Heavy metal contamination in surface water and impacts in public health. The case of Kifissos River, Athens, Greece

Aikaterini-Sofia Partsinevelou, Levkothea Evrenoglou

Abstract—The Kifissos river in Attiki prefecture in Greece, has a length of 22km (14 km in a residential area and 8 km outside) and a basin of 360,7 km². It is the largest river in Attica and flows through the Metropolitan Athens area from the mountains of Parnitha and Penteli until the Egaleo Mountain collecting simultaneously waters from them.

The aim of this study is to establish and evaluate the current situation of Kifissos river in Attica by studying the existing physicochemical parameters in the northern part of Kifissos river, in order to determine if the river is polluted by the already recorded anthropogenic activities.

For determining the degree of pollution of the river Kifissos, a key role is played by the estimate of the total pollution load, with sampling at regular intervals. In particular, the study area concerns the open section of the river, from Philadelphia to Kryoneri including the municipality of Kifisia. 30 water samples were conducted at three different points of the river. Physicochemical characteristics and concentrations of heavy metals were determined by standard methodologies. Recordings of sampling points and anthropogenic activities were introduced into a GIS database.

The results showed that the concentrations of lead (Pb), arsenic (As), mercury (Hg), nickel (Ni), cadmium (Cd), chemical oxygen demand (COD), biological oxygen demand BOD5, suspended solids (SS), total dry solids (TDS), total volatile solids (TVS) and the conductivity was increased in samples of Philadelphia and Kifissia compared with samples Kryoneriou, with a lowest concentration of DO.

By analyzing the results, it is showed that the river's contamination comes from urban and industrial activities. This fact shows that the limited groundwater resources of the study area are endangered by the heavy metal contamination, as the basin is consisted mainly by loose deposits, but most important, there are some severe impacts in public health caused by the continuous exposure to heavy metals.

***Keywords*—**Geographical Information Systems, heavy metal contamination, health impacts, Kifissos River.

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I. Introduction

THE metropolitan area of Athens has experienced a rapid expansion during the last six decades. The population increased from 1.4 million (1950) to 4.5 million (2010), and the town is facing serious environmental problems as a result of the increasing industrialization and traffic, but also related to its geographical relief [1]. The city of Athens and its satellite communities constitute a large urban agglomeration within the Attica basin which is about 600 km2 large.

Kifissos River flows through the Metropolitan Athens area and is the main river of the city, reaching the Saronikos Gulf in the south. In addition to its springs in Parnitha and Penteli, Kifissos River collects also water from the Egaleo Mountain. From its source until Faliro, the river is 30 km long, but the total length of its most notable tributaries is over than 150 km. The River basin covers an area of 372 km2 and is currently the most important natural system in the urbanized wider region of Attica. Hydraulic works have been carried out in Kifissos River since 1900, but the latest works were constructed based on a study of 1971 [2].

The flow management of Kifissos River basin was initiated 35 years ago and accomplished in parts in 2004. The river has been partially trained in the past for discharges of 700, 900, 1100, and 1400 m3/s and return period of 1:50 years. These works do not comprise a coordinated flood control system because they have been constructed in response to specific road transportation needs.

The latest and most radical intervention was the construction of a highway on top of the last 10 km of Kifissos [3]. Thus, the river and its surrounding territory became dumping places for toxic industrial, domestic and institutional wastewater discharge and solid waste disposal. Ten out of twenty trace elements are considered to be toxic for the human body. Of these, five metals, Pb, Cd, Hg, As, and Ni pose a potential threat to humans. The health-related monitoring component of the global environmental monitoring system (GEMS) aims to assess human exposure to pollutants. The long-term objective of the biomonitoring is the assessment of human exposure to toxic metals [4], [5].

The aim of this study was to evaluate the degree of exposure at three different Attica municipalities north and near to the banks of the Kifissos River, allowing to define reference

values of toxic heavy metals, in the current populations and define the impacts in public health. Concentrations of five toxic metals (arsenic, cadmium, mercury, lead and nickel) were analyzed in water samples from the Kifissos River.

II. The Study Area

The study area concerns the north part of the Kifissos River basin (Fig. 1) which is characterized by anthropogenic interventions such as intensive agricultural activities and a dense road network. The intensive urbanization and the hard action of industry (almost 70% of the total river catchment area) represent a major threat to the environment of the study area.

