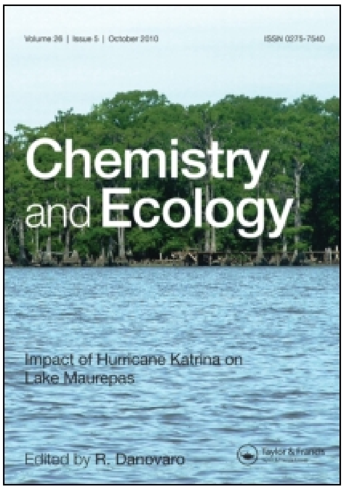

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Transport of pollutants in two estuarine systems on the coast of Georgia

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The aim of the present study was to examine the distribution of pollutants in two coastal systems in Georgia: (1) Kubitskali river which flows into the Black sea through the city of Batumi and is polluted mainly from the effluents of an oil refinery; (2) Paliastomi lake, which is a shallow water body at the south-east of the city of Poti. During 2000–2001, two samplings took place in each system, one in the low-flow period and one in the high-flow period. During these samplings, pH, temperature, dissolved oxygen, and salinity were measured in situ, whereas water samples were collected for the analysis of trace metals, nutrients, and organic pollutants with standard methods. The results of the measurements indicate the significant pollution of both systems by ammonia and in the case of Kubitskali River also by oil products. The need for a sustainable management plan of the activities taking place in the river basin is urgent.

Keywords: Black Sea; Georgia; Kubitskali River; Paliastomi Lake; Pollution

1. Introduction

Urban and industrial activities in coastal areas contribute to the introduction of significant amounts of pollutants into the neighbouring marine environment. In some cases, continuing anthropogenic polluting activities cause significant and permanent disturbances in marine systems and, consequently, environmental and ecological degradation. The disposal of untreated urban or industrial effluents in small coastal systems (rivers, lagoons, etc.) is a common practice in many countries, mainly if the environmental services are not well organized.

Considerable amounts of pollutants enter the marine environment through rivers. Estuarine zones are the sites of major discharges of urban and industrial pollutants. The different kinds of pollutants, during their transport in the river, but mainly during the mixing of fresh and sea

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water that takes place in the estuary, undergo numerous changes as a result of dissolution, precipitation, and sorption phenomena. The suspended load and the pollutants in the riverine water are strongly influenced by changes in major physicochemical variables as well as by various hydrodynamic processes. Flow rate, pH, redox conditions, and ionic strength affect pollutant sorption on particles, formation of authigenic particles, and particle–solution interactions. The distribution patterns of pollutants among the various parts of the estuaries have been found to be very complicated as a result of a great number of physical, chemical, and biological processes involved [1–4].

Lagoons are shallow coastal lakes, sometimes near estuaries, separated from the open sea by a barrier beach offshore, generally paralleling the shoreline. Lagoons are invariably shallow because barrier beaches form only in waters a few metres deep where wave action suspends sediment and transports it along the coast. Coastal lagoons are also very interesting from an ecological and environmental point of view, and although they are recognized as sensitive and fragile systems, many of them are significantly polluted. In most cases, artificial channels that were opened for the easy communication between the lagoon and the sea have significantly influenced their ecology [1, 5, 6].

While there are common basic biogeochemical processes, differences in timescales of mixing and transport, in biological productivity or in sedimentary regimes, lead to major differences in pollutant routes, cycling, and fate in estuarine zones. Although there is some information about the processes involved, there is a need for additional data on the behaviour of pollutants in estuaries. Data from riverine systems and lagoons of differing geology, climatology, and physiography as well as differing anthropogenic influences are needed to better assess natural variability and to provide a basis for differentiating between natural and unnatural values [7, 8].

Most studies concerning the origin and behaviour of pollutants in riverine systems are focused on heavily polluted rivers of the industrialized countries. The study of small riverine systems is rather limited, although some of them are also heavily polluted and have considerable ecological importance. This is also true for Mediterranean and Black Sea regions where the need to study the main riverine systems has superseded the study of small systems [9, 10].

Knowledge of these processes is of great importance not only from a scientific point of view, for the understanding of environmental geochemical and biochemical mechanisms, but also for the planning of environmental management of the estuaries in order to achieve sustainable development. Significant care must be given in small lagoons and rivers, which are systems in danger of environmental deterioration or ecological degradation, without the appropriate management [11, 12].

Monitoring systems are essential for understanding the results of long-existing pollution processes, but the lack of them in many regions makes it very difficult to draw certain conclusions about the long-term results of human activities [13, 14]. The need for sustainable management is urgent.

Concerning the Georgian coast, the main sources of surface water pollution in the region are direct dumping of industrial effluents, run-off of agricultural fields, and urban wastes. It must be noted that the majority of clean-up systems of the industries located in the area need to be repaired or reconstructed, as their operational efficiency no longer meets the sanitary demands. A decrease in Black Sea salmon and trout population has been reported. Moreover, no care has been taken over the management of toxic wastes. Black and coloured scrap metals are dumped near the industries without any kind of treatment, and there are no plans for recycling [15, 16].

