ORGANIC MATTER CHARACTERIZATION AND DISTRIBUTION IN THE LAKE SHKODRA/SKADAR AND THE BUNA/BOJANA RIVER, ALBANIA: A CASE STUDY IN MAY 2009

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ABSTRACT

The Lake Shkodra - River Buna wetland complex (Albania) is included in Ramsar sites, and is one of the most important on the Adriatic coast. Dissolved organic carbon (DOC), particulate organic carbon (POC), surface active substances (SAS), copper complexing capacity (CuCC), and polymeric organic material containing nitrogen atoms (N-POM) were measured in the area. DOC concentrations were in the range 0.335-4.535 mg C L^{-1}, while POC was in the range 0.010-4.147 mg C L^{-1}. SAS concentrations expressed as equiv. of Triton-X-100 were in the range 0.083-0.302 mg L^{-1}. CuCC values were in the range 110-758 nM Cu^{2+}.The measured concentrations were increased only for certain sites (e.g. lagoon site, B1), where the highest DOC, POC and SAS values were measured. At these sites, polymeric organic material (N-POM) was measured. Normalized surfactant activity values (NSA) determined showed that the organic material present in this aquatic system is similar in adsorption properties to the model fulvic acid and protein albumin.

KEYWORDS: Shkodra /Skadar Lake, Buna /Bojana River, organic matter characterization; electroanalytical techniques

1. INTRODUCTION

The concentrations of the dissolved organic carbon (DOC) and particulate organic carbon (POC) in natural waters determine the total concentrations of the aquatic organic matter. A large part of the aquatic organic matter exhibits the property of surfactant activity, and is named surface-active substances (SAS) [1]. SAS accumulate on different phase boundaries (air/water; water/sediment; water/living or non-living suspended particles) influencing the structure and physico-chemical properties of these interfaces and mediating the processes of mass and energy transfer [1]. Surfactant activities of different classes of organic matter as representative for organic matter present in aquatic systems have been determined [2, 3]. Clear evidence of surfactant production by different phytoplankton species based on laboratory and field experiments is also available [4, 5]. A combination of general parameters (DOC and POC) and SAS gives the information about both content as well as the reactivity of organic matter in a particular aquatic system [6, 7].

Metal complexation by inorganic ligands in water (ocean, estuaries, freshwater) is well studied whereas less is known about speciation of metal ions in the presence of organic ligands [8]. With the development of a number of sensitive and selective metal speciation techniques like electrochemical techniques,also metal-organic interactions have been studied [9,10]. Copper is the mostly studied metal ion [11, 12] as it forms very stable organic complexes and is an essential metal ion [8, 13]. Its complexation to organic ligands in all aquatic systems, with the exception of deep ocean water, is >99% [13]. Catalytic and surface activity of nitrogen-containing polymeric organic material (N-POM) could be also analyzed by electrochemical technique of constant current chronopotentiometric stripping analysis (CPSA). Recently, CPSA proved to be a suitable method for determination of low concentrations of N-polymeric compounds in seawater by measuring "presodium" catalytic peak "H" [14].

Our research was performed in May 2009, on the area of the Shkodra/Skadar Lake and the Buna/Bojana River. The area of investigation is the wetland area encompassing «old Drini river»- i.e. the area of former Drini river flow which due to the several interventions in the area (building of dams, errosion, and loading of sediments) has partially changed the flow course. The scope of our research was to determine the concentration and distribution of organic matter in the area with the Buna/Bojana River (river with highest discharge rate in the area) to the southeast Adriatic shelf water. The Adriatic southeast coastal area is an eutrophic area that is strongly affected by freshwater inputs from the Buna/Bojana River system [15].

Dissolved organic carbon (DOC), particulate organic carbon (POC), surface active substances (SAS), copper

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complexing capacity (CuCC) and polymeric organic material containing nitrogen (N-POM) due to hydrological situation in late spring were measured. This is the first research of the freshwater system in this area of Albania regarding the organic matter characterization and distribution.

