JEE Journal of Ecological Engineering

Journal of Ecological Engineering, 2025, 26(2), 48–55
https://doi.org/10.12911/22998993/196377
ISSN 2299–8993, License CC-BY 4.0

Received: 2024.11.14
Accepted: 2024.12.15
Published: 2025.01.01

Determination of phenol levels in some surface water ecosystems of Tirana Area, Albania

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ABSTRACT

The aim of this study was investigating the concentration of phenols in some surface water samples of Tirana area by using UV-VIS technique. Phenols are commonly found in nature because of their natural background and because of human activity including urban wastewater and industrial wastes. Phenol and its derivates are known to have significant ecological toxicity, therefore, determination of its concentrations in water is a valuable parameter for the water quality. UV-VIS method is easy to use, and a low-cost technique but it is also efficient and accurate to determine phenol in trace level. Levels of phenol were measured in four different waterbodies in Tirana area to have an overview about water quality of these important artificial lakes and to find specific reasons and/or phenol sources for them. Water samples were collected in different stations of Tirana artificial lake (10 stations), Paskuqan Lake (8 stations), Farka Lake (8 stations) and Dry Lake reservoir (6 stations). The water sampling was realized monthly from May to October 2024 (except August). Phenol analysis involved method building, method evaluation and quantify of phenol in water samples. Phenols were detected in all the water samples analyzed. The lowest values of phenol were found in the Artificial Lake of Tirana and Dry Lake while the highest values in the Paskuqan Lake and Farka Lake. Almost for all the samples, the concentration of phenols was low in May and high in September. The presence of phenol in these water ecosystems is connected mainly with urban waste. Furthermore, experiments indicated that samples had phenol concentration exceeding 3.4 ppm, a level deemed hazardous to aquatic life by the US Environmental Protection Agency (EPA).

Keywords: phenol, UV-VIS, surface waters, water analysis, urban pollution.

INTRODUCTION

Phenols and their derivatives are often found in the environment and are known as important pollutants of environment [1]. Their presence comes mainly from human activity, and as a result of the complicated bio-mechanism of plants, fungi and the decomposition of organic matter [2]. However, increased industrialization has created new ways for phenol to be present in ecosystems in alarming amounts [3]. Synthesis of polymers (especially resin), dyes and various other organic substances, coal tar, activity of the pharmaceutical and petroleum industries, municipal and industrial wastewater treatment [4], as well as the synthesis and degradation of some pesticides, such as phenoxyherbicides, are just some of the ways that phenols and their derivatives end up in the natural environment, where they usually act as ecotoxins [5]. The toxicity of phenols is often seen in the formation of reactive oxygen species and the formation of organic radicals [6], with hemotoxic and hepatotoxic characteristics, and can also be carcinogenic and mutagenic to living organisms, including humans [7]. Considering the increasing presence of phenols and their derivatives in the environment, as well as accidental pollution, such as transport accidents and pipeline leaks, it is important to analyze the concentration of phenol in water and soil [8, 9]. This can help reduce potential contamination risks as well as enable a more appropriate response to the problem.

Natural waters are estimated to contain about 0.01–2.0 μg/l phenol [1], and in unpolluted waters their concentration is often less than 0.02 mg/l [4]. However, it is important to consider the degradation/elemination of phenol and the fact that its concentration may change depending on anthropogenic water pollution. Toxic effects on aquatic organisms such as fish can be seen at concentrations of 0.01 mg/l and above [10] and phenolic concentrations of up to 5 μg/l can alter the taste of drinking water [11]. The presence of phenol in the environment has also led to its appearance in food. About 5 μg/kg of phenol was found in honey and coffee, as well as 7 and 28.6 μg/kg in sausage and grilled pork, and 37–70 mg/kg in the outer layer of smoked meat [1]. It has been estimated that frequent inhalation of phenol-contaminated air, for example near highly industrialized areas or by occasionally consuming smoked food with high amounts of phenol, can expose a person to toxic concentrations of phenol of 4 mg/day and 2 mg/day respectively [11]. Exposure to 10–240 mg of phenol per person can result in symptoms such as burning pain in the mouth, mouth sores, dark urine and diarrhea [1]. Phenol can also further affect the central nervous system and damage kidney and liver functions [8]. The removal of phenol from various systems, such as drinking water, presents many difficulty. Although some techniques, such as biodegradation, with some suitable microorganisms discovered, seem promising, there are only few data on the purification of drinking water from phenol by means of biofilters [7]. Biofilters are not always suitable for the environment from which phenol must be removed, and the mechanism of degradation of phenols at low concentration is not yet fully understood. The enzymatic approach has also been tried for several years, with its own advantages compared to conventional methods, however, it requires large amounts of enzymes to work, which can often be very expensive [12].

