Proceedings of the 10th World Congress on Mechanical, Chemical, and Material Engineering (MCM'24)
Barcelona, Spain - August 22-24, 2024
Paper No. ICCPE 101
DOI: 10.11159/iccpe24.101

Evaluation of Nutrients and Heavy Metals in the Waters of Seman Basin

Valbona HOXHA[1], Albana JANO[1], Kozeta VASO[2], Enkela PORO[1]
Faculty of Mathematical Engineering and Physical Engineering,
Polytechnic University of Tirana, Albania
v.hoxha@fimif.edu.al, a.jano@fimif.edu.al
[2]Faculty of Natural Sciences,
University of Tirana
Boulevard "Zogu I" Tirana Albania
kozeta.vaso@fshn.edu.al

Abstract - The purpose of this study is to evaluate the water pollution of the Seman River based on the concentration of heavy metals and nutrients, as well as to investigate the possible sources of these pollutants. This study was conducted during the period April - June 2019 for analysis of nutrients and during the period April - May 2019 for analysis of heavy metals.

Water samples were sampled at seven points along the river impacted by human settlements, human activity and agricultural activities. The samples were analyzed for Nickel, Lead, Cobalt and Copper using an Atomic Absorption Spectrophotometer (AAS). Calorimetric methods were used to determine levels of phosphates, total phosphorous, nitrites, and ammoniums. All analyzes were performed using standard analytical methods (APHA, DIN, ISO). Interpretation of results was conducted using descriptive statistics method and compared with international water quality standards.

The average concentration of heavy metals in the analyzed water samples, in ascending order, was Co < Cu < Ni < Pb. This trend was applied to all water samples in both expeditions. The average concentration of lead was the highest at 0.345mg/L, followed by nickel at 0.073mg/L, and by copper at 0.028mg/L. Cobalt was not identified in any of the water samples analyzed. Regarding the average concentration of heavy metals, the waters of this basin are classified as highly polluted waters. heavy – class V of environmental quality. Referring to the measured average values of nitrites, ammoniums, orthophosphates, and total phosphorus, the waters of this basin have a very bad environmental quality and are not suitable for growing fish.

The major sources of both nitrogen and phosphorus in water include municipal wastewater discharges, sewage, urban and agricultural runoff, animal feed lots and industrial wastes. Detergents and other laundry materials are the major contributors of phosphorus in water. Therefore, there is a need to formulate and adopt strict rules for managing and minimizing the causes of pollutants, thus managing and minimizing environmental pollution and the health risks associated with it. The assessment of agricultural activities is also very important, since an increase in the concentration of metals during the rainy seasons due to runoff from these sources has been observed.

Keywords: nutrients, heavy metals, calorimetric methods, AAS

Introduction

Environmental contaminants, as well as pollutants, are chemicals that are present at higher levels than in any section of the environment. [1]-[2]

The term "heavy metals" refers to metals and metalloids that have a density greater than 5 g cm-3 and are associated with toxic effects when present in large concentrations, even though some of them are essential elements for the organism [3]-[4]. For example, copper and zinc are essential elements for the human body, plants and bacteria [3]-[5], but in large concentrations they have a harmful effect on cells [6]. Arsenic, cadmium and lead are classified as priority pollutants, because these metals are not necessary for metabolic activity and can be toxic even at very low concentrations [7] Heavy metals are one of the most serious environmental pollutants due to their toxic effects. They cannot be displaced or removed and can easily bioaccumulate in aquatic ecosystems. [8]-[9]-[10]

Due to the increase in heavy metal pollution and their toxic effects, many countries in the world have established strict regulations regarding the permissible values for the content of heavy metals in water used for drinking, fishing and irrigation of agricultural land, in order to protect human health. [11] The analysis and quality of sediments plays an important role in assessing the state of pollution of an aquatic environment. [12] In order to assess river water pollution, relevant sediment samples should be analyzed, because the concentrations of heavy metals in sediments are many times higher than in water [13]. Heavy metals in surface water systems can be from natural and anthropogenic sources. These metals are found in the geological structure of the earth and therefore can enter water sources through natural processes. Rocks and parent substrate are the main natural sources of heavy metals in the environment [14]. Anthropogenic sources are mainly related to industrial activities, which include: mining, metal smelters, industrial waste, energy production. [15] Some of the heavy metals in water are beneficial, while others are harmful and toxic, for example calcium and magnesium are essential chemical elements, while other metals adversely affect water consumers and wastewater treatment systems. urban pollution.

In this study, we determined the level of copper, cobalt, lead and nickel in the waters of the Seman Basin.