At the north zone of the Kifissos River there are two principal zones for the protection of the natural environment. The A′ protection zone includes all the area located within 50 m from both sides of the river banks and streams. This area is defined as an area of environmental education, outdoor recreation and agricultural uses. Construction and alteration of the natural landscape are not allowed. The B′ protection zone includes the boundaries of A′ zone comprising the limitations that have been determined by coordinates. In this zone agricultural, residential, recreational and cultural uses as well as environmental education and sports are allowed. The construction of fences in the A′ and B′ zones is permitted just for the protection of the habitants and security reasons. Also, in both zones are prohibited the disposal of rubbles, and solid and water wastes.

Geologically, the study area features alpine and post-alpine formations. Alpine formations of mountains cover 65% of the total extent of the river's drainage area. Post-alpine formations (conglomerates, marls, sandstones and alluvial deposits) can be divided into tertiary and quaternary deposits of terrestrial and marine origin. Also, there are artificial embankments made of stone along the main course of the river for the most of its length.

The mountainous and semi-mountainous parts of drainage basin mainly consist of karstified limestones, marbles and schists, while the low-land parts have been totally covered with alluvial depositions and building materials (concrete, slabs etc.). In addition, due to its karstic background, the watershed has a significant groundwater yield [6]. The geological formations of the study area are not correlated with the existence of heavy metals, as the only formations which could enrich the surface water with trace metals are the ophiolitic and metamorphic rocks [7].

The training and the diversion of the rivers Kyklovoros, Profitis Daniil and partially of Ilissos River to Kifissos is one of the most important projects for sewerage and flood protection of Athens. Nevertheless, the surface elevation difference between upland and low-land areas still remain a serious problem for extensive flooding [8]. The last forest fire which was located near the study area was at 2009 and due to lack of data, correlation between the fires and heavy metal concentrations cannot be done.

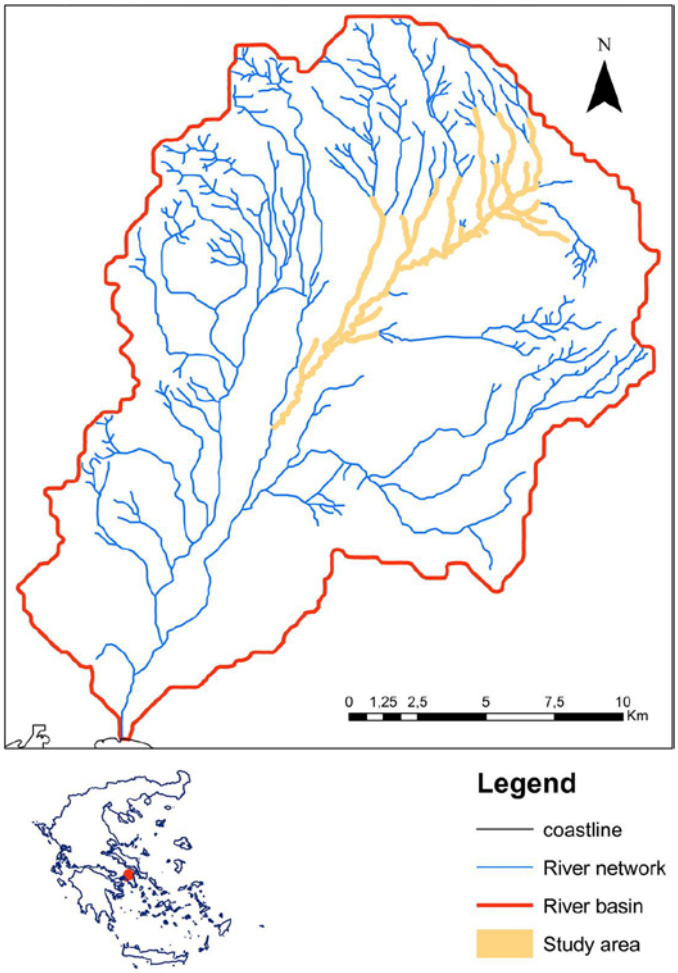

Fig.1 the study area

III. Methodology

Water samples were collected from three different stations, at the municipalities of Philadelphia, Kifisia and Kryoneri. In every station, 5 Kifissos River's water samples were collected (15 samples in total). A Global Positioning System device (Garmin GPS e Trex 10) was used in order to register the sampling stations. The data were stored in a geographic database (Geographic Information System, GIS). The samples were collected according to the guidelines of the Standard Methods for the Examination Water and Wastewater [9].