In the present study, we tried to determine the main environmental problems in two small coastal systems on the coast of Georgia (figure 1), by examining the distribution of the most common water pollutants and the water quality of these systems.

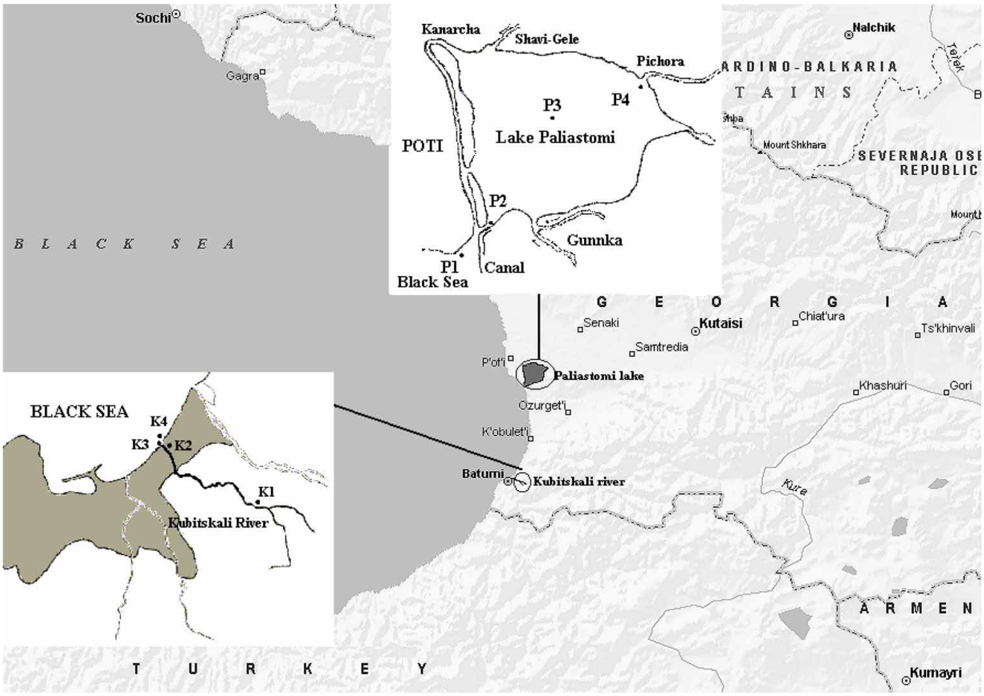

Figure 1. Map of the Georgian coast and the study areas.

2. Materials and methods

2.1 *Study areas*

Kubistskali is a small river (flow range about 1.3–3.9 $m^3\ s^{-1}$), which flows into the Black sea through the city of Batumi. Its length is about 6.5 km, and its catchment area is 6.45 km^2. It never freezes and never gets overly dry. The river bed is slightly widened and consists of sands, pebbles, and stones. Both of its banks are steep, and in some places as high as 8 m. Ferro-concrete walls have been built along some parts of the riverbanks. It has several small tributaries. In the upper part, its water belongs to the hydrocarbonate class, and in the lower section to the chloride class.

It is polluted by the effluents of some industries but mainly from the effluents of one large refinery, which is located near its estuary in the city of Batumi, which is the main port of Georgia. About 5 tonnes of phosphorus, 15 tonnes of synthetic substances, and 275 tonnes of petroleum hydrocarbons were discharged into the river from the refinery. About 400 m^3 of industrial effluents per day were disposed of into the river [17].

During 1976–1989, there was a monitoring system in the river with two sampling stations (upper river and estuary, K1 and K2). A large number of measurements of various environmental parameters were carried out with values of oil products, nutrients, and phenols, exceeding the marginal permissible concentration of the former Soviet Union Legislation by 10–100 times. Now, due to the economic problems of the country, these monitoring systems (and all the relevant systems) have ceased operation [17].

The Lake Paliastomi is a shallow (max. depth 3.2 m) water body of 18.2 km^2, adjoining the Black Sea, located at the south-east of the city of Poti. The lake is part of the ecologically important Kolkheti wetland and apparently represents an old lagoon of the Black sea, which was demarcated in the north by the expanding Rioni river delta and subsequently closed off by a barrier beach formed from shifting river sediments. Paliastomi Lake is a protected area under the Ramsar Convention because it is characterized by unique and endemic biodiversity.

The river Pichora from the east supplies most of the freshwater of Paliastomi Lake. The opening (in 1924) of a channel connecting the lake to the Black sea, for the prevention of floods, has changed the ecology of the area significantly, as the salinity has increased from 2 to 12 ppt. The flow rate through the former natural outlet of the lake, the river Kaparchiva, has been reduced dramatically and the outlet filled. Plankton biomass and benthic populations were decreased by a factor of 15 and 6, respectively, and the economic consequences to the fishing industry were enormous. The opening of the channel has also increased the transport of pollutants through the channel in both directions (e.g. from the lake to the sea for nutrients and from the sea to the lake for hydrocarbons).