Copper (Cu) is a rare component of natural waters that can reach the water from the use of copper pipes or from the dosing of tanks with copper (II) sulfate, which is used to inhibit the growth of algae. It has been proven that copper is toxic to fish and other aquatic organisms in concentrations that do not pose a risk to humans. It has been experimentally proven that the copper (II) ion is the main poisonous form. Copper is an important chemical element for human life and other living things as it plays an important role in metabolic processes, affects a high number of enzymes and hemoglobin synthesis. [16]

Cobalt (Co) is an element that has properties similar to those of iron and nickel. Small amounts of cobalt occur naturally in most rocks, soil, water, plants and animals. Cobalt can enter the environment from natural sources (dust from storms, volcanic eruptions and forest fires) as well as from anthropogenic sources (soil contaminated by airport traffic, highway traffic or other industrial pollution may contain high concentrations of cobalt). [17]

Lead (Pb) is a heavy metal that appears in the +2-oxidation state in water environments and comes from various industrial sources and mines. Organic lead compounds easily reach the human body through the skin and endanger the central nervous system. It reduces enzyme activity, redox reactions in the cell and protein synthesis. [16]

Nickel (Ni) is a hard, silver-white metal that has properties that make it highly desirable to combine with other metals to form alloys. It is released into the atmosphere during its extraction from mines and from industries that produce or use nickel and from nickel alloys or compounds. These industries can also discharge nickel into urban wastewater. Nickel is also released into the atmosphere from oil-burning power plants, coal-burning power plants, and garbage incinerators. [18]

Eutrophication is characterized by excessive plant and algal growth due to the increased availability of one or more limiting growth factors needed for **photosynthesis** [19] such as sunlight, carbon dioxide, and nutrient fertilizers. Eutrophication occurs naturally over centuries as lakes age and are filled in with sediments. [20] However, human activities have accelerated the rate and extent of eutrophication through both point-source discharges and non-point loadings of limiting nutrients, such as nitrogen and phosphorus, into aquatic ecosystems (i.e., cultural eutrophication), with dramatic consequences for drinking water sources, fisheries, and recreational water bodies [21]

Phosphorus Has A Complicated Story. Pure, "Elemental" Phosphorus (P) Is Rare. In Nature, Phosphorus Usually Exists As Part Of A Phosphate Molecule (Po_4^{3-}). Phosphorus In Aquatic Systems Occurs As Organic Phosphate And Inorganic Phosphate. Organic Phosphate Consists Of A Phosphate Molecule Associated With A Carbon-Based Molecule, As In Plant Or Animal Tissue. Phosphate That Is Not Associated With Organic Material Is Inorganic. Inorganic Phosphorus Is The Form Required By Plants. Animals Can Use Either Organic Or Inorganic Phosphate. Both Organic And Inorganic Phosphorus Can Either Be Dissolved In The Water Or Suspended (Attached To Particles In The Water Column) [22]

The bioaccumulation of nitrogenous pollutants like nitrite and nitrate in water and soil pose hazard to humans and plants. Nitrite is also utilized as an additive agent in food industry and it mishandle might lead to excessive amount of nitrite in consumables which is unwholesome to the public health. Organic nitrogen undergoes biochemical oxidation to form nitrate and can be readily converted into the more toxic nitrite by microbial reduction. The WHO recommends $6.5 \times 10{-}5$ M is to be the maximal allowed nitrite concentration in drinking water as per the norms of WHO.[**23**]

Ammonia is a product of the microbiological decay of animal and plant proteins. It can be reused directly by plants to produce protein. Ammonia and ammonia compounds can be applied directly as fertilizer. The presence of ammonia in surface water usually indicates pollution from urban sewage, while its presence in groundwater is normal and is due to microbiological processes [24]

The purpose of this study is to evaluate the water pollution of the Seman River based on the concentration of heavy metals and nutrients, as well as to investigate the possible sources of these pollutants. Water samples were sampled at seven points along the river impacted by human settlements, human activity and agricultural activities.

Materials And Methods

Sampling Sites

The selection of the sampling stations was made in order for the results of the study to give a complete overview of the level of pollution of these waters, starting from the upper flow, in the flow along the city, at the exit of the city, until the canal that flows into the sea Adriatic

Figure 1 gives a map of the water sampling stations

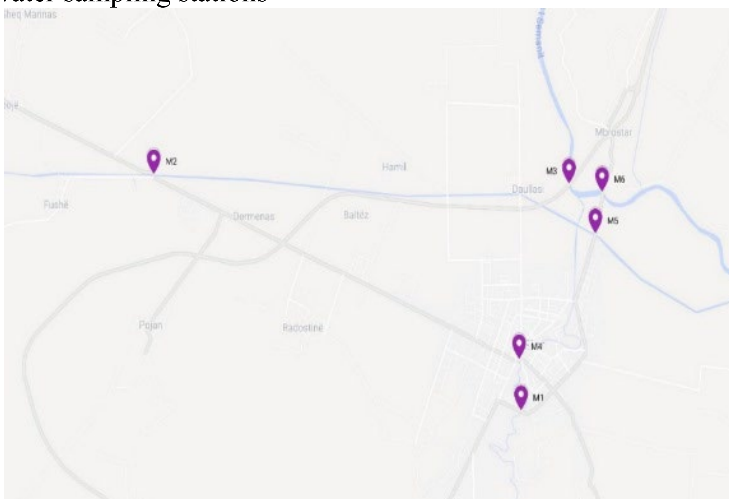

Fig 1. The water sampling stations

Sampling, preservation and conservation at river stations was carried out in accordance with the recommended standard methods. [25]-[26]-[27]-[28]

