EVALUATION OF THE ENVIRONMENTAL STATE AND HUMAN HEALTH RISK DUE TO HEAVY METALS CONTENT IN THE WATERS OF THE KUNE-VAINI COMPLEX LAGOONS, ALBANIA

Alma SHEHU, Majlinda VASJARI, Loreta VALLJA, Nevila BROLI, and Sonila DUKA
Faculty of Natural Sciences,University of Tirana, Albania

ABSTRACT

The heavy metals content in the waters of Kune-Vaini Lagoon and the impact on the human health is here evaluated. Water samples were collected in different periods and from five selected stations of the Kune-Vaini complex for the spatial and temporal distribution of heavy metals concentration. The Atomic Absorption Spectroscopy technique employing electrothermal atomization, GF-AAS was used for the concentration of heavy metals. The extent of metal pollution in the lagoon water was evaluated by comparing the obtained results with the recommended criteria of heavy metals in surface waters, and by calculating some of the most used indexes of the contamination level, such as the Heavy Metal Evaluation Index (HEI); the Contamination Degree Index (CdI) and Water Pollution Index, WPI. Assessment of health risk due to heavy metals in surface water was estimated with regard to dermal contact and ingestion, as the two main routes of humans exposed to heavy metals according to the USEPA (2004) guidelines. The obtained results showed that the average concentration of heavy metals in selected waters followed the order: Fe>Cu>Cr>Mn, while the concentrations of Pb and Cd were below the limit of detection of the method (LOD). Concentration of heavy metals present in waters of the lagoon was below the recommended value as based USEPA, (2001) standards. The waters belong to the moderately polluted to highly polluted class with regard to Cu and to the moderately polluted class with regard to Cr, based on the NIVA (2000) classification. Health risk assessment analysis suggested that the presence of heavy metals in waters of Kune-Vaini complex show minimum hazard effect on human health.
***Keywords*:** heavy metals, water, pollution indexes, health risk assessment, GF/AAS

1. INTRODUCTION

Water contamination with heavy metals have been the main focus of many environmental studies performed in the recent decades as they are considered as severe pollutants due to their toxicity, persistence and bioaccumulation in the living organisms [1]. In surface waters, heavy metals are present in a wide range of physico-chemical forms, both in particulate and dissolved phases [2]. Some heavy metals such as copper (Cu), cobalt (Co) and zinc (Zn) are considered to be essential for the aquatic living organisms and humans and others like cadmium (Cd), chromium (Cr), manganese (Mn), and lead (Pb) are considered to be highly toxic [2,3]. Heavy metals enter into human body through several pathways including food chain, dermal contact and inhalation [4]. Estimation of the health risk of certain hazardous substances, including heavy metals usually is based on the degree of the consumption of that substance [5,6]. Commonly, health risk evaluation is based on the comparison of the estimated concentrations with the recommended guidelines for a certain element in the selected environment but this is not sufficient as it can't provide adequate information on the hazard level as well as on the most important contaminant[7,8,9].The most used methods of health risk assessments with regard to human exposure to different contaminants in the environment are based on the US Environmental Protection Agency, USEPA (USEPA, 2004) recommendations[10].The present study primary aimed to evaluate the environmental state of the Kune Vaini lagoons system waters due to temporal and spatial distribution of heavy metals, and identify the polluted sites and periods which can originate such levels of heavy metals posing any health risk to humans. Among the determined metals were Lead (Pb), Chromium (Cr), Cadmium (Cd), Copper (Cu), Iron (Fe) and Manganese (Mn).

2. MATERIALS AND METHODS

Sampling of water samples

Table 1 informs about the five sites selected for water monitoring on the Kune-Vaini lagoon, with a frequency of every two months, from July, 2018-July, 2019.Field trips were organized in joint groups made up of some eminent personalities in the realm of botany, zoology and chemistry from the Faculty of Natural Sciences, University of Tirana, Albania. The ISO 5667-1:2006 standard method was applied for sample collection [7]. The representative water samples (1 L each) were collected from surface water in cleaned plastic bottles, pre-washed with 20% nitric acid (HNO_3) and deionized water. Samples were filtered *in situ*, and a few drops of HNO_3 were added before samples transport to the laboratory. Samples were stored in a refrigerator at 4 °C till the day of analysis.