Environmental problems in the area are also caused by overfishing, poaching, peat- and sapropel-extraction activities, and water pollution by toxins of decaying unexcavated peat layers and by runoff from upstream agricultural activities. The water quality of the lake was monitored in four sampling stations, but since 1991 the monitoring has not been complete [18].

2.2 *Sampling*

Samplings were carried out in July 2000 and November 2001 to obtain some indication of the variations between the wet and dry period. The position of the sampling stations is shown in table 1. The stations P1 to P4 in Lake Paliastomi and K1 and K2 in Kubitskali River correspond to the positions of the old Georgian monitoring system. Two seaward stations were added in the River Kubitskali inside and outside the mouth of the estuary. A Magellan GPS Colour Track Satellite Navigator was used to define the position of the stations.

Dissolved O_2, temperature, salinity, and pH were measured *in situ* with a Y.S.I.-63 portable pH/temperature/conductivity/salinity meter and a Y.S.I.-57 portable DO/temperature meter.

Water samples were taken with great care using horizontal Hydro-Bios sampling bottles and kept in a portable refrigerator. Upon arrival at the laboratory, the samples were filtered through 0.45 μm Millipore filters using vacuum pumps. All sample handling was carried out in a clean box to prevent contamination.

2.3 *Analytical methods*

Nutrients and total phenols were determined spectrophotometrically using standard methods [19]. Specifically, nitrates and nitrites were determined using a Bran and Luebe

Table 1. Sampling stations in Paliastomi Lake and Kubitskali River.

	Latitude (north)	Longitude (east)	Description
Stations of Paliastomi Lake			
P1	42° 05′ 38″	41° 42′ 12″	Near the sea
P2	42° 06′ 13″	41° 42′ 86″	Under the bridge
P3	43° 07′ 18″	41° 43′ 89″	Centre of the lake
P4	42° 08′ 16″	41° 45′ 16″	Estuary of Pitsora
Stations of Kubitskali River			
K1	41° 38′ 41″	41° 42′ 34″	Upper river
K2	41° 38′ 98″	41° 39′ 88″	Near the estuary
K3	41° 38′ 35″	41° 42′ 85″	Inside the mouth of the estuary
K4	41° 38′ 30″	41° 42′ 92″	Outside the mouth of the estuary

automatic analyser. The principle of the measurement of nitrites is based on the spectrophotometric determination of the coloured azo dye they form after their reaction with sulphanilamide and N-(1-naphtyl)-ethylenediamine dichloride. Nitrates were reduced to nitrites using a cadmium column and were measured accordingly. Ammonium was quantified by the Nessler method, whereby a brown-yellow-coloured salt is formed when ammonium reacts with the Nessler reagent (mercury iodide and potassium iodide). Phosphates were determined by spectrophotometric detection of the blue-coloured complex produced when phosphates react with sulphuric acid, ammonium molybdate, antimony, and ascorbic acid. Silicates are determined by spectrophotometric determination of the blue-coloured complex formed after reaction with ammonium molybdate, metol, and sodium sulphite. Total phenols were determined by the formation of yellow-coloured complexes with amino-antipyrine and potassium ferricyanide. A Varian, Cary 1E double beam spectrophotometer was used for the measurements of phosphates, ammonium, silicates, and phenols. Cuvettes (5 cm in length) were used for samples with low concentrations.

The filters were dried and weighed for the determination of the suspended particulate matter (SPM) and then treated at 90 °C with concentrated HNO_3 in covered PTFE beakers for 16 h to determine the particulate metal content [20]. Blank filters were analysed at each sampling for the determination and subtraction of possible contaminations.

Dissolved trace metals were measured in the filtered water samples by graphite-furnace atomic absorption spectrophotometry (GFAAS) with background correction based on the Zeeman effect (Varian, SectrAA-640Z/GTA-100) and flame atomic absorption spectrometry (Varian, SpectrAA-200) [21].

Fluorescence spectroscopy (Perkin Elmer 512 double beam fluorescence spectrophotometer) was used to determine petroleum hydrocarbons after their extraction with n-pentane. The results are expressed in terms of 'Chrysene equivalents' [22, 23].

The relative standard deviation of the measurements resulting from replicate (four or five) determinations in selected samples and standard addition experiments was 2.5–5% for nutrients and organics, 3–6% for dissolved metals, and 3–7.5% for particulate metals. The results were presented according to IUPAC guidelines for environmental data [24].

3. Results and discussion

In order to provide some measure of comparison between the concentrations of pollutants determined and guideline values, the EU legislation guidelines, maximum admissible concentrations (MAC), are listed in table 2. The types of water considered are 'water for human consumption' (80/778/EEC) and 'fresh water for fish' (78/659/EEC) [25].

3.1 *Kubistskali River*

The data from the two samplings in Kubitskali River are listed in tables 3 and 4. Table 3 also includes historical data from the Georgian monitoring system [17].