2. MATERIALS AND METHODS

2.1. Study area

Albania is rich in water resources including lakes, rivers, springs, and lagoons, with a high quantity of available water. Albanian rivers are characterized by the total annual mean flow of 1308 m^3 s^{-1}, which corresponds to an annual water volume of 42.3x10^9 m^3. The rivers are mainly fed by precipitation (69%) and show a typical Mediterranean regime, with seasonal variation in the flow-rate and high flow from October to May [16, 17].

During the past decades, mining, enrichment and metallurgy industries, as well as organic products and wastes have produced high quantities of solid and liquid wastes, often dumped on river banks or directly into rivers. Some natural characteristics of Albania like geographical (high slopes), pedological, climatological (high precipitation amount) as well as some human impacts (forest mismanagement and gravel mining) have given rise to high erosion rates, and solid matter (TSS) in all rivers is because of that a crucial problem.

The investigated area is the most important wetland system along the Adriatic Sea, and one of the best preserved in the Mediterranean [18]. Its habitat is distinguished about the richness of breeding and refuge habitats for flora and fauna, especially for fishes and waterbirds (after World Database on Protected Areas; http://sea.unepwcmc.org/wdpa/index.htm). Along the Albanian coast, there are extended three wetlands of international importance (Ramsar convention): Butrinti (13500 ha), Karavasta Lagoon (20000 ha), and Lake Shkodra with the River Buna (49562 ha) [19].

The Buna delta has the characteristics of a shovel delta [20], such as the Ebro delta and, in part, the Po delta. The Po in its lower course transports mostly sand whereas, during heavy floods, the Buna transports a lot of gravel too. This type of delta grows by lateral accumulation and the separation of shallow lagoon lakes and pools. This can be seen, in particular, in the eastern half of the Bojana-Buna delta over the last 100 years. The process is related to a strong coastal influence (dune and lagoon development stages). Due to the massive reduction of bed load and suspended load following the construction of the dams in the upper Drini basin, the delta is today more and more eroded by the coastal regime. Together with reduced discharges of the rivers and the slight raising of sea level due to climate change, the erosion phase will be intensified [20]. In Fig. 1, the sampling stations are denoted. One sampling area includes the Shkodra Lake and the Buna River (B15,

B8, B7, B5), and the other is the area of Drini River (B2, B3, B4, B14) and the two lagoons (B1, B6).

2.2. Analytical methods

2.2.1. DOC and POC determination

For DOC and POC determination, samples were collected directly from the Niskin samplers in dark 1.3-L bottles, previously washed with chromic-sulfuric acid and rinsed with organic free water (Milli Q water) and water samples. The filtration was performed immediately after sampling (Whatman GF/F filters, pore size 0.7 μm). Filtered samples for DOC analysis were collected in duplicates in 22-ml glass vials washed with chromic-sulfuric acid, rinsed with Milli-Q water and combusted for 4 h at 450 ^{o}C. The samples were preserved with mercury chloride (10 mg/L) and stored at +4 ^{o}C in the dark until analysis. After collection of the DOC subsamples, GF/F filters were rinsed with a few ml of Milli-Q water to remove salts from the filter and stored in liquid nitrogen at -80 °C until POC analysis. The DOC concentrations were analyzed in duplicate using the sensitive high temperature catalytic oxidation (HTCO) method [21]. A Model TOC-V$_{CPH}$ (Shimadzu) with platinum on silica catalyst and nondispersive infrared (NDIR) detector for CO_2 measurements was used. Samples acidified with hydrochloric acid (pH 2) were purged with organic free air for 10 min prior to analysis to remove inorganic carbonate fraction. DOC concentrations were calculated by subtracting the measuring system and Milli-Q water blanks. Potassium hydrogen phthalate as a standard was used. The concentration was calculated as an average of three to five replicates. The average instrument and Milli-Q blank correspond to 0.03 mg/L (n=32), and the reproducibility was high (1.6 %). POC was analyzed with a solid sample module SSM-5000A associated with a Shimadzu TOC-V$_{CPH}$ carbon analyzer calibrated with glucose. After acidification with hydrochloric acid (2M) to remove inorganic carbonate fraction, the filters were folded in an alumina ceramic sample boat and dried at 50 ^{o}C for 12 h. The prepared samples were burned in a flow of oxygen at 900 ^{o}C. The CO_2 produced was detected by the NDIR detector. POC concentrations were corrected on the basic of blank filter measurements. The average filter blank including instrument blank corresponded to 0.005 mg/L. The reproducibility obtained for the glucose standard was high (≤3 %).