MATERIAL AND METHODS

Some data about study areas

This study was carried out in four waterbodies of Tirana area:

1) The Artificial Lake of Tirana is close to the city of Tirana, surrounded by a large vegetation park with an area of about 157 ha. The lake was built in 1955–1957 using several small rivers and rainfall. The 400 m dam was built to prevent water from flowing towards the city of Tirana. It has a surface of 45 ha.
2) Paskuqani Lake is to the North of Tirana city. It is one of its very important artificial sources. It was built in 1983 with the aim of irrigating agricultural lands. It has an area of 85 ha.
3) Farka Lake is an artificial lake built in the 1980s to irrigate the area below the dam. The water of the lake comes from the stream of Farka. The lake has an area of 75 hectares. It is to the East of Tirana.
4) Dry Lake of Tirana is to the South-Eastern part of Tirana city. It was built by a dam about 120 m in 60’. A small stream and rainfall supply it with water; therefore, its surface is constantly changing (max. 1 ha).

Note that, after the 90s, residential buildings and businesses were built near these lakes. In recent years, around these lakes, pedestrian walkways and recreational areas have been built for the residents of the area, and investment has been made in the growth of vegetation to serve as a place of rest and entertainment for the residents of the area and the citizens of Tirana. These areas stand out for their biodiversity and attractive hilly landscape, as well as for their natural heritage.

Water sampling in four artificial lakes of Tirana

Water samples were collected in different stations of Tirana artificial lake (10 stations), Paskuqan Lake (8 stations), Farka Lake (8 stations) and Dry Lake reservoir (6 stations). The water sampling was realized monthly from May to October 2024 (except August). One litre of water sample was taken for each station. Water samples were taken according to the ISO 5667-14:2016 methodology. They were transported and kept at +4 °C before analytical measurements in the laboratory. The sampling stations for each lake were shown in Figure 1.

Building of method for determination of phenol level by using UV-VIS technique

Before the analysis of phenol in water, the method was built in the UV-VIS apparatus and its evaluation was done as follow: A certified