The fluctuations of water temperature was typical for small rivers. During the summer low-flow period, the temperature ranged from 25.8 to 27.9 °C, whereas during the winter high-flow period, the range was 10–12 °C. The pH and salinity values were similar in both seasons. Higher pH (8.0) and salinity values (9.7) were observed at station K4, at the mouth of the river.

Dissolved oxygen (DO) ranged between 5.78 and 9.60 mg l^{-1} during the summer months, while during the high-flow period, all the concentrations of DO were similar to the saturation

Table 2. EC guideline values of major physicochemical parameters in fresh waters (potable-fish culture).

Parameter	Freshwater for fish (*Kyprinides*)	Water for human consumption: Guide level	Water for human consumption: Maximum admissible level (MAC)
Temperature (°C)	≤28		
	≤10 (cold-water species)	12	25
DO ($mg\,l^{-1}$)	≥4		
pH	6–9	6.5–8.5	
Nitrites ($\mu gat\,N\,l^{-1}$)	≤0.65 (guide level)		2
Ammonium ($\mu gat\,N\,l^{-1}$)	≤56 (mandatory)	2.7	27
Nitrates ($\mu gat\,N\,l^{-1}$)		400	800
Phosphorus ($\mu gat\,P\,l^{-1}$)		3	35
Zn ($mg\,l^{-1}$)	0.3–2	0.1–5	
Cu ($mg\,l^{-1}$)	0.005–0.112	0.1–3	
Pb ($mg\,l^{-1}$)			0.05
Cd ($mg\,l^{-1}$)			0.005
Polycyclic aromatic hydrocarbons ($\mu g\,l^{-1}$)			0.2

theoretical values. The small depth of the river favours the saturation of water with dissolved oxygen, but some low values in areas of reduced flow rate indicated the elevated organic load in the system.

The pH, temperature, and DO values were below maximum guideline levels. Based on the data of the Kubitskali monitoring system for the period 1978–1989, a significant difference between stations K1 and K2 existed because of the discharge of industrial effluents from the oil refinery downstream of Station K1. The decrease of pH (from 7.34 to 6.92) and of dissolved oxygen (from 10.2 to 5.84 $mg\,l^{-1}$), as well as the increase of BOD (from 1.2 to 31.5 $mg\,l^{-1}$) indicates the deterioration of water quality downstream [17].

The concentrations of nitrates and nitrites were higher in November, whereas silicates were higher during July (table 3). The concentrations of phosphates and ammonium were similar in both seasons. The higher concentrations of nitrates in the high-flow period were lower than the EC guideline values and can be attributed to the enhanced runoff. On the contrary, the concentrations of nitrites and ammonia exceeded the guideline values in both sampling periods.

The nutrient concentrations measurements during the 2000–2001 samplings were found to be at the same levels as the corresponding data from 1989.

In most undisturbed aquatic systems, the main form of nitrogen is nitrates [26]. However, in the case of Kubitskali River, ammonium values were higher than the corresponding nitrate values, and this is an indication of direct discharge of urban effluents. In figure 2, the percentages of inorganic nitrogen forms in Kubitskali River are presented.

The concentrations of silicates were determined at the expected levels for riverine waters. The concentrations of phosphates on the contrary were rather low. Phosphates are the limiting factor for phytoplankton growth in the area. The possibility of the development of eutrophic phenomena in the river estuary is dependent on the phosphorus load, and a possible increase may be dangerous [27, 28].

As expected, high concentrations of oil products were determined in Kubitskali, because of the direct dumping of untreated wastewaters from the Batumi oil refinery into the river. The increase was observed more clearly during the summer and can be attributed to lower water flow (table 3). The comparison of the oil products levels of the current work with the historical

Table 3. Physicochemical parameters, nutrients, and oil products in the Kubitskali River.

	T (°C)	pH	S (ppt)	DO ($mg\,l^{-1}$)	NO_3^- ($\mu gat\,N\,l^{-1}$)	NO_2^- ($\mu gat\,N\,l^{-1}$)	NH_4^+ ($\mu gat\,N\,l^{-1}$)	PO_4^{3-} ($\mu gat\,P\,l^{-1})^-$	Si ($\mu gat\,Si\,l^{-1}$)	Oil products ($mg\,l^{-1}$)
July 2000										
K1	25.8	6.8	0.1	9.6	24.2	1.43	65.6	0.42	174	0.115
K2	26.5	7.2	0.1	5.78	20.2	2.41	77.8	0.26	145	0.135
K3	26.4	7.1	0.1	6.2						0.16
K4	27.9	7.99	9.7	7.5						0.09
November 2001										
K1	10	6.7	0.1	11.7	58.1	2.85	66.1	0.21	57.6	0.017
K2	11.5	6.8	0.1	11.9	53.5	3.22	83.3	0.21	103	0.014
K3	11.7	7	0.1	7.8						0.04
K4	12	8	9.4	9.4						0.02
	Range 1989	Range 1989	Range 1989	Range 1978–1979	Range 1989	Range 1989	Range 1989	Range 1989	Range 1989	Range 1978–1979
K1		7.1–7.57		3.28–13.2	4.03–29.8	0.22–4.20	26.1–107	0.05–0.42		nd–0.26
		7.34		10.2	16.9	2.21	66.6	0.24		0.1
K2		6.73–7.1		2.12–12.0	13.7–33.9	0.22–3.70	38.3–131	0.10–0.42		0.1–8.7
		6.92		5.84	23.8	1.96	84.7	0.26		2.5

Table 4. Trace-metal concentrations in the Kubitskali River.