Water samples were collected using a polyethylene bottle of 1 L volume, at a depth of about 15 -20 cm below the water surface, prewashed and properly labeled. The storage of water samples for the determination of heavy metals is done in accordance with ISO method. [27] To have a pH<2 in the sample, 0.5 ml of concentrated nitric acid is added to 100 ml of the sample. They are transported to the laboratory in freezer boxes at about 4˚C [29]

All standard analytical methods used, are recommended by APHA [29], DIN [30]- [31]-[32] and [34], and EN/ISO standard methods, [34], [35]. All nutrients were determined by UV- VIS spectrophotometry technique [29]-[30]-[31]-[32]-[33]-[34]. All heavy metals were determined using atomic absorption spectrometry with a graphite furnace. [35]- [36]

Results and Discussions

Heavy Metals

Heavy metals are the most dangerous pollutants as they are persistent and accumulate in water, sediments and in the tissues of living organisms, through two mechanisms, called 'bio-concentration' (uptake from the ambient environment) and 'biomagnification' (uptake through the [37] Fish are able to aspire to take up and retain heavy metals dissolved in water by active or passive processes. [38]

For this study, the micropollutants Cu, Co, Pb and Ni were determined with the SAA technique with a graphite furnace.

The concentration profile of heavy metals in the first expedition is shown in figure 2. High concentration values for copper were found at M4 station (0.07mg/L) and the lowest value at station M5. Regarding the concentration of copper, the waters of all stations taken in the study are classified as heavily polluted waters - class V of environmental quality. For lead, the highest concentration value resulted in the M5 sampling site and the lowest in the M1 sampling site. Regarding the concentration of lead, the waters of all stations taken in the study are classified as heavily polluted waters - class V of environmental quality.

Cobalt was not identified while nickel was only identified in the sample taken at M4 station. Regarding nickel concentration, waters where nickel has been identified are classified as heavily polluted waters - class V of environmental quality

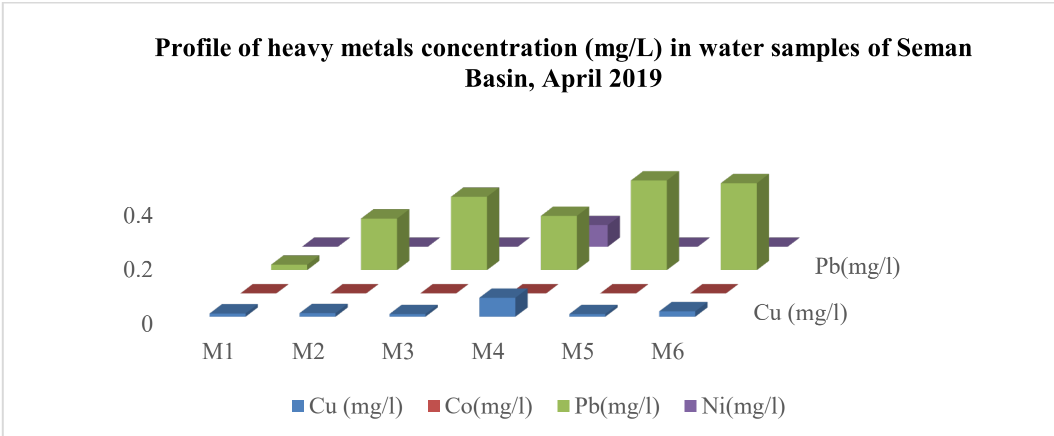

Fig. 2. Profile of heavy metals concentration (mg/L) in water samples of Seman Basin, April 2019

The profile of heavy metals concentration in the second expedition is shown in figure 3. It is noted that high concentration values for copper were found at M1 station (0.06mg/L) and the lowest value at station M5. Regarding the concentration of copper, the waters of all stations taken in the study are classified as heavily polluted waters - class V of environmental quality.

For lead, the highest concentration value resulted in the M1 sampling site of 0.43mg/L and the lowest in the M5 sampling site. Regarding the concentration of lead, the waters of all stations taken in the study are classified as heavily polluted waters - class V of environmental quality. Cobalt was not identified while nickel was only identified in the sample taken at M1 and M4 stations. Regarding nickel concentration, waters where nickel has been identified are classified as heavily polluted waters - class V of environmental quality.