2.2.2. Copper complexing capacity (CuCC) measurements

The experiments were performed on an electrochemical system consisting of a 663 VA-Stand (Metrohm, Herisau, Switzerland) connected via an IME663 module to a computer-controlled μ-Autolab instrument (EcoChemie, Utrecht, The Netherlands). The working electrode was a static mercury drop electrode (SMDE, drop surface area 0.52 mm^2). The reference electrode was a double-junction Ag/AgCl (3 M KCl) electrode, and the counter electrode was a glassy carbon rod. The solutions were stirred during the deposition step of measurements. Potential of deposition was -0.6 V vs. Ag/AgCl ref. electrode with the depo-
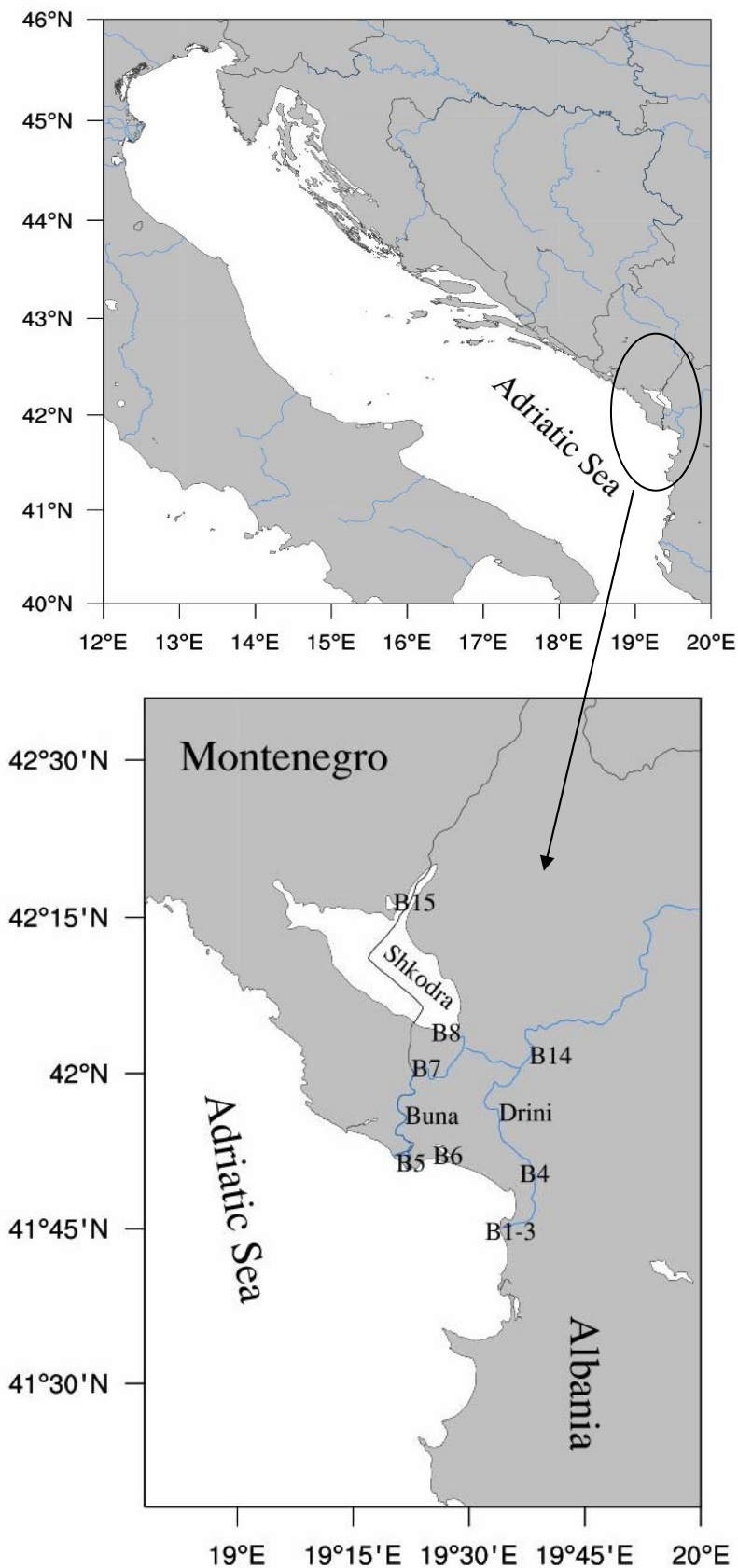
FIGURE 1 - **Map of the Adriatic Sea with inserted area of sampling stations in the Shkodra Lake and the Buna River, Albania. The sampling stations were: B1, B2, B3, B4, B5, B6, B7, B8, B14 and B15.**