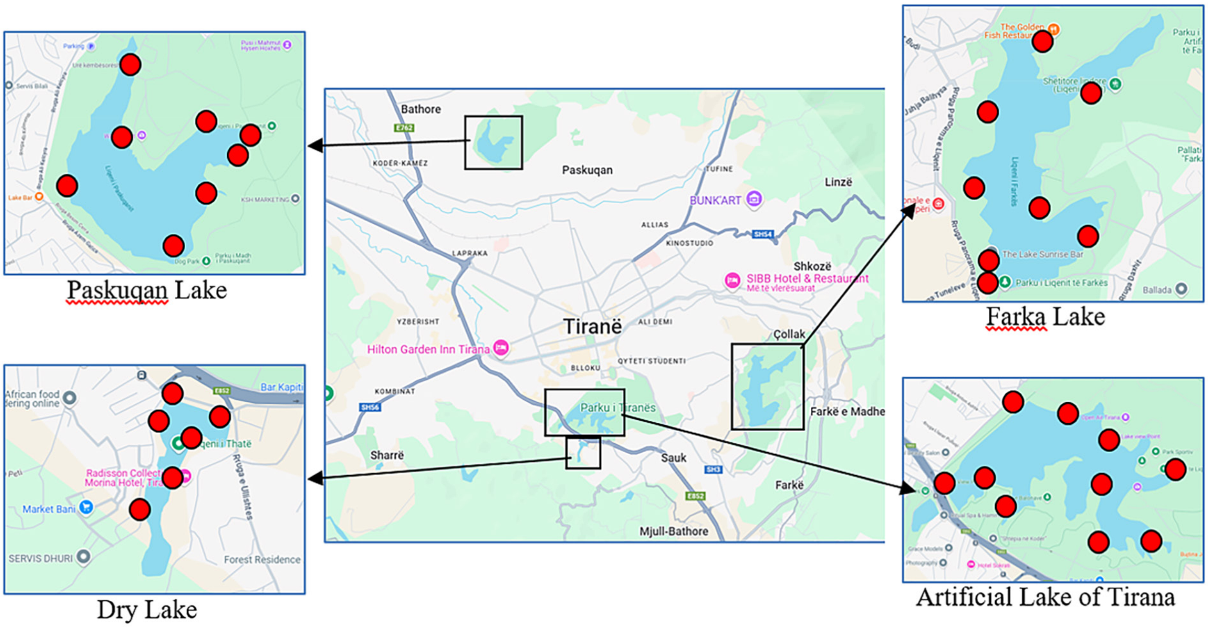

Figure 1. Sampling stations for surface waters of Tirana, Albania

standard solution with a concentration of 1000 ppm ± 10 ppm obtained from Fisher scientific company with catalog number LC 183301 was used. Initially, a working solution with a concentration of 100 ppm (250 ml) was prepared and from it, solutions with concentrations of 50, 25, 10, 5, 2.5 and 1 ppm were prepared in 50 ml flasks. Bi-distilled water was used for phenol dilution. The phenol solution with a concentration of 25 ppm was used to derive the absorption curve of phenol. Its scanning was performed automatically in a UV-VIS spectrophotometer model Varian Cary 50 UV-VIS Photometer and by using Cary WinUV software. It was scanned for every nm in the wavelength range from 200–1100 nm. The scanning speed was chosen to be 10 nm/sec. The selected, wavelength for the phenol quantitative analysis, λ max = 270.1 nm was selected. In Figure 2, the spectrum of the 25 ppm solvent for phenol was given.

Method evaluation for phenol determination

Measurements for different concentrations of phenol were made at λ_{max} = 270.1 nm as follow: o ppm (A = 0), 1 ppm (A = 0.0331), 2.5 ppm (A = 0.0665), 5 ppm (A = 0.0782), 10 ppm (0.1546), 25 ppm (A = 0.3597), 50 ppm (A = 0.7854) and 100 ppm (A = 1.5678). The absorbance data for these concentrations was used to build the phenol calibration curve (Figure 3). These data were used to evaluate the method parameters such as,