Table 1. Sampling stations

Station	Station information
Ceka 1	Ceka, northern part, Lezha.
Ceka 2	Ceka, central part, in front of the new communication tidal channel,
Ceka 3	Ceka, southern part, Lezha.
Zaje 1	Zaje close to the communication channel with the Drini River, Lezha.
Merxhani	Merxhani, at its southern part, in front of tidal channel near Kune, Shengjini.

Procedure of heavy metals determination

All filtered and acidified samples were analyzed for metals (Cu, Fe, Cr, Mn, Pb, Cd) via atomic absorption spectroscopy technique, with electrothermal atomization, AAS/ETA [13]. All samples were analyzed in triplicates together with standards and blanks. Quality control of the obtained results was carried out by analyzing a Certified Reference Material (CRM) for the content of heavy metals in water such as the CRM SPS WW-14. Statistical treatment of the obtained results was carried out by using MINITAB 19 and the Excel Analysis Tool Pack. Basic statistics such as mean and standard deviation were computed along with the descriptive statistics. Boxplot were used to evaluate the spatial and temporal distribution of each metal in selected stations.

Pollution assessment indices

Several standards with regard to the recommended limits of heavy metals in surface waters were employed to determine the pollution status of waters of the Kune-Vaini System lagoon such as the USEPA Water Quality Standards [14] and the Norwegian Institute for Water Research classification [15]. Besides that, the water quality was evaluated by using also different pollution indices, including Heavy Metal Evaluation Index (*HEI*) and the Contamination Degree Index (*CdI*). Accordingly, *HEI* presents the overall surface water quality with respect to heavy metals content and is computed by using the following equation [12]:

$$HEI = \sum_{i=1}^{n} \frac{Mi}{MACi}$$

where *Mi*and MAC_i are the monitored value and maximum admissible concentration of the ith metal, respectively. Classifications of surface water quality based on *HEI* values are: <10 for low pollution; 10 - 20 for moderate pollution and >20 high pollution. Whilst, the Contamination Degree Index *CdI* indicates the overall detrimental impact of the HMs on surface water [12], and it is determined according to formula:

$$CdI = \sum_{i=1}^{n} Cfi \text{ where } Cfi = \frac{Mi}{MACi} - 1$$

where *Cfi* is the contamination factor for the ith metal. The categories used to represent pollution due to heavy metals on the basis of *CdI* are: <1 for low, 1-3 for moderate and >3 for high pollution of in the surface water body [12].

Human health risk assessment

Exposure determination was estimated by involving the average daily dose exposure value of a human body to a certain metal. The key exposure routes include direct ingestion and dermal absorption. We have determined exposure by employing ingestion and dermal routes since these are the two important routes of heavy metals exposure from an aquatic ecosystem [16]. The exposure assessment was computed as:

$$ADDi = \frac{Ci \times IR \times EF \times ED}{BW \times AT} \quad ADDd = \frac{Ci \times SA \times Kp \times ET \times EF \times ED \times CF}{BW \times AT}$$

The non-carcinogenic risks were determined by applying the hazard quotient (*HQ*) of USEPA [16]. The sum of the non-carcinogenic risk of an individual metal is presented as the Total Hazard Index (HQ_{tot}) for the two exposure routes, and computed as:

$$HQi = \frac{ADDi}{RfDi} \quad HQd = \frac{ADDd}{RfDd}$$

$$HQ_{tot} = HQ_i + HQ_d \text{ and } HI = \Sigma HQ_m$$

HQ_{tot} of a single metal and *HI* of all metals present in a water media categorizes health risks into two types; HI < 1 indicates a low detrimental impact of metals on human health, while $HI \geq 1$ represents greater chances of harmful health effects.