sition time of 60 s. The complexing capacity was determined in non-filtered seawater samples after thawing deep frozen samples (-20 °C) within one month after sampling. The reproducibility of the method is $\pm 2 \times 10^{-9}$ M Cu^{2+} from which the detection limit equal to 6×10^{-9} M Cu^{2+} can be calculated. Determination was performed by the direct titration method of the sample with increasing amounts of copper ions, and their electrochemical response was measured by the method of differential pulse anodic stripping voltammetry (DPASV) [22, 23]. Total Cu ion concentrations were determined in UV-irradiated (for 24 h) and acidified samples. To obtain complexing capacity values and conditional stability constant, titration data are linearly transformed assuming 1:1 metal to ligand complexes [24, 25]. The equation used for calculation is: [Cu]/[CuL] = [Cu]/CuCC + 1/KCuCC, where Cu is the copper ions detected by anodic stripping voltammetry, CuL is the copper ion bound in a complex with ligand L, CuCC is the total concentration of binding ligands (i.e. complexing capacity), and K is the apparent stability constant. The plot of [Cu]/[CuCC] vs. [Cu] yields a straight line with a slope of 1/CuCC and intercept 1/KCuCC.

2.2.3. SAS determination

Surface active substances were analyzed electrochemically by a.c. voltammetry [6] using a Metrohm 797 VA Computrace instrument. A three-electrode cell system was used: hanging mercury drop electrode (HMDE), as a working electrode, Ag/AgCl (3 M KCl) as the reference electrode, and platinum electrode as the counter electrode. The deposition potential of -0.6V vs. Ag/AgCl ref. electrode and deposition time of 30 s controlled by stirring were applied. Surfactant activity was expressed in terms of surfactant equivalents of the non-ionic surface active compound Triton-X-100 (MW=600 mg/L), with detection limit of 0.01 mg/L and reproducibility of 3%. Surface active substances were determined in both non-filtered (SAS_T, total,

i.e. dissolved + particulate) and filtered (SAS_{diss}, dissolved) samples immediately after sampling. Normalized surfactant activity (NSA) values were calculated by dividing the concentration of SAS in mg/L equiv. of Triton-X-100 with the DOC in mg C L^{-1} [6].

2.2.4. N-containing polymeric material (N-POM)

Measurement conditions for electrochemical constant current potentiometric stripping analysis (CPSA) method were as follows: accumulation potential E_a = -0.6 V and time of accumulation t_a = 60 s, with stirring, constant reduction current I = -1 µA and maximum time of measurement = 5 s. CPSA measurements were performed on unfiltered samples, in the presence of oxygen, while instrument and cell were as in CuCC determination. The results were expressed as the equivalents of the model polymer substance i.e. protein human serum albumin (HSA, Sigma, USA, MW = 67 kDa) and/or as equivalents of N atoms present in HSA taking into account the 15.7 % of N content in HSA [26] .

