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Year-round assessment of water pollutants in five Greek rivers

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Abstract Globally, an estimated 80% of industrial and municipal wastewater is discharged into the environment without any prior treatment, with adverse effects on human health and the ecosystem. The current study was conducted for a year-round assessment of water pollutants in five Greek rivers (Glafkos, Assopos, Kifissos, Messapios and Rematia-Halandri). The rivers were selected based on their vicinity to municipal or industrial areas. All values of parameters determined were below permissible limits for the rivers selected. Only Kifisos River showed relatively elevated concentrations for arsenic and manganese. In Assopos River, manganese was slightly higher in spring while in Glafkos was increased in winter. Chromium in Messapios River in Evia was found to be much higher than in other surface waters. Nitrates in Rematia – Halandri were higher than the other surface waters

Keywords: pollution, river, hexavalent chromium

1. Introduction

According to the 2021 World Water Development Report released by UNESCO [1], the global use of freshwater has increased six-fold in the past 100 years and has been growing by about 1% per year since the 1980s. With the increase of water consumption, water quality is facing various challenges. Industry, agriculture and urban life have resulted in the pollution of the environment, adversely affecting the water bodies (rivers and oceans) necessary for life, ultimately affecting human health and the environment [2].

The current study was conducted to assess the physical and chemical water quality parameters of five Greek rivers. Chemical contaminants of water contain 65 parameters such as Inorganic Contaminants (IOCs), Volatile Organic Contaminants (VOCs), and Synthetic Organic Contaminants (SOCs). The parameters used in this study for water quality assessment include temperature, pH, conductivity, Total Dissolved Solids, nitrates and trace elements.

The parameters are:

P1. Air Temperature (˚C)
P2. Water Temperature (˚C)
P3. pH
P4. Conductivity (μs/cm)
P5. Total Dissolved Solids (ppm)
P6. Chromium (ppb)
P7. Manganese (ppb)
P8. Nickel (ppb)
P9. Copper (ppb)
P10. Arsenic (ppb)
P11. Cadmium (ppb)
P12. Nitrate (mg /L)
P13. Phosphates (mg/L)

The permissible limits for drinking water are pH 6.5-9.5, conductivity 2500 μs/cm, Chromium 50ppb, Manganese 50 ppb, Nickel 20 ppb, Copper 2000 ppb, Arsenic 10ppb, Cadmium 5 ppb, Nitrates 50 mg/L, and Phosphates 5 mg/L.

2. Materials and methods

Sampling locations are depicted in Pictures (1-5) below. The water samples were collected in 2022-2023 during four different seasons. Samples were collected in 50mL plastic falcons. Filtration was performed using a 0.22μm syringe filter, while a non-filtered sample was also collected. Samples used for trace element determination were acidified prior to the measurement. All samples were kept at 4ºC for 5 days or at -40ºC for longer preservation.

Trace elements were determined using ICP-MS 7700 (Agilent, USA). All measurements were conducted using external calibration, according to US EPA Method 8, Revision 5.4: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry. Phosphates and nitrates were determined by Hach Test Kits. Water and air temperature, conductivity, total dissolved solids as well as salinity were also measured on site using a HI-9835 Hanna conductivity meter.

3. Results and discussions

3.1 Five Greek Rivers

Glafkos is the biggest river of Patras region and the city's main groundwater reservoir. It is 26.3 km long sourcing from Panachaiko mountain and it flows into the Gulf of Patras (Ionian Sea) south of the city. A hydroelectric

power plant had been built on the river in 1927 but today serves only as a museum. Overpumping of water, during the last years, has resulted to a decrease of water level in several wells.