Every water sample from the surface of the river (without sediments), was stocked in two different polyethylene bottles, one for the physicochemical analysis and one for the determination of heavy metals which contained 5 mLhigh-purity concentrated nitric acid (Merck, Darmstadt, Germany) as a preservative. The samples were transported to the laboratory and kept at 4 °C until the analysis.

The physicochemical analysis involved measurements of physical and chemical parameters of the water samples, such as total dry solids (TDS), volatile suspended solids (VSS, oven J.P. Selecta s.a.), suspended solids (SS,), pH (826 pH meter, Metrohm), diluted oxygen (DO, WTW Oxi 315i), conductivity (Lovibond Con 200), nitrate (NO3-N, HACH DR 2000), biochemical oxygen demand (BOD5, Thermostat Cabinet

Lovibond and WTW Oxi 315i) and chemical oxygen demand (COD, AquaLytic CSB/ COD Reactor AL 31 and HACH DR 2000). Portable electrochemical devices were used for in situ measurements as pH, temperature, diluted oxygen and conductivity were also done. The determination of the other parameters was done in the laboratory, based on the guidelines of the Standard Methods for the Examination of Water and Wastewater [9]. The methodology for the determination of heavy metals in water samples is the same to the one described above.

IV. Results

Overall, some 470 installations of human activities, including agricultural and industrial activities were registered with the Garmin GPS e Trex 10 in the study area. The majority of industries are placed around the municipalities of Philadelphia and Kifisia. Industrial processing of marble, car repairs, refinishing, wood industries, veterinary medicines, pharmaceutical, plastics, metal, food, beverage, and dairy industries are some of the activities in the study area. We can observe from the data, that industrial development that is within the industrial zone is not exclusively specified by the law development which has spread to the A′ and B′ protection zone.

Heavy metal concentrations were also determined at three water stations of the municipalities Kryoneri, Kifisia and Philadelphia, along the Kifissos River (Fig. 2). Table I shows the number of samples (N), arithmetic means (MA), standard deviations (SD), geometric means (GM), and the minimum (Min) and maximum (Max) concentrations expressed by micrograms per liter (μg/L) of arsenic (AsW), cadmium (CdW), mercury (HgW), lead (PbW) and nickel (NiW) concentrations in river's water for every sample station. The Kolmogorov–Smirnov Z test with a significance level 0.05, revealed a significant normal distribution of AsW (p=0.057), CdW (p=0.550), PbW (p=0.138) and NiW (0.052) concentrations in the three municipalities' river water. The mercury concentrations were below the sensitivity of the instrument (electrothermal atomization atomic absorption spectrometry Zeeman Perkin Elmer A Analyst 600, with graphite furnace and background correction system, b0.05 μg/L) and were therefore not included in the analysis. The Levene's and Brown–Forsythe's variance homogeneity tests do not show statistically significant differences in As, Cd and Ni water concentration for the municipalities of Kifisia and Kryoneri, unlike the concentration of PbW. The t-test confirms the difference between the samples from these municipalities for AsW (p=0.000), CdW (p=0.000) and NiW (p=0.000) concentrations. The one-way ANOVA also confirms the statistical difference of PbW (p=0.000) concentration. Also, statistical difference was confirmed by t-test for concentrations of AsW (p=0.000), CdW (p=0.000), PbW (p= 0.000) and NiW(p=0.000) between the municipalities of Philadelphia and Kryoneri.

No statistically significant t-test differences were observed for AsW (p=0.295), CdW (p=0.441) and PbW (p=0.163) concentrations between the municipalities of Kifisia and Philadelphia. A statistically significant difference was found only for NiW (p=0.031).

The discharges of Kifissos River's natural springs have diminished significantly, mainly due to illegal human interventions, thus, river flow is not continuous through the whole year but it depends on the amount of the annual rainfall [10]. Chemical characteristics of urban rivers are sometimes profoundly altered by the pollutants of urban environments. The concentrations of heavy metals in the Kifissos River show that the river is characterized by pollution sources and differs chemically from other natural Greek rivers. In comparison with the research of Skoulikidis et al. [11], on the environmental quality of the Greek rivers, only mercury concentration was lower than that of the Evros River.