3. RESULTS AND DISCUSSIONS

Descriptive statistics

Table 2 shows some statistical parameters such as mean, minimum, maximum and relative standard deviation of the obtained results regarding metals concentration in water samples. As it can be seen, Fe and Cu were found to be in higher concentration, compared to other elements while the content of Cd and Pb have resulted to be lower than the limit of detection of the method, being respectively 0.005 and 0.1 µg/L. The metals concentration in selected samples followed the order: Fe>Cu>Cr>Mn while the variations relating to their content between the sampling time and sites, estimated as relative standard deviation ranged between 39% (Fe) to 190% (Mn).

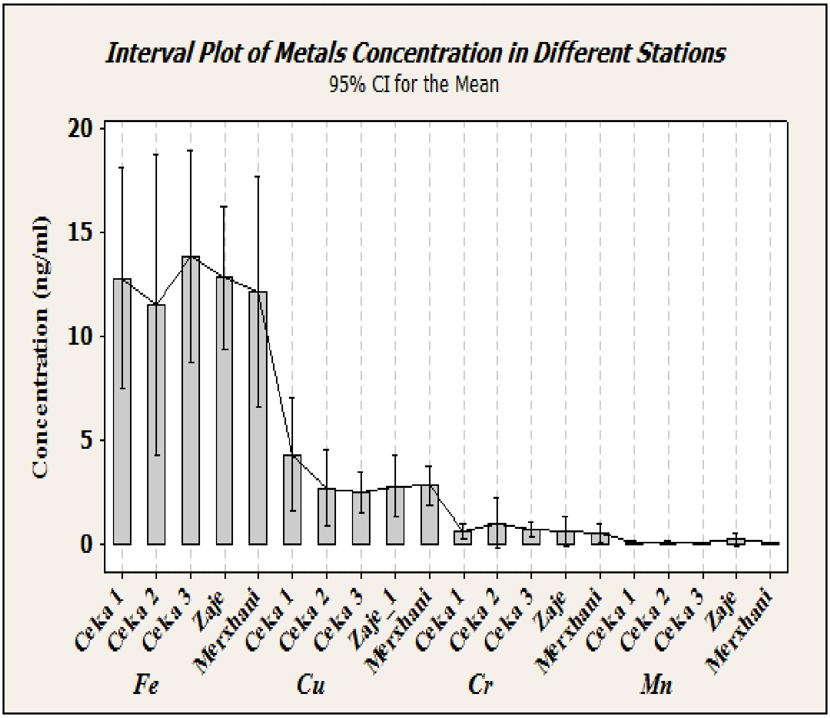
Table 2. Descriptive statistics for metals content in selected water samples (µg/L)

Parameter	Fe N=30	Cu N=30	Cr N=30	Mn N=30
Mean	12.628	3.027	0.676	0.079
Median	12.330	2.585	0.410	0.010
RSD	39.0	54.6	94.1	190
Minimum	2.880	1.330	0.090	0.010
Maximum	22.590	8.250	3.220	0.760
MAC (EPA, 2001)	200	3.1	50	50

Spatial and temporal distribution pattern of the elements

The Figure 1 depicts the heavy metals distribution in the waters of Kune-Vaini system, and the forthcoming paragraphs discusses in details this distribution. Box Plots were used to evaluate the temporal and spatial variation of each element concentration in the selected stations in different periods of sampling.