Picture 1. Glafkos River

Assopos River is located north of Athens, flows along Boeotia and northern Attica. It is 57km long having its main sources in the mountain Kitheronas and flowing in the southern EviaBay. In antiquity it was the natural border between Thebes and Plataea with the famous battle fought on its banks. In 1969, the river was characterized as a "canal for treated industrial waste" without, though, securing the waste treatment by the neighbour industries. Since then, it has been the object of many environmental studies due not only to the sever industrial but also agricultural activities taking place. High (Cr^{6+})concentrations were attributed to untreated industrial discharges and the whole basin in addition to the river itself have suffered environmental degradation.

Picture 2. Asopos River

Kifissos river in Attica, is the main urban river of the capital of Greece having a length of 27 km. Its sources are between Penteli and Parnitha mountains and it flows through the whole capital into the Saronic Bay. Inthe last decades its southwestern part several heavy-duty industries have been a creating major environmental impact. Kifisos has been canalized since 2000 being fully boxed for 13km. Although heavily polluted, it still keeps its natural characteristics at its upper part and hosts several fish populations.

Picture 3. Kifisos River

Messapios is a torrent located in central Eviaand is formed from four smaller rivers with a total length of 34km.

Picture 4. MessapiosRiver

Rematia-Halandristream sources from the southwestern sides of mountain Penteli and runs through Maroussi and Halandri suburbs intoto Kifissos river. It is one of the very few streams with constant flow and it is of great importance for Attica basin due to its morphology and flora

Picture 5. Rematia-Halandi River

3.2Parameters measured

The average year-round values of the parameters measured are presented in table 1:

Table 1 Parameters estimates in five Greek rivers

Parameters	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P10**	**P11**	**P12**	**P13**
Rivers													
Glafkos	12.5	14.6	6.95	498	248	0.6	6.9	0.9	0.9	0	0	3.5	3.5

Asopos	17.0	17.1	6.9	1412.8	784.5	3.8	17.4	12.0	2.4	0.8	0.0	4.1	-
Kifisos	20.5	18.2	7.3	12725.0	6367.5	1.8	31.4	4.8	7.8	7.1	0.0	2.9	2.7
Messapios	23.0	18.4	7.7	713.5	358.0	8.3	2.1	2.9	0.0	0.0	0.0	0.7	0.4
Halandri	12.5	14.5	6.6	1154.0	570.3	0.5	1.8	1.8	1.1	0.0	0.0	20.8	-

3.2Discussion of the parameters estimated

3.2.1Glafkos river

The water samples from the Glafkos River in Patras (from which the city is watered) were analyzed every three months (21/6/22, 21/9/22, 22/12/22, 22/3/23). All the values of all parameters measured were below drinking water levels, although Manganese was increased during the winter.

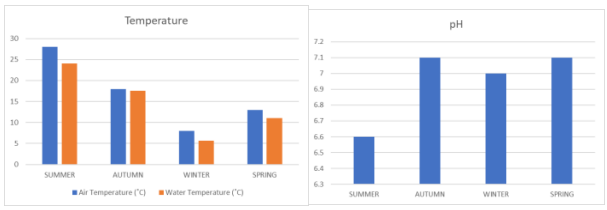

Figure 1. Temperature and pH seasonal distribution in Glafkos river

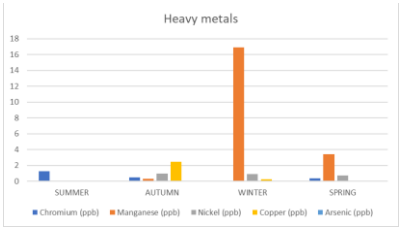

Figure 2. Heavy metal seasonal distribution in Glafkos river

3.2.2 Assopos river

The analysis of the water samples from the Assopos River in Halkoutsi was carried out every three months (21/6/22, 21/9/22, 22/12/22, 29/3/23). All the values of all parameters were in satisfactory levels. Manganese is somewhat increased in the spring and of course chromium, which is significantly higher than other surface waters we measured in Attica and Achaia. This latter is in agreement with earlier observations.