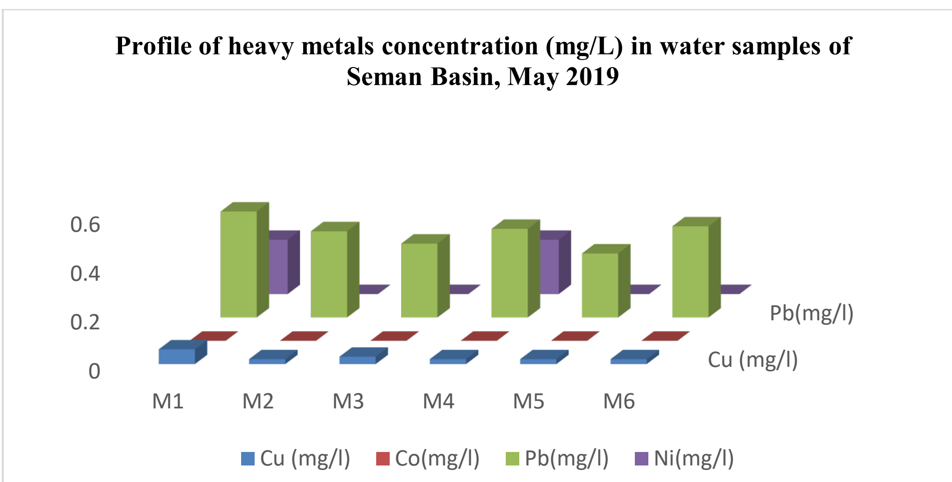

Fig 3. Profile of heavy metals concentration (mg/L) in water samples of Seman Basin, May 2019

The average concentration of heavy metals in the analyzed water samples, in ascending order, was $Co < Cu < Ni < Pb$. This trend was applied to all water samples in both expeditions. The average concentration of lead was the highest at 0.345mg/L, followed by nickel at 0.073mg/L, and by copper at 0.028mg/L. Cobalt was not identified in any of the water samples analyzed.

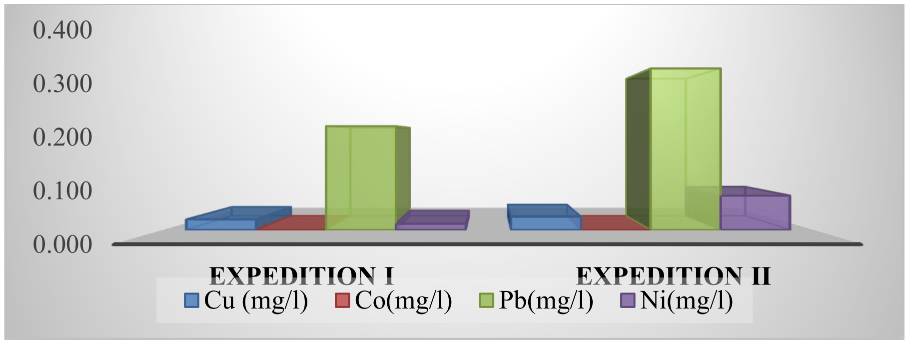

Fig.4. The average concentration of heavy metals

Nutrients – Nitrogen and Phosphorus

The parameters that were analyzed for nitrogen are nitrites and ammoniums, while for phosphorus they are phosphates and total phosphorus.

Nitrites. Table 1 presents the results obtained from the statistical processing of the nitrite parameter in the waters of the Seman basin.

Table 1. The results of the statistical processing of the NO_2^- - N (mg/L) parameter in the waters of the Seman Basin

NO_2^- - N (mg/L)	M1	M2	M3	M4	M5	M6
Mean	0.097	0.215	0.029	0.085	0.156	0.011
Median	0.104	0.236	0.030	0.103	0.180	0.008
Standard Deviation	0.073	0.040	0.002	0.070	0.044	0.008
Minimum	0.020	0.168	0.027	0.008	0.105	0.005
Maximum	0.166	0.240	0.030	0.144	0.184	0.021

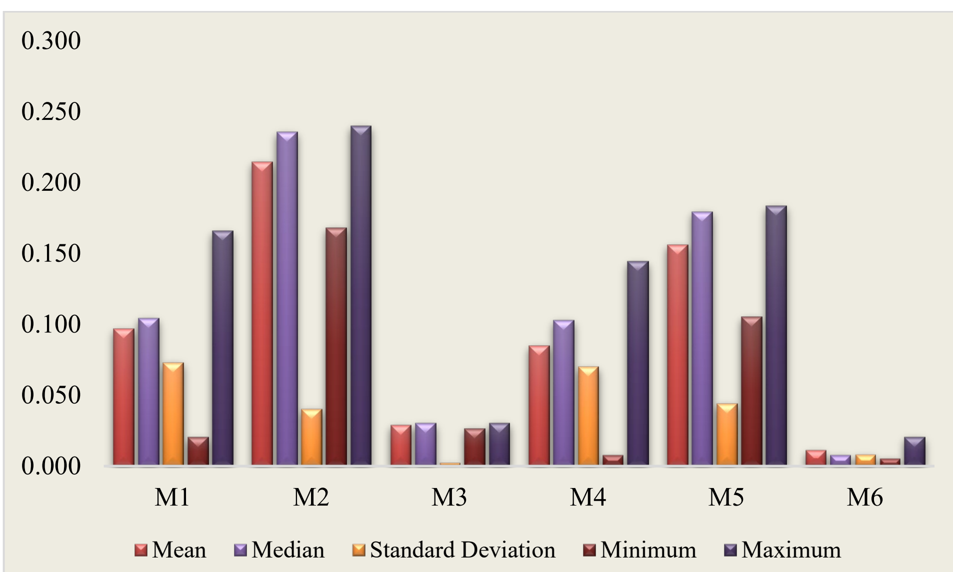

Figure 5. Variation of nitrite concentration by stations NO_2^- - N (mg/L)

This parameter has also been qualified as an indicator of surface water quality, as it has stronger toxic properties than nitrates in humans and animals. For this, limit rates of its presence in waters have been set, and on the basis of its content, we can also classify their quality.