Urban and industrial wastewaters, as well as surface runoff of the city are the main sources of pollution. Different kinds of industries, such as paint production plants, as well as food, beverage, and dairy industries are in the area between Kryoneri and Philadelphia. From these sources heavy metals (Cd, Pb, Zn, Cr, and Ni) may leach into the river [12]. The highest concentration of NiW was measured in the municipalities of Kifisia and Philadelphia where industry is the main activity.

Another important source of contamination of surface waters and human exposure is the air of the Attica basin that is polluted by heavy metals. The concentrations of Pb, Cd, As and Ni in the atmospheric PM2.5 particles have common sources, such as vehicle emissions/oil combustion, re-suspended road dust and industrial activity. Lead concentration values were mainly emitted by motor vehicles, the main emission source in Attica basin [13]. Lead concentrations in

Municipalities																		
	Philadelphia (urban) (μg/L)						Kifisia (urban) (μg/L)						Kryoneri (sub-urban) (μg/L)					
Metal	N	MA	SD	MG	Min	Max	N	MA	SD	MG	Min	Max	N	MA	SD	MG	Min	Max
AsW	5	4.224	0.201	4.2	4.05	4.56	5	4.518	0.551	4.28	4.2	5.5	5	1.234	0.155	1.31	1.04	1.4
CdW	5	0.176	0.034	0.17	0.14	0.23	5	0.2	0.057	0.18	0.16	0.3	5	0.038	0.008	0.04	0.03	0.05
HgW	5	[a]	[a]	[a]	[a]	[a]	5	[a]	[a]	[a]	[a]	[a]	5	[a]	[a]	[a]	[a]	[a]
PbW	5	5.088	0.705	4.78	4.67	6.34	5	5.94	1.021	5.64	5.15	7.63	5	0.304	0.079	0.26	0.23	0.4
NiW	5	61.44	2.254	60.9	59.2	65.2	5	68.74	5.85	68	63	78.3	5	6.002	0.10	6.04	5.89	6.1

N number of children, *MA* arithmetic mean, *SD* standard deviation, *MG* geometric mean, *Min* minimum concentration, and *Max* maximum concentration.
[a] All mercury concentrations were lower than 0.05 μg/L, below the sensitivity of the instrument.