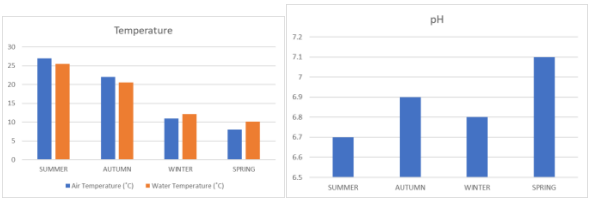

Figure 3. Temperature and pH seasonal distribution in Assopos river

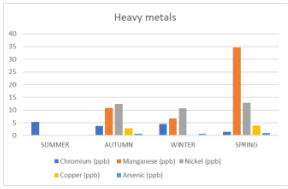

Figure 4. Heavy metal seasonal distribution in Assopos River

3.2.3 Kifissos river

The analysis of the water samples at the Kifissos estuary were carried out every three months (21/6/22, 21/9/22, 22/12/22, 29/3/23).. The water along its route is significantly polluted and is discharged into the Saronic Baywith increased concentration levels. Arsenic in Kifissos was constantly higher than all other river samples, reaching in autumn almost the upper limit of 10ppb. In addition, manganese was severely increased during spring time, up to 65μg/L exceeding the upper limit of 50μg/L. It should be noted that at the end of Kifissos there is seawater intrusion. Salinity expressed as NaCl had an average value of 8200ppm, while seawater salinity is 35000ppm. Seawater has a conductivity of 53 mS/cm, while the average value we measured is 12.7 mS/cm. It is evident that there is seawater mixing at a level of almost 25%. This means that the concentrations before mixing should be about 30% higher than what we measured.

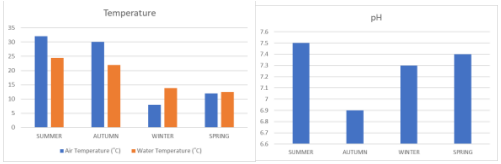

Figure 5. Temperature and pH seasonal distribution in Kifissos river

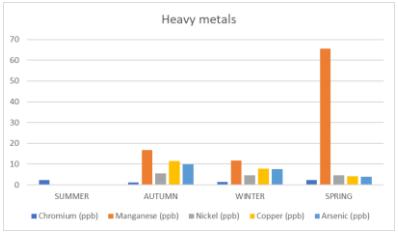

Figure 6. Heavy metal seasonal distribution in Kifissos river

3.2.4 Messapios river

The analysis of the water samples in the Messapios River in Psachna Evia were on 21/6/22 and 29/3/23. In autumn and winter there was no water as it is a torrent,

but it has flooded in the past with significant consequences for the residents. Satisfactory levels of values of most parameters. However, as has been the case in the past, an important problem for the area is chromium, which was found to be much higher than in other surface waters we studied. Chromium (Cr) is a common heavy metal existing in nature with an average concentration of 100mg/kg in the Earth's crust and is present in two abundant oxidation states, trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}) [3]. Kazakis et al [4] found that Cr^{6+}in the groundwater of Sarigkiol Basin, Northern Greece originated from both the ophiolite weathering products in the soils, and the local leaching of $Cr^{6+}$from the diffused fly ash located in the area surrounding the lignite power plant. Remoundaki et al. [5] discussed the relationship between heavy metals mobilization from soils to groundwater and the composition of irrigation water, in solutes that influence the generation rates and mobility of soluble heavy metals species in Psachna, Evia, in Greece.This region is characterized by elevated geogenic Cr in soils and intense agricultural activity.