The graph in the figure 5 shows variation of nitrite concentration by stations. The results of statistical processing, it is noted that the average value of nitrite concentration varies from 0.0112mg/L at M6 station to 0.215mg/L at M2stationThe nitrite concentration is higher in stations where there are urban, industrial and agricultural discharges. According to the European Directive, the recommended level for salmonid waters is <0.01 mg/l, while for cyprinid waters it is <0.03 mg/l. Compared to the European Directive, the waters taken in the study do not meet these conditions. So, they are not suitable for growing fish.

Ammoniums

Table 2 presents the results obtained from the statistical processing of the ammoniums parameter in the waters of the Seman basin.

Table 2. The results of the statistical processing of the NH_4^+-N (mg/L) parameter in the waters of the Seman Basin

NH_4^+-N (mg/L)	M1	M2	M3	M4	M5	M6
Mean	0.097	0.215	0.029	0.085	0.156	0.011
Median	0.104	0.236	0.030	0.103	0.180	0.008
Standard Deviation	0.073	0.040	0.002	0.070	0.044	0.008
Minimum	0.020	0.168	0.027	0.008	0.105	0.005
Maximum	0.166	0.240	0.030	0.144	0.184	0.021

Ammonia is the reduced inorganic form of nitrogen and includes the dissolved form NH_3 and the ionic form NH_4^+. It is formed when organic matter containing nitrogen is destroyed by microbial activity. High concentrations of ammonia are found when urban waste, chemical and organic, agricultural or industrial fertilizers containing ammonium or its salts, are discharged into water. Ammonia can also result from natural reduction processes under anaerobic conditions.

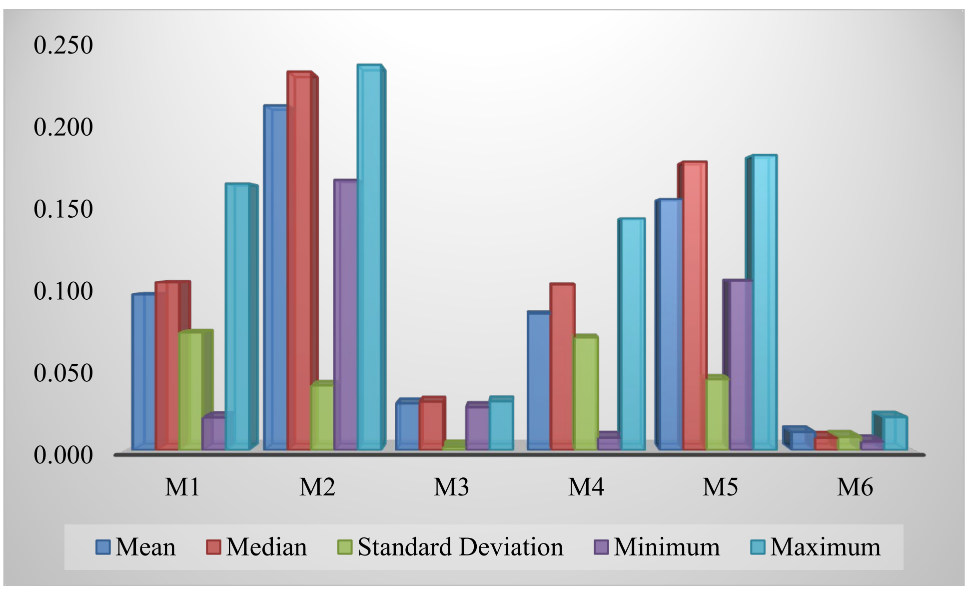

Figure 6. Variation of ammoniums concentration by stations (NH_4^+-N mg/L)

Looking at the graph in figure 6, it is noted that the highest values of ammonium, as nitrogen were measured at M2 station. Regarding the average concentration values of ammonium as nitrogen, it is noted that they range from 1.655mg/L at M6 station to 5.318 mg/L at M2 station.

What is noticed is that the content of ammonium, in the stations taken in the study, has a variation as well as nitrites, since both of these parameters depend on the amount and content of urban, industrial or agricultural discharges. Compared to the European standards, we say that: according to the European Directive that supports the growth of fish, the recommended level for salmonid waters is < 0.04 mg/L and for cyprinid waters < 0.2 mg/L. As mentioned above, the waters taken in the study are not suitable for growing fish. According to UNECE, the waters taken in the study belong to category V of environmental quality "very bad".