	July 2000			November 2001		
Stations	D-Cu ($\mu g\, l^{-1}$)	D-Pb ($\mu g\, l^{-1}$)	D-Zn ($\mu g\, l^{-1}$)	D-Cu ($\mu g\, l^{-1}$)	D-Pb ($\mu g\, l^{-1}$)	D-Zn ($\mu g\, l^{-1}$)
K1	8	4.6	62	7.16	4.25	74.1
K2	12	5.2	120	9.74	4.8	68.8
K3	10.5	4.9	100	10.3	5.2	98
K4	8.7	3.8	75	6.35	4.5	52
	P-Cu ($\mu g\, l^{-1}$)	P-Pb ($\mu g\, l^{-1}$)	P-Zn ($\mu g\, l^{-1}$)	P-Cu ($\mu g\, l^{-1}$)	P-Pb ($\mu g\, l^{-1}$)	P-Zn ($\mu g\, l^{-1}$)
K1	2.02	2.11	12	2.5	1.75	13.5
K2	1.74	2.09	27.1	3.2	1.95	24.3
K3	1.19	1.86	22.2	4.4	1.52	26.2
K4	2.21	1.71	12.4	2.8	1.6	18.2

Note: D: dissolved; P: particulate.

data showed a significant decrease for station K2, but still the levels are much higher than the MAC of water for human consumption. This is an environmentally positive trend. However, we do not have any information on the production processes of the refinery and the possible installation of a treatment plant in the industry, so we cannot be certain of the cause of this decrease, and we cannot consider it as a permanent fact. In any case, it is clear that there is an urgent need to establish a wastewater-treatment plant in the industry.

The determination of heavy metals has shown increased concentrations mainly during the low-flow period and especially for zinc (table 4). The values of trace metals increase downstream and are again reduced at station K4 because of the mixing of river and sea water. The distributions of Cu and Pb in the dissolved and particulate form along the Kubitskali River for

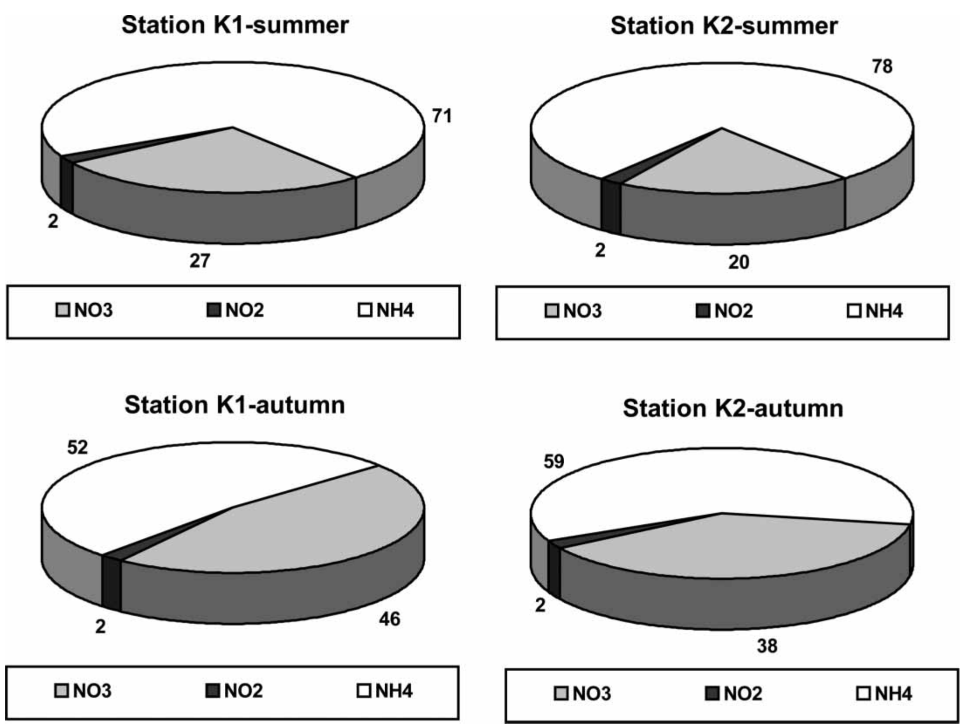

Figure 2. Percentage distribution of nitrogen forms.