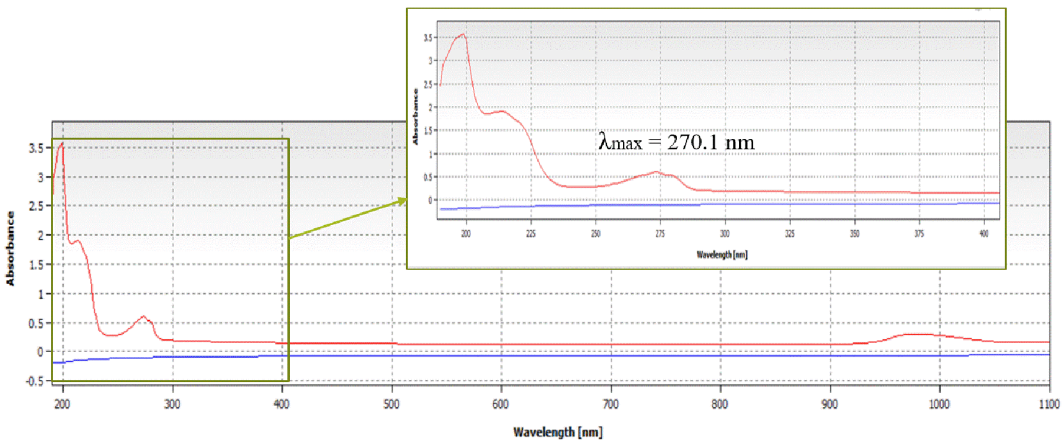

Figure 2. Absorption curve for phenol with concentration of 25 ppm

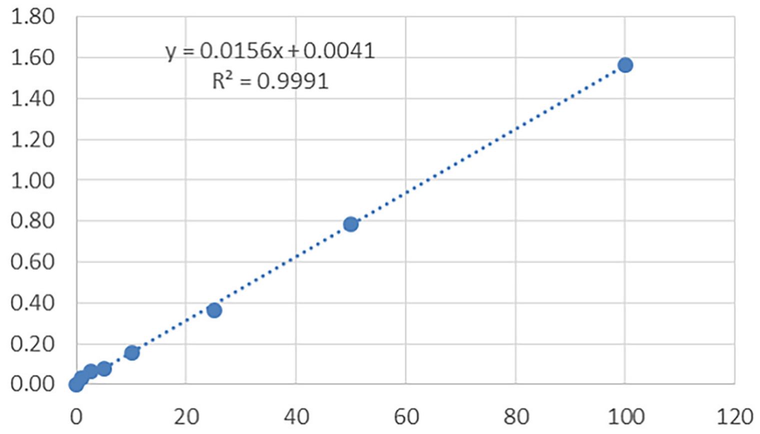

Figure 3. Calibration curve of phenol by using UV-VIS technique

the slope (0.0156), LOD (0.3 ppm), LOQ (0.9 ppm) and correlation coefficients (R^2 = 0.9991) as well as the linear range of measurements (0–100 ppm). The recovery of phenol was performed in a 1 liter solution with a concentration of 10 ppm (98.5–103.8%). A set (10 parallel measurements) of phenol solution of 10 ppm concentration were analyzed within one day and on 10 different days to calculate the STDEV, reproducibility (10.014 ± 0.0086) and repeatability (10.025 ± 0.0114) of the measurements. Measurements of the control solution of 10 ppm were analyzed on two other devices by other analysts to observe the reproducibility of the method (10.085 ± 0.0512). Also from these data the measurement error value was calculated (bias < 0.021% or 0.00021 ppm). Blank measurements were regularly performed during the measurements for validation procedure. The method validation was done according to ISO 17025 recommendations.

Analyzes of phenol levels at water sample

Water samples were first filtered with Whatman filter paper with diameter of 125 mm, grade no. 42 for removing suspended solid matter and then transferred to a 25 ml measurement flask. Three parallel measurements were performed for each water sample (for each station at each sampling period). Average value was selected as representative of phenol concentration for each analyzed sample.

RESULTS AND DISCUSSION

In this study, phenol levels were determined at four important aquatic ecosystems located in the Tirana area. Water samples were taken at 32 different stations for each month from May to October (with the exception of August). Measurements of phenol concentrations were performed using the UV-VIS technique, directly in water samples without the need to add reagents or other treatments that increase the cost of analysis and often lead to sample loss/contamination and obtaining incorrect results. This is a simple and low-cost technique that provides reliable results for phenol levels in the range of 0–100 ppm. The study was conducted at 10 stations from the Artificial Lake of Tirana, 8 stations from the Farka Lake, 8 stations from the Paskuqani Lake and 6 stations from the Dry Lake (of Tirana). These waterbodies are located near the city of Tirana. They are artificial lakes built before the 90s with the main purpose of irrigating agricultural lands and controlling water flooding in the city. After the 90s, residential houses and businesses were built near them, which have directly affected the quality of their waters. The impact of urban waste which are discharged directly into the waters of these lakes is one of the main reason for their pollution with phenol and other pollutants. This fact is supported by the results obtained from this study. Phenol was detected in all samples taken for analysis regardless of the lake or the study period (Table 1).