Iron was the metal found in higher concentrations in waters of Kune-Vaini lagoon, ranging from 2.8µg/L (Ceka-2/July 2018) to 22.6µg/L (Ceka-2 /January 2019), followed by Cu, which concentration ranged between 1.33 µg/L (Ceka-2/September 2018) to 8.25 µg/L (Ceka-1/January 2019). Higher concentration of Cr (3.22 µg/L) was observed in station Ceka-2 during September, 2018 and the lowest during May, 2019 in three stations, Ceka-1, Zaje and Merxhani. Manganese was the metal found at a lower concentration rate, ranging from 0.01 to 0.76 µg/L in station Zaje, during September 2018. The average values for copper were 2.69 µg/L in Ceka waters, 2.34 µg/L in Zaje, and 2.39 µg/L in Merxhani; based on the Norwegian classification of lake water quality [15], these values belong to quality III (1.5-3 µg/L), showing significant pollution, while in certain months the quality was IV (heavy pollution). The average for chromium was 0.52 µg/L in Ceka, 0.25 µg/L in Zaje, and 0.25 µg/L in Merxhani, quality II (0.2-2.5 µg/L), corresponding to moderate pollution. Higher variation of Fe and Cu content between stations was observed during July 2018 and January 2019. Cr concentration varied mostly during September and November, 2018 while Mn during July and September, 2018.The results obtained by the Analysis of Variance, ANOVA (Table 3) confirmed that no significant differences were observed with regard to metals distribution between the selected stations ($P>0.05$), while significant differences existed between the content of Cu and Cr with regard to different sampling periods. Pollution with copper and chromium is expected in Kune-Vaini lagoons, affected somehow by the waters of the Mati delta; the basin area of this river is traditionally known for the processing of copper and chromium minerals. Concentration of all studied metals have resulted to be lower than the recommended values of heavy metals in surface waters, according to the USEPA, 2001 [14].



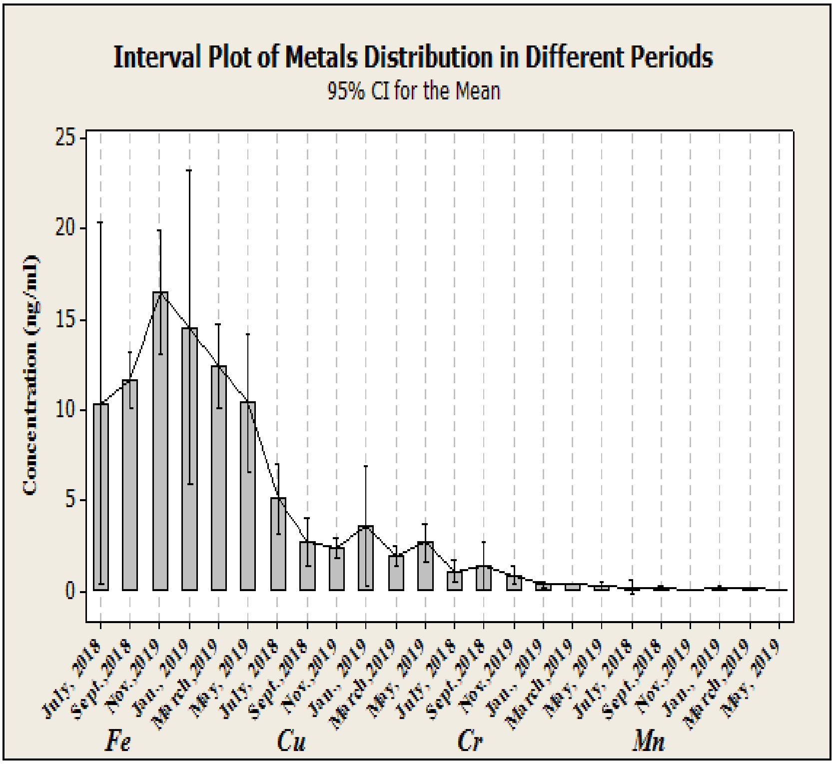


Fig. 1: Box Plots of metals spatial and temporal distribution.