CuCC and N-POM were determined at the same time after thawing the deep-frozen nonfiltered samples. Samples were analyzed within one month after sampling.

3. RESULTS

All the results are summarized in Table 1. The average concentrations determined for all the parameters (DOC, POC, SAS_{diss}, and CuCC) were lower for the area of Shkodra Lake and the Buna River (B15, B5, B7, B8), while in the Drini River area (B2, B3, B4, and B14) and, especially, in the lagoons (B1, B6), the determined average concentrations were higher. DOC and POC concentrations were measured also for the stations B14A and B15A (not denoted in Fig. 1., which are situated a few 100 m upstream of stations B14 and

TABLE 1 - Salinity, temperature, pH, DOC, POC, SAS $_{diss}$, CuCC, logaritmic value of apparent stability constant for copper complexation (log K_{app}) and N-POM for all stations measured.

	S	T (^{0}C)	pH	DOC mgC/L	POC mgC/L	SAS $_{diss.}$ equiv.mg/L T-X-100	CuCC nM	logK_{app}	N-POM equiv µg/L HSA
The Shkodra Lake, The Buna River									
B15	0	-	8.02	1.363	0.453	0.139	432	9.2	0.0
B8	<1	21	8.30	0.947	0.134	0.082	320	9.0	0.0
B7	<1	16	7.87	1.031	0.230	0.077	302	9.2	0.0
B5	<1	15	7.32	0.954	0.180	0.051	-	-	0.0
Old Drini									
B14	0	-	8.78	0.619	0.225	-	678	8.4	0.0
B4	<1	22	8.15	1.090	0.274	0.127	758	8.2	10.8
B3	21	23	8.04	1.446	0.498	0.132	490	7.6	31.5
B2	2	22	7.69	1.470	0.517	0.153	473	8.3	10.5
Lagoons									
B1 (Kune-Vain)	14	25	8.71	4.535	4.147	0.172	446	8.0	17.4
B6 (Vilun)	17	26	8.52	3.119	0.615	0.153	110	7.0	0.0

- not measured

B15). The measured values were for B14A: DOC was 0.553 mg C/L and POC was 0.161 mg C/L; for B15A: DOC was 0.335 mg C/L and POC was 0.010mg C/L. These are very low values characteristic for a pristine systems at the eastern coast of the middle Adriatic like the karstic Krka River [27].

Part of the Drini area and lagoons are influenced by the intrusion of seawater, which could be observed from the salinity values measured there (Table 1.).

There exists a correlation between different parameters with a statistical significance. DOC is correlated with POC for stations B1, B2, B3, B4, B6 and B14 with a correlation coefficient of $R^2= 0.842$. In Table 1, the values for SAS $_{diss}$ are quoted as there are very small differences in the SAS concentrations determined in filtered and unfiltered samples. Values for SAS$_{diss}$ were used for calculation of the normalized surfactant activity (NSA) as presented in Fig. 2. DOC vs. SAS$_{diss}$ values are presented together with the straight lines which represent the relationship for SAS and DOC for selected model substances: (1) nonionic surfactant Triton-X-100; (2) polysaccharide Dextran-T-500; (3) protein-albumine; (4) fulvic acid, and (5) microbial polysaccharide xanthan. It can be observed that most of the results for the samples are close to the lines for albumine/fulvic acid and xanthan, which is to be expected for the unpolluted natural waters [28]. In Fig. 3, the frequency distribution of NSA for Albanian coastal seawater samples (data are from [29]) and Albanian freshwater samples (the Buna/Bojana river and Shkodra/Skadar lake - this paper) are presented. It can be observed that Albanian freshwaters have the NSA frequency distribution in a higher-value range which indicates that the materials determined there have a more hydrophopbic character than the samples from the Albanian coastal sea (measured at the same time as the freshwater samples in May 2009), which showed higher frequency distribution for lower NSA values, pointing to the more hydrophylic material in Albanian coastal sea, probably of autochtonous origin.
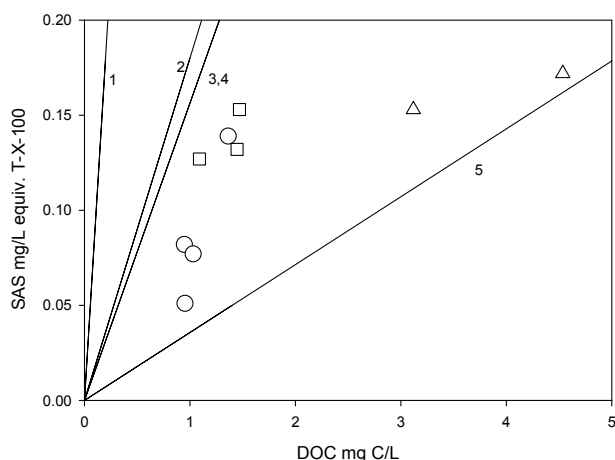