Table I heavy metals in the studied water samples

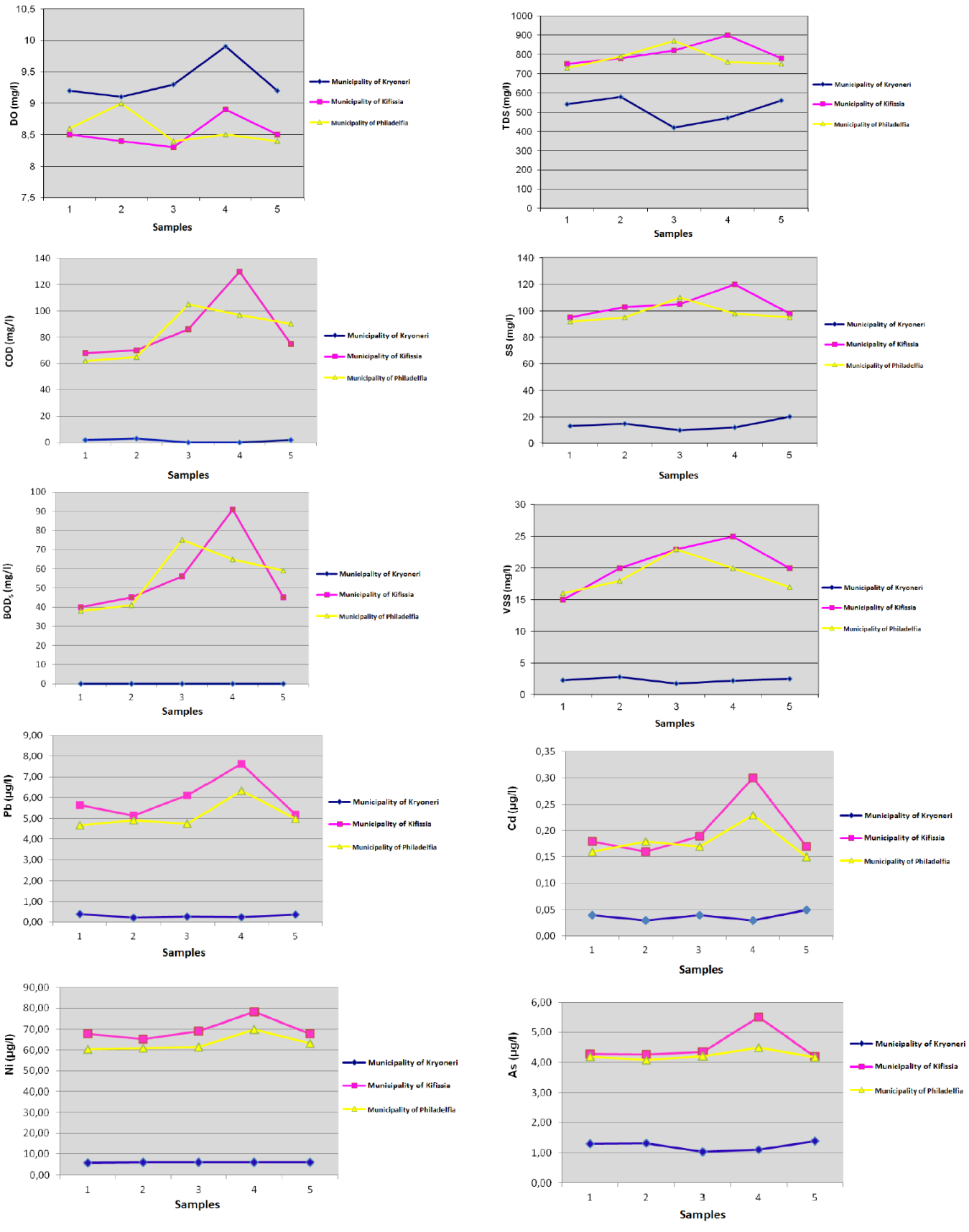

Fig.2 results of the water samples measurements

the atmosphere of Athens were in the range 55–4049 μg/g with an overall average of 1293±916 μg/g and an average value for the street locations of 1318±101 μg/g [14].

V. Impacts in Public Health

Continuous exposure to low levels of heavy metals may result in bioaccumulation and health deterioration in humans [15].

The discharges of Kifissos River's natural springs have diminished significantly, mainly due to illegal human interventions, thus, river flow is not continuous through the whole year but it depends on the amount of the annual rainfall [10].

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De Burbure et al. [16] have shown that exposure to As, Cd, Hg and Pb concentrations can cause effects on children's renal and dopaminergic systems without clear evidence of a threshold. This finding reinforces the need to control all the potential heavy metal emissions into the environment in order to protect children's health.

VI. Conclusions

Human activities release toxic pollutants such as heavy metals like lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn) and organic compounds in the environment.

All the arithmetic mean values of trace elements that were analyzed in this study such as arsenic (AsH), cadmium (CdH), mercury (HgH) and lead (PbH) in hair were higher in the area of Kifisia than in the other two areas. All the mean values for the same trace element were the lowest in Kryoneri, while the values of Philadelphia were between those of Kifisia and Kryoneri. These observations may confirm the fact that the area of Kifisia (particularly its northern part near the banks of the Kifissos River) is exposed to major environmental pollution, due mainly to the human activities (traffic exhaust and industrial emissions).

The observed lowest concentrations of heavy metals, at the municipality of Kryoneri (which doesn't have major anthropogenic activities), compared to Kifisia and Philadelphia concentrations, suggest that the river is contaminated namely by anthropogenic activities near and along the river banks.

Most of the industrial activity is located near the municipality of Kifisia. Thus results in higher, contaminant concentrations in Kifissos River. Moreover the exposure of children to heavy metals as lead, arsenic and nickel is also increased in comparison with the other municipalities.

This is probably because heavy metals existing in water bodies and sediments may be released back into the water column and atmosphere due to the modification of water physicochemical parameters and biological activity [17]. Thus, in several cases, urban rivers can be physically and biologically hazardous due to their abrupt changes like e.g. in the water flow velocity, in the hydraulic water level, water quality and sediment [18]. Another possible pathway of exposure is the concentrations of heavy metals that remain in the atmosphere (as suspended particles) and can be inhaled so penetrate in the human body.

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