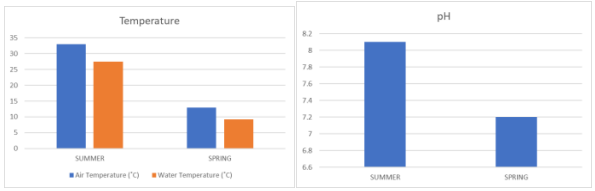

Figure 7. Temperature and pH seasonal distribution in Messapios river

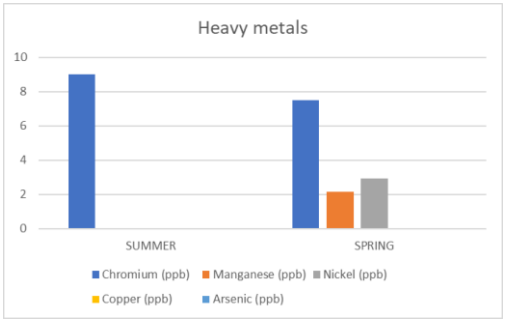

Figure 8. Heavy metal seasonal distribution in Messapios river

3.2.5Rematia-Halandri river

The analysis of the water samples in Rematia in the municipality if Halandri were carried out every three months (21/6/22, 21/9/22, 22/12/22, 29/3/23) and the seasonal differences were also determined. Nitrates were a bit increased, but all basic parameters were within specifications (pH at the lower limit of drinking water legislation). Arsenic and cadmium were not detected while measurements of all other metals were close to quantification limits. Phosphate concentrations were also low (below 0.4 mg/l).

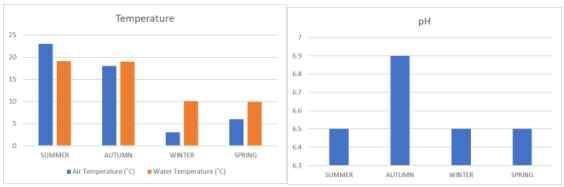

Figure 9. Temperature and pH seasonal distribution in Rematia-Halandri river

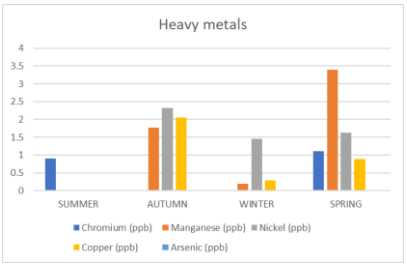

Figure 10. Heavy metal seasonal distribution in Rematia-Halandri river

4. Conclusion

All values were below the permissible limits for drinking waters suggesting a satisfactory quality level for the rivers selected according to the parameters monitored. The high conductivity of Kifisos River samples was due to sea water intrusion. Water samples from Kifisos River had the highest concentration of manganese followd by Assopos River. Manganese was increased during the winter in Glafkos. Arsenic level was quite high in Kifisos reaching the upper limit value during autumn. Rematia – Halandri showed relatively increased nitrates especially in winter, yet lower than the upper limit. The highest concentration of chromium was detected in Messapios River in Evia, followed by Assopos. Assopos River exhibited also the highest concentration of nickel, compared to all other surface waters.

References

[1] UNESCO 2021 World Water Development Report,https://www.unesco.org/reports/wwdr/2021/en/download-report

[2] Xu, X., Yang, H., and Li, C. (2022a). Theoretical Model and Actual Characteristics of Air Pollution Affecting Health Cost: A Review. Ijerph 19, 3532 doi:10.3390/ijerph19063532.

[3] WHO (2017) Guidelines for drinking water quality: fourth edition incorporating the first addendum. World Health Organization, Geneva.

[4] Kazakis N, Kantiranis N, Kalaitzidou K, Kaprara E, Mitrakas M, Frei R, Vargemezis G, Tsourlos P, Zouboulis A, Filippidis A (2017) Origin of hexavalent chromium in groundwater: the example of Sarigkiol Basin, Northern Greece. Sci Total Environ 593–594:552566 https://doi.org/10.1016/j.scitotenv.2017.03.128

[5] Remoundaki, E., Vasileiou, E., Philippou, A., Perraki, M., Kousi, P., Hatzikioseyian, A., Stamatis, G., Groundwater Deterioration: The Simultaneous Effects of Intense Agricultural Activity and Heavy Metals in Soil, (2016) Procedia Engineering, 162, pp. 545-552.