Phenol concentrations in the Artificial Lake of Tirana were given in Figure 4. Their levels increased from 6.05 ppm in May to 8.29 ppm in September. This is related to the pollution of the lake waters both from urban pollution and from the decomposition processes of plants and living things during this period. Note that, for the period from May to September has been a dry period without any significate precipitation. The lowest

Table 1. Statistical data of phenol in artificial lakes of Tirana area

Study area	Month	Mean	Min	Max	Median	STDEV
Artificial Lake of Tirana (10 stations)	May	6.051	4.520	9.372	5.585	1.399
	June	7.257	5.291	11.571	6.895	2.148
	July	7.213	5.282	11.204	7.010	1.738
	September	8.285	6.254	11.251	8.320	1.444
	October	7.860	5.392	9.273	8.415	1.319
Paskuqani Lake (8 stations)	May	9.040	7.361	13.315	8.611	1.982
	June	9.436	6.441	14.935	9.180	2.629
	July	9.430	7.503	11.809	9.414	1.730
	September	11.807	9.250	15.986	11.546	2.264
	October	11.518	9.052	13.173	11.958	1.488
Farka Lake (8 stations)	May	9.107	5.614	14.688	8.708	3.122
	June	10.446	6.120	16.475	10.212	3.509
	July	10.601	8.277	17.556	10.106	3.162
	September	11.761	8.322	14.515	11.725	2.605
	October	10.802	7.251	14.531	11.442	3.111
Dry Lake (6 stations)	May	7.033	5.225	10.832	6.422	1.985
	June	8.048	6.115	12.150	7.531	2.185
	July	8.365	6.104	12.947	7.731	2.375
	September	9.209	7.225	10.705	9.467	1.466
	October	9.191	6.231	10.716	9.913	1.662

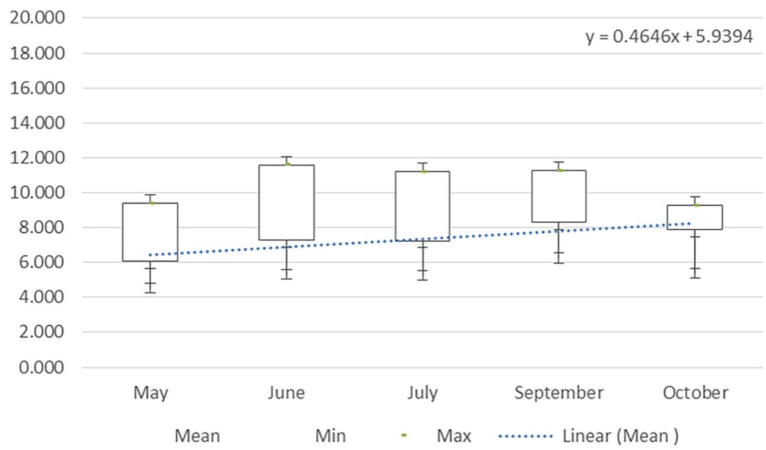

Figure 4. Levels of phenol in Artificial Lake of Tirana

level of phenol in October should be related to this fact (some intense rain fell at the end of September). The decrease of flow during the summer into the lake and the water evaporation may be other reasons for the increase of phenol level during this period. Also, its trend fluctuates depending on the number of residents near the lake, for example, in July there is a slight decrease. The presence of phenol seems clearly related to urban pollution and decomposition processes near the lake. The amount of precipitation and effluent flows directly affects the found levels. For all analyzed samples, the levels were higher than the 3.4 ppm limit set by the EPA for surface waters.