FIGURE 2 - SAS vs. DOC concentrations (○ for B15, B8, B7, B5; □ for B2, B3, B4; and △ for B1, B6,). Lines correspond to different model substances; no. 1: nonionic surfactant Triton-X-100; no 2: model polysaccharide Dextran-T-500; no. 3: model fulvic acid, no. 4: protein-albumin; no. 5: microbial polysaccharide xanthan.
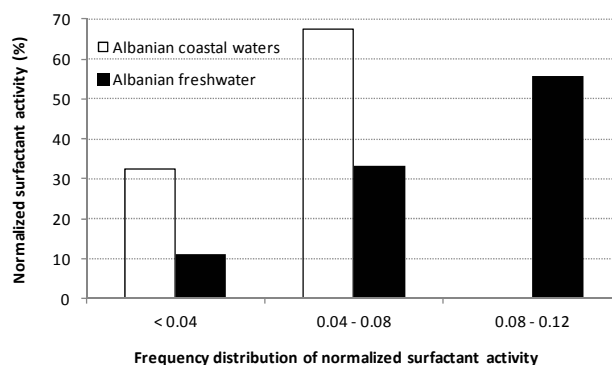

FIGURE 3 - Frequency distribution of normalized surfactant activity values for the freshwaters' and Albanian's coastal seawater samples.
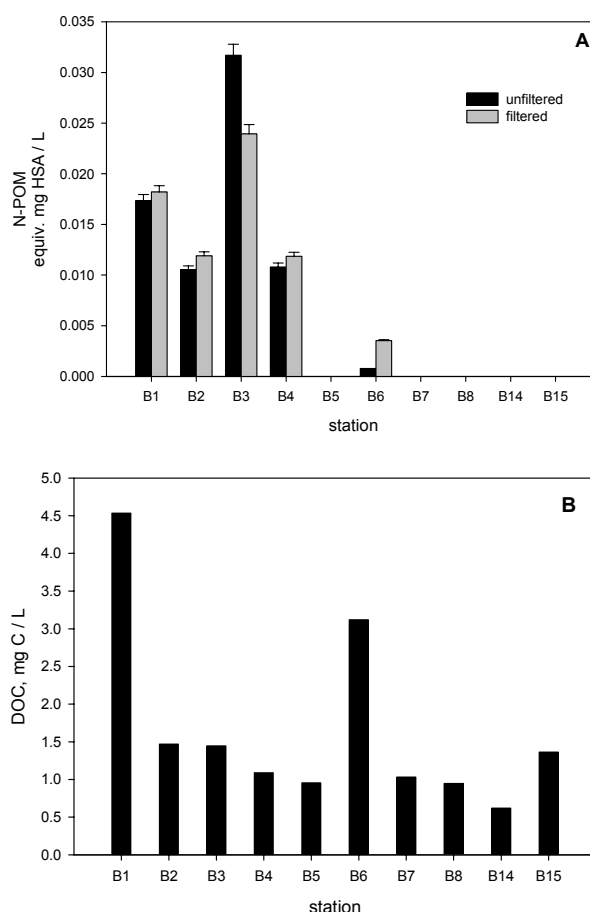

FIGURE 4 - A) N-POM concentrations for all the stations for filtered and unfiltered samples; B) DOC concentrations measured on the sampling stations B1-B15.