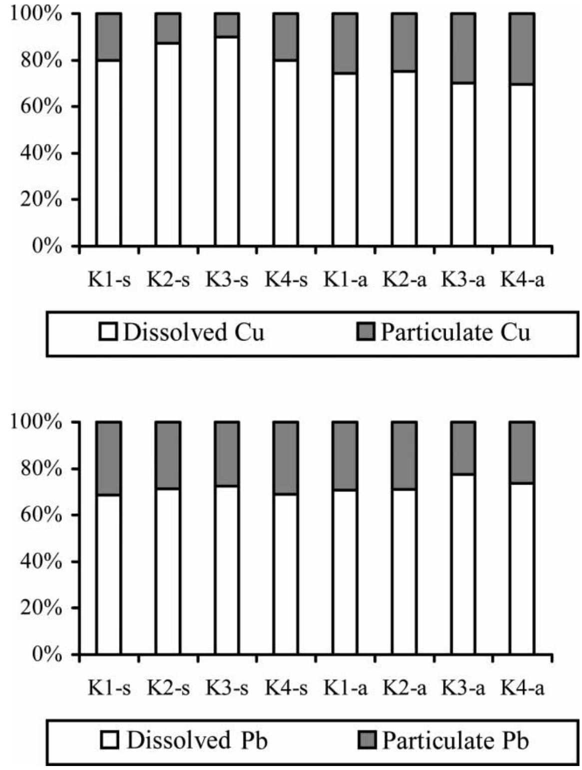

Figure 3. Distribution of Cu and Pb between the particulate and dissolved phase (a: autumn, s: summer).

both sampling periods are presented in figure 3. The dissolved form prevails in both seasons and all sampling stations. The same trend is observed in the case of Zn.

The trace-metal concentrations of Kubitskali River were below the guideline levels for freshwater cultures of Kyprinides. Table 5 was compiled to provide a comparison between the results of Kubitskali River with similar river systems. The range concentrations of nutrients and trace metals for three rivers in Greece and two rivers in Bulgaria characterized by various levels of pollution are presented. In general, the pollution level of the chosen rivers was Louros > Sperchios > Acherontas, and Kamchiya > Ropotamo. The Laboratory of Environmental Chemistry produced the data used in table 5 for various research projects [26, 29, 30, 31].

Nitrate and phosphate levels in Kubitskali River were lower than the corresponding levels in most of the rivers under comparison. Silicate levels were similar, while the values of nitrites and ammonia in Kubitskali were much higher than the observed levels of the other rivers except the polluted Kamchiya in Bulgaria.

Concerning trace-metal concentrations, the levels in Kubitskali are higher than the levels in the other rivers. In some cases (Cu and Pb), the highest values of Kubitskali River were lower than the corresponding values in some of the other rivers, but in all cases the minimum metal concentrations in Kubitskali were the highest among the minima.

3.2 *Paliastomi Lake*

The data from the two samplings in Paliastomi Lake are presented in table 6. The temperature of the lake water during summer was higher than 29 °C, while during winter it ranged between

Table 5. Concentrations of the studied parameters in various rivers.

Parameter	River Ropotamo, Bulgaria 2003	River Kamchiya, Bulgaria 2003	Sperchios River, Greece 2003	Louros River, Greece 2002	Axerontas River, Greece 2002	Kubitskali River, Georgia 2000–2001
Nitrates (μgat N l^{-1})	24.8–34.1	40.6–473	0.90–145	12.5–120	14.1–61	20.2–58.1
Nitrites (μgat N l^{-1})	0.32–0.66	0.04–0.25	0.02–1	0.04–9.84	0–0.72	1.43–3.22
Ammonium (μgat N l^{-1})	3.08–9.32	7.16–208	0.5–6.3	0.01–39.2	0–0.97	65.6–83.3
Phosphorus (μgat P l^{-1})	0.10–2.40	0.20–14.8	0.03–7	0.02–3.26	0.01–0.22	0.21–0.42
Silicates (μgat Si l^{-1})	79–141	64–135	130–170	65.8–141	51.9–133	57.6–174
Dis Zn (μg l^{-1})	11.8–42.3	26.3–34.3	0.53–9.3	3.13–92.1	3.37–29	62.0–120
Part Zn (μg l^{-1})	1.06–2.79	1.35–3.95	3.61–19.4			12.0–27.1
Dis Cu (μg l^{-1})	2.71–53.2	1.07–4.08	0.18–1	0.08–33	0.21–46.1	8.00–12.0
Part Cu (μg l^{-1})	0.17–0.45	0.23–0.72	0.03–6.83			1.19–2.21
Dis Pb (μg l^{-1})	0.04–7.82	0.31–4.71	0.17–0.85	0.20–15	0.03–7.58	3.80–5.20
Part Pb (μg l^{-1})	0.43–0.71	0.48–2.34	0.06–7			1.71–2.11

Table 6. Data from the Paliastomi Lake.