Phenol concentrations and trends in Paskuqan Lake was shown in Figure 5. Their levels range from 8.44 ppm in June to 11.81 ppm in September. The pollution of the lake waters mainly could be from urban pollution, decomposition processes of living organisms (during the summer period the process is intense), agricultural and new arrivals from the effluents of this lake. Again, for this

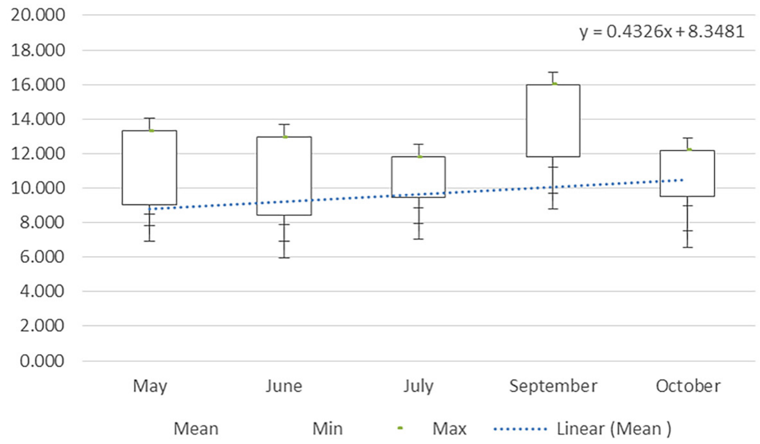

Figure 5. Concentrations of phenol in Paskuqani Lake

ecosystem, precipitation and the number of population (habitants) affect the levels of phenols in this ecosystem. It was clear that the levels of phenol in Paskuqan Lake were higher than in the Artificial Lake of Tirana for the same period. This must also be related with impact of animal farms and agricultural near the lake that can affect in a constant way. Degradation of pesticides and other chemical can impact directly phenol levels. Also, for all samples analyzed from this lake, the levels were higher than the limit set by the EPA for surface waters.

Figure 6 shown phenol concentrations in Farka Lake for the period from May to October 2024. Their minimum level was in May (8.67 ppm) and the maximum in July (17.56 ppm). Again, these levels should be related to the pollution of the lake waters mainly from urban pollution, organism decompositions and agricultural activity. Compared to other ecosystems, the September value does not represent the maximum level. This belongs to July. This can be related to any punctual source for the phenol (or compounds that generate it from the degradation process e.g. pesticides) in this period in the lake. Adding that, near Lake Farka there is a large number of new buildings that are built and/or in building process. The discharges from agricultural activity and animal farms here are limited (compare to Paskuqan Lake) but again the levels of phenol were higher compare to Artificial Lake of Tirana. This can be related to new arrival from the Farka Stream that supplies this lake with water. Note that, the self-cleaning processes of these lakes are very slow and can affect to the concentration of phenol (and other pollutants) in the water. All analyzed samples from Farka Lake, were in higher level than the limit set by the EPA for surface waters.

Phenol concentrations in the Dry Lake (of Tirana) are given in Figure 7. Their levels range from 7.03 ppm in May to 9.21 ppm in September and October. There seems to be an increasing trend from month to month. This is closely related to the lack of precipitation during this period. The Dry Lake has as its main supply rainfall, so