In the area of the Drini River and the lagoons (at B1, B2, B3, B4 and at B6, where the concentration was at the limit of detection), the polymeric organic material containing nitrogen atoms (N-POM) has been measured [26, 29], while in the area of Shkodra lake and the Buna River (stations B5, B7, B8 and B15), such organic material was not detected (Fig. 4A). N-POM has been measured in non-filtered and filtered samples (Fig. 4A). Practically, at all stations concentrations of N-POM did not differ sigifi-

cantly between filtered and nonfiltered samples (Fig. 4A). In Fig. 4B, the DOC concentrations for the stations are presented.

Usually, higher DOC concentrations measured mean that also higher N-POM concentrations [26, 29] were measured as well. In Albanian samples, this was not the case, meaning that their N-POM was not the main component in organic matter with high DOC concentrations.

Complexing capacity values were in the range 110-758 nM, which is higher than for the karstic Krka River [30], but comparable to the results obtained for the Kotor Bay, the area strongly influenced by freshwater imput [31]. Concentrations of copper ions were significantly correlated with DOC for the Shkodra Lake and the Buna River ($R^2 = 0.9168$) which means that the loading of metal ions to the water is connected with the concentration of organic matter in the system. The concentrations of copper ions in the area were in the range 2-9 nM, with the only exception at station B1 (lagoon Kune) where it was 13 nM. At B1 station, for all the parameters, the highest concentrations were measured.

4. DISCUSSION

DOC, POC, CuCC and SAS concentrations in the samples were not high, especially regarding DOC and POC concentrations for the area of Shkodra Lake and the Buna River. The Buna River in the southeastern area of Adriatic and the Po River in the northwestern Adriatic area account for more than one third of the freshwater entering the coastal area in their respective area [15]. The median DOC concentration in the Po River in the period 1995-2007 was 2.24 mg C/L [32], and in the Buna River, a maximum of 1.36 mg C/L (and three other DOC concentrations were even lower, app. 1 mg C/L) was measured which means that the Po River is contributing more to the overal DOC budget in the Adriatic Sea than the Buna River. Also the type of organic material was different in the Albanian coastal seawater samples than in the fresh water samples visible from the NSA frequency distribution (Fig. 3). Nevertheless, the measurable influence of the Albanian rivers was observed in Albanian coastal waters from the inverse dependence of the DOC concentrations and salinity data [29]. Also, in the sampling station which was the closest to the Albanian shore, a very high concentrations of silicate was measured (up to 380 μg/L; [29]). The results for NSA, for the freshwater samples, point to the type of organic matter which regarding its adsorption properties resembled those of model fulvic acid and/or model for proteinaceous organic matter like albumine, which gave the same line for NSA [27]. NSA for B1 and B6 samples, which are lagoon samples, are closer to the line for microbial polysaccharide xanthan, which means that such a type of material could be present, indicating biological activities and the influence of the seawater intrusion there. In the coastal sea, the lower values for NSA were detected also

corresponding to the low NSA values for model polysaccharide xanthan.

CuCC values were similar to the ones determined in the closed Kotor Bay [31], while log K values were all quite high (9.0-9.2) especially in the Shkodra Lake and in the Buna River samples, which could point to the ligands with high affinity for binding copper ions [8].