Orthophosphates

Table 3 presents the results obtained from the statistical processing of the orthophosphates parameter in the waters of the Seman basin.

Table 3. The results of the statistical processing of the PO_4^{3-} - P(mg/L) parameter in the waters of the Seman Basin

PO_4^{3-} - P(mg/L)	M1	M2	M3	M4	M5	M6
Mean	0.097	0.215	0.029	0.085	0.156	0.011
Median	0.104	0.236	0.030	0.103	0.180	0.008
Standard Deviation	0.073	0.040	0.002	0.070	0.044	0.008
Minimum	0.020	0.168	0.027	0.008	0.105	0.005
Maximum	0.166	0.240	0.030	0.144	0.184	0.021

Phosphorus is a nutrient for living things, but it is a polluting substance if it is present in high concentrations under specific environmental conditions. The addition of phosphorus as phosphate ion to natural waters is one of the most serious environmental problems due to its contribution to the processes of artificial eutrophication of waters. In natural waters and aquatic wastes, phosphorus is present almost exclusively in the form of phosphates, which can be dissolved and as insoluble compounds (mainly with iron, aluminum and calcium) in solid particles and sediments.

Figure 7 shows the average values of orthophosphate concentration as phosphorus and the minimum and maximum values for each station.

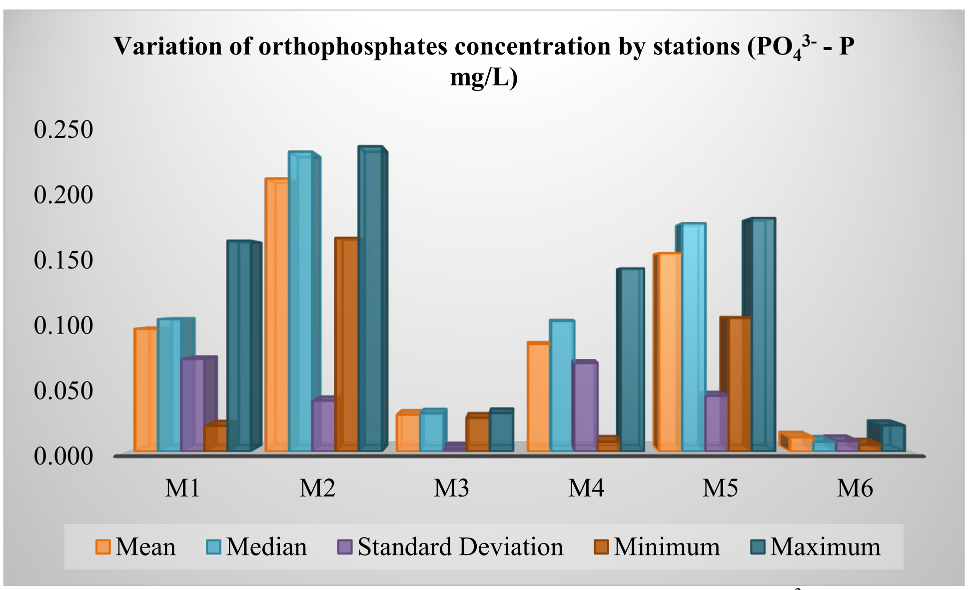

Figure 7. Variation of orthophosphates concentration by stations (PO_4^{3-} - P mg/L)

It is noted that the highest values of the concentration of phosphates were measured in the M2 station (in the Hoxhara channel which flows into the Adriatic Sea. This channel brings all the spills of Ballsh industry) during the three expeditions carried out during the study. These high values are also followed by the M5 station (at the Ngjala Line which flows into the

Adriatic Sea. This channel like the M2 station, brings all the spills of Ballsh industry). The minimum values of PO43--P were measured at M6 station.

Total phosphorous

Table 4 presents the results obtained from the statistical processing of the total phosphorous parameter in.the waters of the Seman Basin.

Table 4. The results of the statistical processing of the total P (PO_4^{3-} - P mg/L) parameter in the waters of the Seman Basin

Total P (PO_4^{3-} - P mg/L)	M1	M2	M3	M4	M5	M6
Mean	0.097	0.215	0.029	0.085	0.156	0.011
Median	0.104	0.236	0.030	0.103	0.180	0.008
Standard Deviation	0.073	0.040	0.002	0.070	0.044	0.008
Minimum	0.020	0.168	0.027	0.008	0.105	0.005
Maximum	0.166	0.240	0.030	0.144	0.184	0.021

Figure 8 shows the variation of total phosphorous concentration by stations (PO_4^{3-} - P mg/L).

From the graph, it can be seen that the total phosphorus concentration values are higher for M2 stations and M5 station, and the average values vary from 0.118 mg/L phosphorus for M6 station to 1.070 mg/L at M2 station. These concentration values have the same trend as the concentrations of orthophosphates.