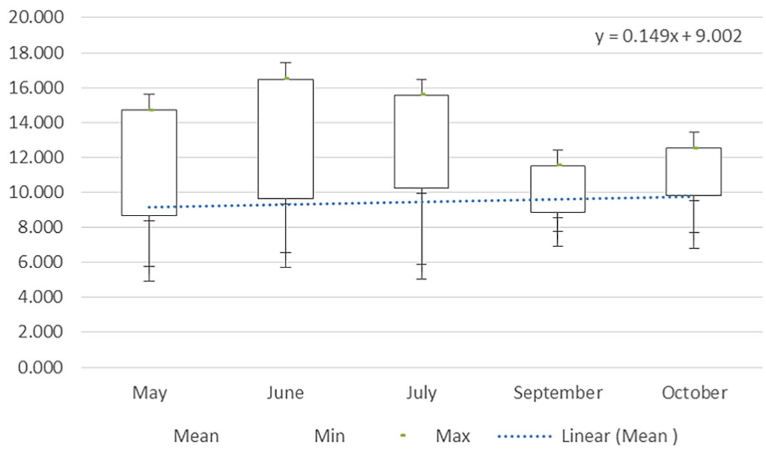

Figure 6. Concentrations of phenol in Farka Lake

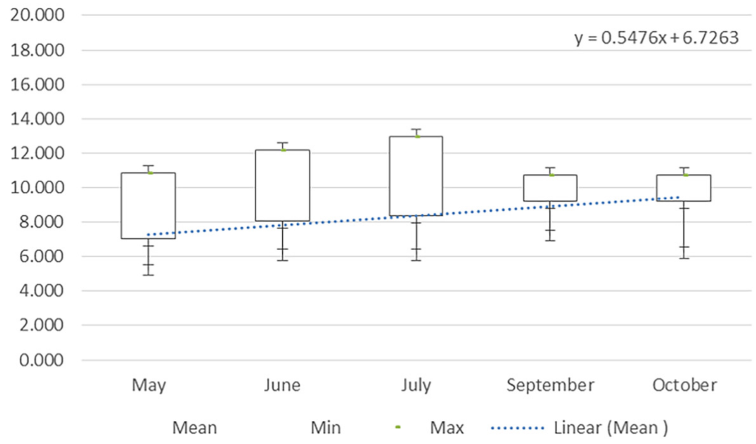

Figure 7. Concentrations of phenol in Dry Lake

their lack increases the concentration of pollutants in the water. Phenol presence for this lake could mainly be because of urban pollution and organism degradation process. Overall, the phenol levels found for this lake were similar to those of the Tirana Artificial Lake and lower than the found levels in Paskuqan and Farka lakes. Even for this lake, the levels of phenol in water samples were higher than the limit set by the EPA.

CONCLUSIONS

Analysis of phenol concentrations in natural water samples by using UV-VIS technique shown a reliable method which is fast, low-cost and with reliable results. One of the useful characteristics of UV-Vis spectrophotometer turned out to be its simplicity, versatility and fast result time. On the over hand, it did not always provide consisting results and it is not known how well it can distinguish phenol from other similar pollutants, such as benzene and toluene, leaving a room for errors. Thus, this is mostly a fast, simple and easily applicable way to determine relative phenol concertation in water, which can also be helpful when comparing different water sources and the water pollution in general. Determination of phenol levels in natural waters is an important data connected directly to the water quality. In this study the analyzes were performed at wavelength = 270.1 nm by using satisfactory parameters such as $R^2 = 0.9991$, LOD = 0.3 ppm and LOQ = 0.9 ppm, etc. Evaluation of method was done for each parameters recommended by ISO standards.

Measurements in four waterbodies of Tirana shown relatively high amount of phenols, especially when taking into consideration US Environmental Protection Agency (EPA) which stated [13] that for aquatic life, the concentration of phenols should not exceed 3.4 ppm at any time. In all the samples that were taken for analysis for the Artificial Lake of Tirana, Paskuqan Lake, Farka Lake and Dry Lake (of Tirana), the concentration of phenols were higher than 3.4 ppm. The highest concentrations were found for Paskuqan Lake and Farka Lake with maximum in September over 10 ppm (3 times higher than limit of phenol in surface waters) and the minimum was for Artificial Lake of Tirana and Dry Lake. Note that, the concentration of phenols generally were lower in May was the highest concentration was in September. Lack of rainfall, urban waste discharges, decomposition of organisms, waste discharges from animal farms and/or agricultural can be considered as the main pollution sources of phenol in these ecosystems. Also, this can be influenced by the dry and hot weather in summer period and the characteristics of each of these artificial lakes. Adding that, this study present the first published data on phenol levels in water systems of Albania. Recommend that, the responsible institutions for surface water quality in Albania, to apply this method to assess phenol level for these and/or other ecosystems, as a hazard water pollutant.

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