Stations	T (°C)	pH	S (ppt)	DO (mg l^{-1})	NO_3^- (μgat N l^{-1})	NO_2^- (μgat N l^{-1})	NH_4^+ (μgat N l^{-1})	PO_4^{3-} (μgat P l^{-1})$^-$	Si (μgat Si l^{-1})	Oil products (mg l^{-1})
July 2000										
P1	29.8	8.2	11.5	12	10.8	0.74	131	2.47	53.6	0.11
P2 surface	29.2	8.47	10.5	12	3.37	0.15	155	1.5	64.6	0.097
P2 depth		8.29	11.3	7.5						
P3 surface	29.4	8.46	10	12	0.81	0.28	155	1.13	52.1	0.078
P3 depth		8.46	10	2						
P4	31.1	8.4	9	12	4.79	0.31	194	1.94	78	0.08
November 2000										
P1	10.5	6.9	9.5	10.9	54.1	2.84	132	0.26	34.8	0.105
P2	11	6.7	8.2	9.56	54.1	3.56	116	0.26	34.8	0.088
P3	12.5	6.9	5.1	12	53.5	4	100	0.21	63	0.056
P4	10	6.8	4.2	9.65	54.1	3.21	116	0.26	46.5	0.045
				Range 1991–1999	Range 1991	Range 1991	Range 1991	Range 1991		
P1				4.86–11.74	2.58–22.6	0.02–0.39	23.3–278	0.15–1.14		
				9.62	12.6	0.2	151	0.64		
P2				5.79–11.92	2.26–38.7	0.07–1.23	34.4–278	0.12–1.47		
				9.54	20.5	0.65	156	0.8		
P3				5.60–11.87	2.58–24.2	nd–4.07	26.7–348	0.06–1.27		
				9.47	13.4	0.65	187	0.67		
P4				5.45–11.82	0.97–16.1	nd–2.54	8.89–309	0.10–1.21		
				9.25	8.54	0.65	159	0.66		

10 and 12.5 °C. The highest values during summer and the lowest during winter were observed at station P4. This can be attributed to the influence of the water from the river Pichora.

The salinity of the lake during summer ranged between 9.0 (at P4 near the river Pichora) and 11.5 (at P1 near the sea). The inlet of sea water into the lake through the channel is clear. The values were slightly lower during winter due to the increase in the inflow of freshwater.

The fluctuations of pH values were similar to those of salinity. The pH of the lake ranged between 8.20 and 8.47 during the summer, indicating the influence of the sea water. During winter and spring, the pH ranged between 6.70 and 6.90, indicating the decrease in the percentage of saline marine water in the lake.

High temporal and spatial variations were observed in the concentrations of dissolved oxygen. The lake water was saturated with dissolved oxygen during winter, but during summer the dissolved oxygen was drastically decreased near the bottom water layer of the central station P3, and the conditions were hypoxic with DO = 1–2 mg l^{-1}. The organic load that enters the lake due to the runoff of the catchment area is the main cause for this phenomenon, which poses a risk to the ecological health of the lake [9].

Some low dissolved oxygen values had been observed in the past, but there was no recorded development of anoxic conditions. The BOD levels of the lake were between 1 and 3 mg l^{-1}, with the higher values in stations P3 and P4 indicating a minor contribution of organic load from the Pichora River [18].

As far as nutrients are concerned, the main characteristic of Lake Paliastomi was the high values of ammonia (more than 100 $\mu\text{gat N l}^{-1}$), exceeding the EU MAC and indicating the pollution of the lake by urban effluents.

Nitrites also exceeded the EU MAC during the high-flow season. The concentrations of nitrates were also high, especially during the high-flow season (more than 10 $\mu\text{gat N l}^{-1}$), but remaining lower than the ones of ammonia and the EU MAC. The concentrations of silicates (35–78 $\mu\text{gat Si l}^{-1}$) were similar in both periods. Phosphates showed a trend opposite that of other nutrients and were higher in the low-flow period, but generally their levels were low and below the EU guidelines for drinking-water. The percentage distribution of nitrogen forms for station P3 is presented in figure 4.

The nitrate and nitrite levels of 1991 were lower than the corresponding values of November 2001. On the contrary, the mean values of ammonium and phosphates in 1991 were higher than the corresponding levels of the 2000–2001 samplings. Such variations are observed in similar systems, and safe conclusions about decreasing or increasing trends must be based on long-term data, which are unfortunately unavailable [10].

As in the case of the Kubitskali River, phosphorus is the limiting factor for phytoplankton growth, and probably its lack prevents the development of eutrophic phenomena in the lake. It is clear that the management plan of the lake has to deal with the possible development of eutrophication, which has to be avoided.

