako: Visualization, Methodology.

Sources of Funding for Research Presented in a Scientific Article or Scientific Article Itself

No funding was received for conducting this study.

Conflict of Interest

The authors have no conflicts of interest to declare.

APPENDIX

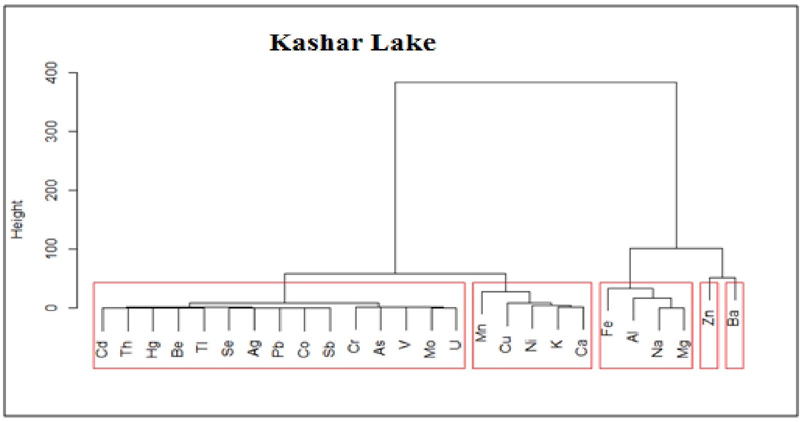

Fig. 2: Dendrogram with clusters of major and trace metals by mean concentration levels in Kashar Lake

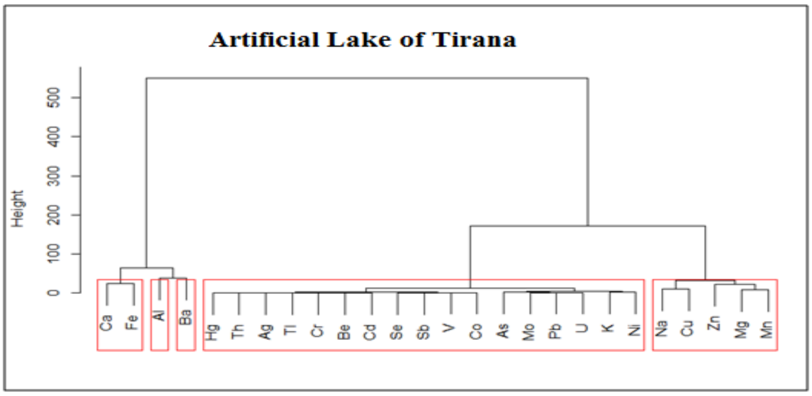

Fig. 3: Dendrogram with clusters of major and trace metals by mean concentration level in Artificial Lake of Tirana

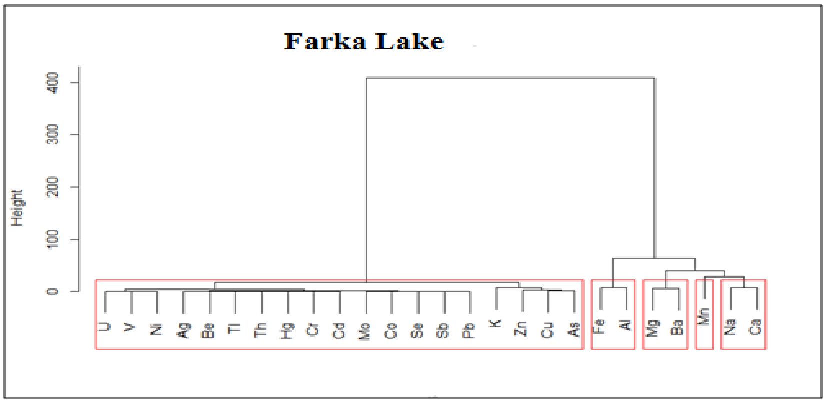

Fig. 4: Dendrogram with clusters of major and trace metals by mean concentration levels in Farka Lake

Table 2. The concentration of major and trace elements in water samples of three lakes of Tirana

	Kashar Lake Concentration (μg/L)			Artificial Lake of Tirana Concentration (μg/L)			Farka Lake Concentration (μg/L)		
	Station 1	Station 2	Station 3	Station 1	Station 2	Station 3	Station 1	Station 2	Station 3
Na	23.58*	24.31*	23.25*	26.86*	26.82*	27*	10.61*	12.89*	12.9*
Mg	23.16*	23.95*	23.13 *	17.32*	17.54*	17.51*	13.99*	17.12*	17.01*
K	4.11*	4.29*	4.93 *	4.23*	4.22*	4.58*	2.45*	3.12*	2.98*
Ca	5.27*	5.58 *	4.48 *	22.99*	23.37*	23.03*	39.45*	47.64*	45.05*
Fe	26.63	16.46	42.50	36.6	40.71	17.82	31.11	66.76	20.02
Cu	1.83	1.67	5.94	1.04	1.45	2.01	5.26	9.91	10.02
Be	Nd	Nd	Nd	0.0016	0.0053	0.0024	0.0065	0.013	0.004
Al	19.42	14.14	19.44	39.02	42.93	12.85	51.86	73.32	20.45
V	0.63	0.61	1.10	0.63	0.75	0.61	0.42	0.63	0.39
Cr	1.26	0.19	0.52	Nd	Nd	Nd	Nd	0.035	0.001
Mn	5.21	20.27	10.77	41.12	24.94	35.77	11.675	22.365	22.65
Co	0.15	0.19	0.13	0.11	0.097	0.09	0.13	1.00	1.002
Ni	6.88	6.74	5.44	0.72	0.68	0.73	1.68	2.305	1.65
Zn	21.58	35.40	68.75	1.46	1.38	3.31	24.055	26.4	27.03
As	0.87	0.88	2.00	1.23	1.23	1.27	1.36	0.675	1.00
Se	0.35	0.37	0.32	0.11	0.11	0.13	0.24	0.295	0.28
Mo	0.93	1.16	1.10	0.25	0.18	0.22	0.54	1.95	0.51
Ag	0.20	0.29	0.01	Nd	Nd	0.01	0.01	0.005	0.009
Cd	0.04	0.03	0.02	Nd	Nd	Nd	0.01	0.025	0.013
Sb	0.14	0.15	0.21	0.14	0.14	0.14	0.185	0.33	0.22
Ba	52.96	59.14	47.23	15.3	18.25	12.83	80.215	57.5	40.7
Hg	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Tl	Nd	Nd	Nd	0.0014	0.008	0.001	Nd	Nd	Nd
Pb	0.16	0.20	0.37	0.09	0.16	0.16	0.61	1.21	1.2
Th	0.00	0.00	0.01	Nd	Nd	Nd	Nd	Nd	Nd
U	1.24	1.25	1.06	0.44	0.45	0.43	0.99	1.24	1.2

**Concentration (mg/L)*

Table 3. Results of ANOVA calculation for the concentration of metals in water samples in three lakes.

Ind Residuals	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Kashar Lake	2 75	88 16970	44.03 226.27	0.195	0.824
Artif. Tirana Lake	2 75	102 31612	51.2 421.5	0.121	0.856
Farka Lake	2 75	57 11641	28.53 155.22	0.184	0.832