Table 3. Analysis of Variance, ANOVA of metals distribution

	Fe		*Cu*		*Cr*		*Mn*		
Source of Variation	*F*	*P-value*	*F*	*P-value*	*F*	*P-value*	*F*	*P-value*	*F crit*
Stations	0.17	0.95	1.88	0.15	0.75	0.57	1.79	0.17	2.87
Months	1.13	0.38	3.82	0.01	4.06	0.01	0.98	0.45	2.71

Pollution assessment indices

The overall water quality was observed by calculating the Heavy Metals Evaluation Index, *HEI* and the Contamination Index *CdI* which represents the overall detrimental impact of the HMs on surface water [12].Based on the *HEI* values, surface water quality is classified as “low polluted” (HEI<10); “moderately polluted” (HEI between 10 – 20) and “highly polluted”(HEI>20)while based on the CdI values three classes can be used, accordingly CdI<1 for low, 1-3 for moderate and >3 for high pollution of the surface water body from heavy metals[12].HEI was calculated for each metal in all selected stations in different months. Obtained results show that, except for the highest value of HEI observed in station Zaje, during July, 2018 which suggests a moderate pollution in this station due to metals concentration, the environmental state of the other stations can be classified as low-polluted (Fig.2). The results of CdI values showed that the water quality in most parts of the selected stations could be classified as low-polluted. In station Zaje, during July, 2018, and station Ceka 3, during September 2018 the quality of water was classified as very polluted. During September, 2018 and January, 2019 the quality of water in stations Ceka 1, Ceka 2 and Zaje was classified as moderately polluted (Fig.3).

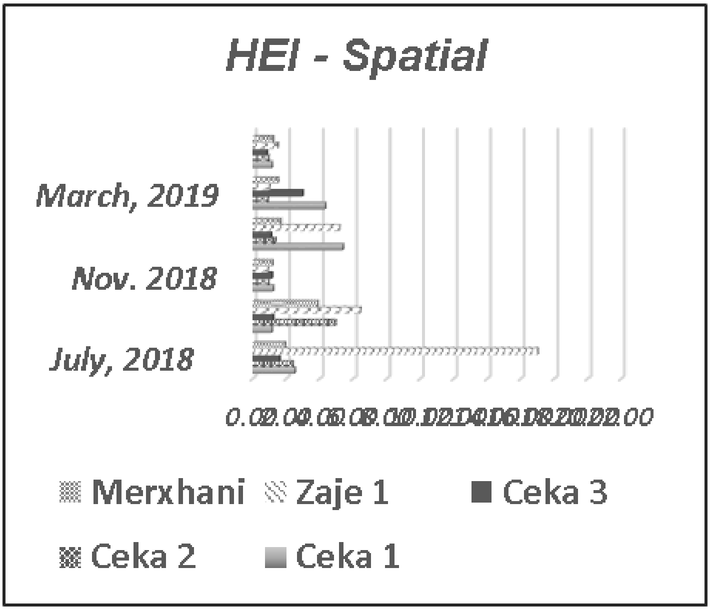


Fig. 2: HEI values of heavy metals in lagoon.

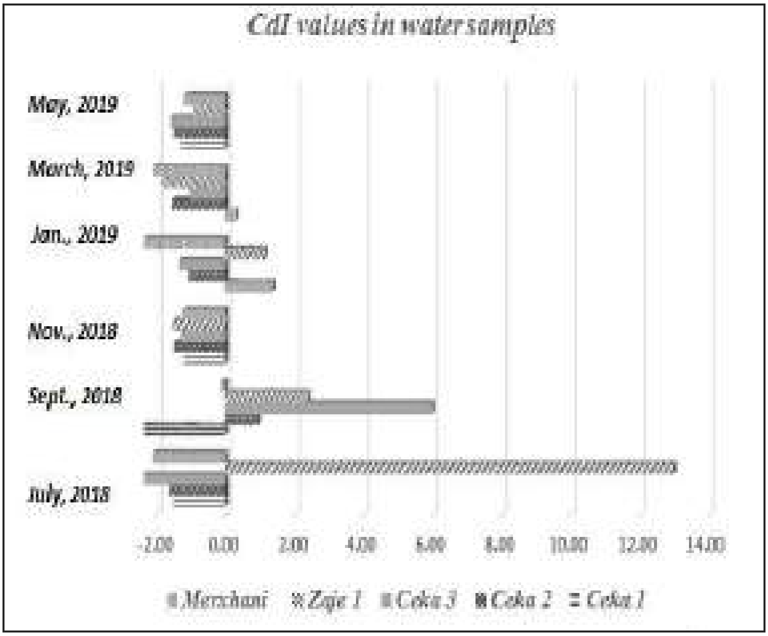


Fig. 3: Contamination degree Index, CdI.