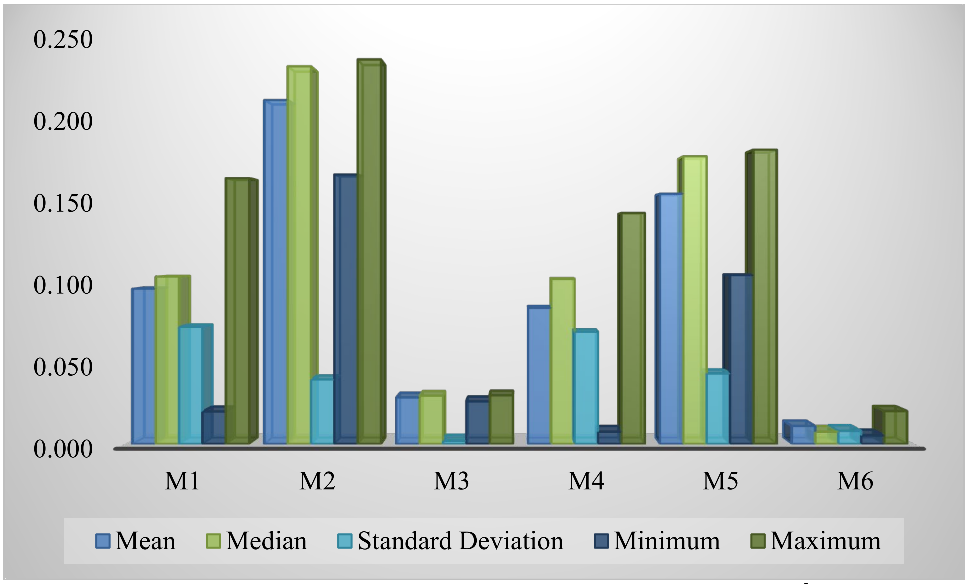

Figure 8. Variation of total phosphorous concentration by stations (PO_4^{3-} - P mg/L)

Compared to European standards:

- Based on the classification according to NIVA, all the stations taken in the study belong to environmental quality class V (very bad), thus resulting in very polluted, in terms of total phosphorus concentration.
- According to UNECE M1, M2, M3, M4 and M5 stations belong to class V resulting in the environmental class "very bad" and M6 station belongs to class IV resulting in the environmental class "bad".

Conclusions

Based on the above results, we understand, that the waters of the Seman basin are very polluted waters and do not meet the conditions according to international standards.

The major sources of both nitrogen and phosphorus in water include municipal wastewater discharges, sewage, urban and agricultural runoff, animal feed lots and industrial wastes. Detergents and other laundry materials are the major contributors of phosphorus in water. Referring to the measured average values of nitrites, ammoniums, orthophosphates, and total phosphorus, the waters of this basin have a very bad environmental quality and are not suitable for growing fish.

It is also noted that the highest values of nutrient concentrations have resulted in M2 station followed by M5 station, these stations are more influenced by anthropogenic activity and industrial discharges (brings all the spills of Ballsh industry and discharges from agricultural lands).

The average concentration of heavy metals in the analyzed water samples, in ascending order, was Co < Cu < Ni < Pb. Regarding the concentration of copper, lead and nickel, the waters of all stations taken in the study are classified as heavily polluted waters - class V of environmental quality. It is noted that the average values of heavy metal concentrations are higher in the second expedition, conducted in May 2019, a month associated with rain and storms. This is explained by the fact that the non-point sources of metals are runoff from roads and parking lots, runoff from waste, agricultural lands where metal-containing sludge, fertilizers and pesticides have been applied.

Therefore, there is a need to formulate and adopt strict rules for managing and minimizing the causes of pollutants, thus managing and minimizing environmental pollution and the health risks associated with it. The assessment of agricultural activities is also very important, since an increase in the concentration of metals during the rainy seasons due to runoff from these sources has been observed.

References

[1] Masindi V., Muedi K.L. (2018). *Heavy Metals.* Intech; Environmental contamination by heavy metals. [Google Scholar]

[2] Walker C.H., Sibly R.M., Hopkin S.P., D.B.P (2012). *Principles of Ecotoxicology; Group, T. And F., Ed.; 4th Edition.* CRC Press; [Google Scholar]

[3] Adriano, D.C. (2001). Trase elements in terrestrial environments, Bichemistry, biavalibility and risk of metals, Springer-Verlag, New York.

[4] Alloway, B.J., (1995) Heavy metals in soils, Blackie Academic&Professional, 2nd edition, London.

[5] Harrison, R.M., (1999) Understanding our environment, The Royal Society of Chemistry, Cambridge, UK.

[6] Siegel, F., (2002) Environmental geochemistry of potentional toxic metals, Springer-Verlag, Berlin Heidelberg, Germany.

[7] US EPA (U.S. Environmental Protection Agency), (1999). Integrated Risk Information System (IRIS). National Center for Environmental Assessment, Office of Research and Development, Washington DC, USA.

[8] Öztürk. M, Özözen. G, Minareci. O, Minareci. E (2009). Determination of heavy metals in fish, water and sediments of Avsar Dam Lake in TurkeyIran. J. Environ. Health. Sci. Eng., Vol. 6, No. 2, pp. 73-80.