Statistically significant correlations between DOC and POC denote that transformation reactions between DOC and POC are prominent in the area. It was revealed that floodplain interactions increase DOC concentrations, alter dissolved organic matter compositions, and reduce nitrogen loading [33]. Polymeric organic material (N-POM) is mainly in colloidal phase which passes through the pores of 0.7-μm GF/F filters used for filtration. This was observed through almost the same concentration of N-POM measured in filtered and unfiltered samples. The presence of the organic matter which could complex copper ions is of great significance as it is known that the most toxic form of metal ions is that of free metal ions, while complexed metal ions are usually not bioavailable [12]. Recently, the metal ions in the sediments of the area have been measured [34], and they did not show increased values (except for Ni) and could be classified as background or unpolluted. The other rivers in Albania like Mati, Ishmi, Shkumbini and Sumani have been investigated to a higher extent [16, 17]. The concentration of copper ions in water samples in the above-mentioned rivers were determined to be much higher, between 43 nM and 153 nM. Nutrient concentrations in these Albanian rivers were determined to be: for N-NO_3, the range was 0.51-1.44 mg/L; for N-NO_2, it was 13.6-278.5 μg/L; for N-NH_4, it was 0.24-6.64 mg/L; and for P-PO_4, it was 5-417 μg/L. These values for nutrients are comparable to other river systems in Europe. In the Shkodra Lake, on the sampling stations in the Montenegrian part of the lake, mean total phosphorus (TP) concentrations of surface samples ranged from 4 to 54 μg/L. Mean total nitrogen concentrations ranged from 0.15 to 1.28 mg/L [35]. Chlorophyll a concentrations ranged from 0.12 to 39.78 μg/L with a yearly average of 5.9 μg/L [35]. According to Vollenweider and Kerekes [36], this average chlorophyll a value classify the Shkodra Lake as being mesotrophic [35]. Later on, the Shkodra Lake was classified to be eutrophic due to the new measurements of chlorophyll a concentrations and due to the presence of phytoplankton communities which become dominant in the lake on the sampling sites in Montenegro [37]. Regarding the trophy valences of the bioindicator species of diatoms in the Lake Shkodra, measured at sampling points on the Albanian site of the lake, the highest number of diatoms belong to oligo-mesotrophic and tolerant groups, which shows a good situation of the lake for sustaining life [38].

One parameter, total suspended solids (TSS) measured in Albanian rivers, is very high (38-108.9 mg/L). This is enormously above the concentrations recommended by European Water Framework Directive (WFD) [39] of 25 mg/L. Only 4% of all river water samples in Albania had

TSS levels below 25 mg/L [16, 17]. This is because of very high errosion rates for the rocks in the area, being mainly composed of silica material [20]. That is the reason while very high concentrations of silicate (up to 380 µg/L) in the seawater close to the Buna River estuary were determined [29]. For the investigated area of the Skhodra Lake, the Buna river and the old Drini area, there are no published data for the measured parameters related to organic carbon content and distribution.

5. CONCLUSIONS

It is important to preserve the sensitive watershed area which will help to prevent damage to biodiversity and humans, and help to retain the original beauty of the landscape. The Albanian territory is important for the water supply on the Eastern Adriatic coast. Sustainable watershed management in the area would guarantee the fulfillment of related tasks on a regional and international level. Further measurements there would be of importance as in comparison to other rivers in Albania (e.g. Ishmi, Fani, Tirana, Lana, Semani, Shkumbini), the area of Shkodra Lake and the Buna River as well as that of Drini River showed relatively low level of human impact. Although, the wastes from mining and metallurgy were dumped in the area, the concentrations of copper ions in the water were generally low. The organic matter (DOC, POC, SAS, CuCC, N-POM)measured there did not show high concentrations.The transformation of the organic matter was measured through the correlation between DOC and POC, and the presence of the N-POM on wetland and lagoon area. Elevated DOC and POC concentrations were measured in the area of lagoons (station B1) which, in the case of metal ions dumped in the area, could have a beneficial role, being able to bind metal ions in a form of organic complexes which are less toxic to biota. These studies could serve as a platformn to raise the awareness regarding the importance of monitoring and preserving such environmentally important sites.

ACKNOWLEDGEMENT

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