Human health risk assessment

Health risk assessment of each element made by means of Hazard Risk Quotients for ingestion and dermal routes of exposure, HQ_{ing} and HQ_{derm}, total Hazard Quotient, HQ_{tot}, and based on the Hazard Index, HI (Table 4). The results showed that estimated values of HQ_{tot} and HI was<1, suggesting an acceptable level of health risk in all selected stations and months due to the analyzed metals. Cu and Fe exhibited higher values of Hazard Quotient due to ingestion compared to the other metals while Cr exhibited higher Hazard Quotient values due to dermal contact. With regard to the total HQ, Cr was the metal which has exhibited higher values of the total Hazard Quotient, HQ_{tot} ranging from 1.44E-03 to 5.15E-02 followed by Cu, for which the HQ_{tot} values ranged between 1.03E-03 and 6.37E-03. Total Hazard Quotient values of metals in water of the Kune-Vaini System lagoon followed the order: Cr>Cu>Fe>Mn.

Table 4. Mean, minimum, and maximum values of non-carcinogenic human health risks posed by heavy metals in water of study area via different pathways.

	HQi			HQd			HQtot		
	mean	min	max	mean	min	max	mean	min	max
Fe	5.15E-04	1.18E-04	9.22E-04	1.01E-05	2.74E-06	1.81E-05	5.25E-04	1.21E-04	9.40E-04
Cu	2.33E-03	1.03E-03	6.37E-03	1.95E-05	8.61E-06	5.32E-05	2.33E-03	1.03E-03	6.37E-03
Cr	1.29E-05	1.71E-06	6.13E-05	1.1E-02	1.44E-03	5.15E-02	1.1E-02	1.44E-03	5.15E-02
Mn	1.61E-05	2.04E-06	1.55E-04	9.44E-07	1.2E-07	9.12E-06	1.61E-05	2.04E-06	1.55E-04
HI	2.87E-03	1.15E-03	7.51E-03	1.10E-02	1.45E-03	5.16E-02	1.39E-02	2.59E-03	5.90E-02

4. CONCLUSIONS

In this study, the environmental state of the Kune-Vaini System lagoon waters due to heavy metals was evaluated in five different stations, for a period of 11 months. The metals concentration in selected samples followed the order: Fe>Cu>Cr>Mn, while the variations relating to their content between the sampling time and sites, estimated as relative standard deviation ranged between 39% (Fe) to 190% (Mn).

Based on the results obtained by the Analysis of Variance, ANOVA it was confirmed that no significant differences were observed with regard to metals distribution between the selected stations ($P>0.05$) while significant differences existed between the content of Cu and Cr with regard to different sampling periods. Pollution with copper and chromium is expected in Kune-Vaini lagoons, affected somehow by the waters of the Mati delta; the basin area of this riveris traditionally known for the processing of copper and chromium minerals.

Concentration of each metal analyzed has resulted to be lower than the recommended values set for heavy metals levels in surface waters, according to the USEPA.

Health risk assessment of each element was evaluated by means of Hazard Risk Quotients for ingestion and dermal routes of exposure, HQ_{ing} and HQ_{derm}, total Hazard Quotient, HQ_{tot} as well as based on the Hazard Index, HI. Obtained results showed that estimated values of HQ_{tot} and HI have resulted to be <1, suggesting an acceptable level of health risk in all selected stations and months due to the analyzed metals. Cu and Fe exhibited higher values of Hazard Quotient due to ingestion compared to the other metals while Cr exhibited higher Hazard Quotient values due to dermal contact. With regard to the total HQ, Cr was the metal which has exhibited higher values of the total Hazard Quotient, HQ_{tot} ranging from 1.44E-03 to 5.15E-02 followed by Cu, for which the HQ_{tot} values ranged between 1.03E-03 and 6.37E-03. Total Hazard Quotient values of metals in water of the Kune-Vaini System lagoon followed the order: Cr>Cu>Fe>Mn.