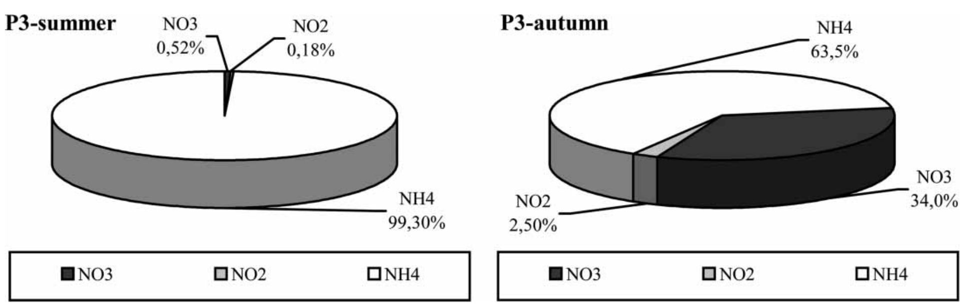

Figure 4. Percentage distribution of nitrogen forms at station P3.

Table 7. Concentrations of the studied parameters in lagoons.

Parameter	Korissia lagoon, Greece 2005	Moustos lagoon, Greece 2005	Paliastomi Lake, Georgia 2000–2001
Nitrates (μgat N l^{-1})	0.17–0.43	110–150	0.81–54.1
Nitrites (μgat N l^{-1})	0–1.02	0–0.30	0.15–4.00
Ammonium (μgat N l^{-1})	0.08–2.32	3–5	100–194
Phosphorus (μgat P l^{-1})	0.01–0.08	0–0.10	0.21–2.47
Silicates (μgat Si l^{-1})	77.7–205	100–120	34.8–78

Concerning oil products, the concentrations in station P1 are higher than in P4, indicating the influence of the sea and not Pichora River. During the high-flow season, the concentration in P4 was smaller than in the low-flow period due to dilution of the river discharges.

Table 7 contains concentrations of nutrients for two coastal lagoon systems in Greece. Both areas are designated wetlands protected under the Natura 2000 network. The Laboratory of Environmental Chemistry produced the data used for various research projects [32, 33].

A comparison of nutrient concentrations between lake Paliastomi and the two lagoon systems in Greece reveals that, except for silicates, the nutrient levels in Korissia lagoon were lower than in Paliastomi, and especially for ammonium significantly lower. The concentrations of nitrates and silicates in Moustos lagoon were higher than the corresponding values in Paliastomi. The increased ammonium concentrations of Paliastomi can be attributed to human activities. The two Greek lagoon systems are far away from populated areas, and there are no significant anthropogenic polluting activities in their vicinity. Furthermore, the freshwater supply of these two Greek lagoons is from the aquifer. The increased concentrations of nitrates in Moustos can be attributed to aquifer nitrification, which is often observed in agricultural areas of Greece [32–34].

4. Conclusions

The study of the concentrations, the temporal and spatial fluctuations, and the overall geochemical behaviour of a series of significant pollutants in the Kubitskali River and Paliastomi Lake led to some interesting conclusions about the influence of human activities in the surface water quality in developing countries, in regions like the Black Sea. The studied systems are affected by a large number of human activities, which introduce significant polluting loads and result in the observation of elevated levels of pollutant concentrations that are generally higher than the maximum EU admissible concentrations [25]. These include urban activities, agriculture, industries or handicrafts, traffic, and rainwater-land-washout canals are some of them. Land washout plays a very important role in the enrichment of the water in pollutants, mainly nitrates. The coexistence of point and non-point polluting sources in combination with the seasonal variations of water flow, of the main physicochemical parameters (DO, pH, temperature) and of the suspended load, affect the distribution and chemical behaviour of pollutants in various ways and lead to characteristic spatial and temporal distributions. In small water systems, the introduction of rather low quantities of pollutants, like phosphates, lead, or hydrocarbons, may cause a significant increase in their concentrations in the neighbouring part of the system. Large fluctuations in pollutant concentrations are common in such systems, which may cause a significant deterioration in the water quality and thus may have dangerous effects on the local ecosystems. The results on concentration levels and the chemical behaviour of nutrients indicate that the systems studied are enriched, mainly in ammonia. Phosphates and nitrites are present in significantly lower concentrations. The case of phosphorus is the most interesting because it can cause significant problems in areas where phosphorus is the limiting factor for phytoplankton growth. Concerning trace-metal concentrations, the River Kubitskali is more affected compared with those rivers of Greece and Bulgaria that are not heavily polluted, but less affected in comparison with various European rivers from industrialized countries [35]. The pollution of the Kubitskali River by petroleum hydrocarbons has increased, although less so than the previous decade. The marine environment is the main source of oil products in Paliastomi Lake. The systems studied contribute a significant load of pollutants to the sea, which has to be reduced by the proper management of human activities in order to avoid ecological damage. The appearance of concentration maxima of various pollutants, in some cases exceeding EU MAC for human consumption or fish cultures, indicates environmental problems in both systems. These systems have to be managed very carefully, since the small size of the ecosystems makes them considerably fragile. The need for sustainable management is urgent as the economical development may increase the environmental pressure on the systems. The establishment of treatment plants and the re-operation of the monitoring systems combined with implementation of existing national or EU legislation could lead to improvements in the environmental quality of the region.

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