[9] Odu NN, Igwiloh NJPN, Okonko IO, and Njoku HO, (2011). Heavy metal levels of some edible shellfish from Kalarugbani Creek in River State, Nigeria. Journal of American Science;7(9) http://www.americanscience.org.

[10] Censi P, Spoto SE, Saiano F, Sprovieri M, Mazzola S, Nardone G, Di Geronimo SI, Punturo R, Ottonello D, (2006) Heavy metals in coastal Water system.Chemosphere 64: page1167-1176.

[11] Goletić, Š. (2005), Teški metali u okolišu. Mašinski fakultet u Zenici: 39-72.

[12] Samir M. Saeed and Ibrahim M. Shaker. (2008) Assessment of heavy metals pollution in water and sediments and their effect on oreochromis niloticus in the northern Delta Lakes, Egypt. 8th International Symposium on Tilapia in Aquaculture.

[13] Cullaj A. (2010). *Environmental Chemistry* (2nd Ed.) (in Albanian). Perlat Voshtina, Tirana, Albania.

[14] Mohamed M. El Bouraie, Ahmed A. El Barbary, Mohamed M. Yehia & Eman A. Motawea (2010). Heavy metal concentrations in surface river water and bed sediments at Nile Delta in Egypt Suoseura - Finnish Peatland Society ISSN 00395471 Helsinki 2010 Suo 61(1): 1–12.

[15] Bradl. H.B, (2005). Heavy metals in environment Elsevier.

[16] Bujar H. DURMISHI, (2005). "Determining the levels of water pollution of Shkumbin River (pena) with heavy metals and other effluents with spectrometry and "striping" voltammetry". Master's thesis.

[17] .https://www.atsdr.cdc.gov/PHS/PHS.asp?id=371&tid=64
[18] https://www.atsdr.cdc.gov/phs/phs.asp?id=243&tid=44
[19] Schindler, D. W. (2006). Recent advances in the understanding and management of eutrophication. Limnology and Oceanography 51, 356-363
[20] Carpenter, S. R. (1981). Submersed vegetation: an internal factor in lake ecosystem succession. The American Naturalist 118, 372-383
[21] Carpenter, S. R, Caraco N. F. , Correll D. L. , Howarth R. W. , Sharpley A. N. , Smith V. H. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8, 559-568.
[22] https://archive.epa.gov/(2009).Monitoring and Assessing Water Quality. Volunteer Monitor, Volume 20, Number 1, PDF.
[23] Gauthama, B.U., Narayana, B., Sarojini, B., Bello K. , Suresh N., (2020). Nitrate/Nitrite determination in water and soil samples accompanied by in situ azo dye formation and its removal by superabsorbent cellulose hydrogel. SN Appl. Sci. 2, 1225. https://doi.org/10.1007/s42452-020-3016-5)
[24] (1975) American public health association, American water works association, and Water pollution control federation, Standard Methods for the Examination of Water and Wastewater, 14th edition,
[25] ISO (2020) ISO 5667-1, Water quality – Sampling - Part 1: Guidance on the design of sampling programms.
[26] ISO (2020). ISO 5667-2, Water quality – Sampling - Part 2: Guidance on sampling techniques.
[27] ISO (2020).ISO 5667-3, Water quality – Sampling - Part 3: Guidance on the preservation and handling the water sampling.
[28] ISO (2020). ISO 5667-6, Water quality – Sampling - Part 6: Guidance on sampling river and stream.
[29] APHA (2017). Standard Methods for the Examination of Water and Wastewater (23rd ed.). Washington DC: American Public Health Association
[30] DIN 38409: (1986) - German standard methods for the examination of water, waste water and sludge. DIN, Berlin, Germany.
[31] DIN (1993). DIN EN ISO 2677 (D10): 1993 - Standard method for water quality; determination of nitrite; molecular absorption spectrometric method.
[32] DIN (2004). DIN EN ISO 6878 (D11): Standard Method for water quality - Determination of phosphorus - Ammonium molybdate spectrometric method.
[33] DIN. (1983). DIN 38 406 – E5: German standard methods for the examination of water, waste water and sludge; parameters characterizing effects and substances determination of nitrite; molecular absorption spectrometric method.
[34] ISO (2018). ISO 15681-2:2018(E) Water quality — Determination of orthophosphate and total phosphorus: Ammonium molybdate spectrometric method. ISO, Geneva, Switzerland.
[35] ISO (2018). ISO 15587-2Water quality – Digestion for the determination of elements in water – Part 2; Nitric acid digestion.
[36] ISO (2020) ISO 15586 :2020. Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace.
[37] Garbisu, C.; Alkorta, I (2011). Phytoextraction: A cost-effective plant-based technology for the removal of metals from the environment. Biore-sour.Technol.2011,77, 229–236.
[38] Burns N Aykin, Ercal N, Gurer-Orhan, (1999). Toxic metals and oxidative stress part I: mechanisms involved in metal-induced oxidative damage