ACKNOWLEDGEMENTS

This study has been carried out in the framework of the project “Construction and sustainability of the Kune-Vain lagoon system through access to the ecosystem (EbA)” supported by UNEP, GEF and the Albanian Government.

REFERENCES

1. **Forstner U, Wittmann GTW. 1981.** Metal Speciation in the Aquatic Environment, 2nd ed., 26, Springer-Verlag.

2. **Murray JW. 1987.** Mechanisms controlling the distribution of trace elements in oceans and lakes, p. 153-184. Zn R. A. Hites and S. J. Eisenreich [eds.], Sources and fates of aquatic pollutants. **ISBN13:** 9780841209831 **e ISBN:** 9780841223981**Copyright © 1987 American Chemical Society**

3. Mallk Qa**,** Khan MS**. 2016.** Effect on Human Health due to Drinking Water Contaminated with Heavy Metals. Environmental Science. *Journal of Pollution Effects and Control.* **5(1):**1000179.

4. **Hussein FH, Baqir SJ, Karam FF. 2014.** Seasonal Variation in Heavy Metals Contamination in Surface Water of Shatt Al-Hilla River, Babylon, Iraq. *Asian Journal of Chemistry*; **26**, Supplementary Issue, S207-S210.

5. **Eftimi R. 2005**. Hydrochemical characteristics of some lithologicaly different karst massifs of Albania. https://www.researchgate.net/publication/327406188.

6. **Miho A, Mitrushi R. 1999.** Phytoplanktonic data and trophic state of Lezha lagoons. *Albanian Journal of Natural and Technical Sciences* (AJNTS) (Academy of Sciences, Tirana, Albania) **1/1:** 69–76.

7. ISO 5667-1:2006. Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques.

8. **Balistrieri LS, Murray JW, Paul B. 1992.**The cycling of iron and manganese in the water column of Lake Sammamish, Washington. *Limnology and Oceanography*, **37**: 510 – 528.

9**. Nicolau R, Galera CA, Lucas Y. 2006.**Transfer of nutrients and labile metals from the continent to the sea by a small Mediterranean river, *Chemosphere*, **63 (3):** 469 - 476.

10. **Zafiri C, Marazioti C, Kornaros M, Angelopouos K, Lyberatos G. 2009.**The deterioration of the environmental state of the shallow Koutavos lagoon in Kefalonia, Greece. *Fresenius Environmental Bulletin*, **18 (6):** pp. 935-947.

11. **Hirsch RM, Hamilton PA, Miller TL. 2006.** U.S. Geological Survey perspective on water-quality monitoring and assessment. *Journal of Environmental Monitoring*, **8(5):** 512-518.

12. **Beckman B, Bodis D, Lahermo P, Rapant S, Tarvainen T. 1998.** Application of a groundwater contamination index in Finland and Slovakia. *Environmental Geology*. **36 (1-2):**55-64.

13. American Public Health Association, American Water Works Association, and Water Environment Federation, Washington (APHA/AWWA). 2017. Standard methods for the examination of water and wastewater.

14. US EPA. 2001. Parameters of Water Quality. Interpretations and Standards. Ireland.

15. **Bratli LJ. 2000.** Classification of the Environmental quality of freshwater in Norway. In: Hydrological and limnological aspects of lake monitoring. John Willey & Sons Ltd, pg. 331-343.

16. **US EPA.1992.** Guidelines for Exposure Assessment, EPA/600/Z-92/001, Risk Assessment Forum, Washington, DC.