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Environmental assessment of water quality of the Mati River (Albania) based on the use of physico-chemical parameters and aquatic insects as bioindicators

Еколошка проценка на квалитетот на водата од реката Мати (Албанија) базирана на употреба на физичко-хемиските параметри и водните инсекти како биоиндикатори

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The aim of this study was the assessment of the water quality of the Mati River based on the use of selected physico-chemical water quality parameters and benthic insects as bio-indicators.
Four stations positioned along the Mati River (Burrel, Shkopet, Rubik, Milot) are selected in the frame of this study.
In this paper, are reported 2896 individuals, from 3 phyla (Arthropoda, Mollusca and Annelida) and 5 classes (Insecta, Malacostraca, Gasteropoda, Bivalvia and Clitellata). The most represented class is Insecta with 30 families. The insect orders with the biggest number of the families are *Ephemeroptera*, *Plecoptera, Trichoptera* and *Diptera,* followed by orders *Coleoptera* and *Odonata*.
EPT (Ephemeroptera, Plecoptera, and Trichoptera) - Biotic Index and Biotic Index parameter (Stroud Water Research Center) are used for water quality bio-classification.
Water quality parameters (pH, electrical conductivity, dissolved matter, dissolved oxygen, total suspended solids and nutrients) have been measured in those 4 different stations along the Mati River. The waters quality assessment is based on: NIVA classification (Heinonen et.al., 1997) and the European Community Directive (EEC/EEAC/EC 78/659) on "Quality of fresh waters supporting fish life".
The conclusions from the chemical analyses are in good accordance to those obtained from biological parameters.

Key words: Mati River, bio-indicators, bio-monitoring, eutrophication, physico-chemical parameters, water quality.

Introduction

Benthic macroinvertebrates are organisms that live in and on the bottom substrates of rivers and streams. The use of benthos data has proven to be a reliable monitoring tool, as benthic macroinvertebrates are sensitive to subtle changes in water quality. The benthic community also integrates the effects of a wide array of potential pollutant mixtures [Schmiedt K., Jones R.L., Brill I., Pikalw., 1998., SWRC Bouchard R.W.Jr., 2004. , 2007].

Using benthic macro-invertebrates as indicators of localized conditions aids interpreting water quality data because they lead stationary lives and re-

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spond quickly to stress from storrm events and illegal dumping [Environmental Protection Agency. 1996].

The Mati River is located at the North part of Albania and runs among an area rich with sulfide and chromites minerals [Cullaj, A., Lazo, P., Baraj, B. 2008] The fact that some urban and rural areas are positioned along the river makes the monitoring of storm water runoff within the city essential to characterize pollutant loading from different land uses and to estimate annual pollutant loading.

Material and methods

Sampling sites

Four sampling stations were selected along the Mati River and its tributaries, the Big Fani and the Small Fani Rivers. The selected sites present various levels of human impact, from near natural to severe impacted sites. The details of each station are given below:

Ma 1 – Shkopet (N41.669578, E19.854012)
Ma 2 – Rubik (N41.767727, E19.784317)
Ma 3 – Mati Bridge (N41.701884, E19.735222)
Ma 4 – Near the delta of the Mati River (N41. E656497,19.586563)

Four sampling expeditions were carried out in each season every 3 months during the year 2010.

Sampling procedure is implemented according to standard operation methods [APHA, AWWA, WPCF (ed), 1998; ISO Norme Internationale Nos. 5666 (1986), 8288 (1990), 9174 (1999)].

Methods of chemical analysis

Water quality physico-chemical parameters (pH, electrical conductivity, dissolved matter, dissolved oxygen, total suspended solids and inorganic nutrients) are used to asses the environmental situation of Mati River. The parameters have been measured in those 4 different stations along the Mati River.

The analyses were performed using spectropho-

Table 1. Water bio-classification by Schmidt et al. (1998)

EPT - Biotic Index	0 – 3,75	3,76 – 6,50	> 6,50
Water quality	*No impact*	*Moderate impact*	*High impact*

Table 2. EPT - Biotic Index calculated for all the sampling stations for 2009-2010 of Mati river

	TAKSON	TV	Density				TV*Density			
			St.1	St.2	St.3	St.4	St.1	St.2	St.3	St.4
Ephemeroptera (*Mayflies*)	*Baetidae*	4	384	116	99	25	1536	464	396	100
	Heptagenidae	4	548	25	8	13	2192	100	32	52
	Ephemerellidae	1	66	13	5	4	66	13	5	4
	Potamanthidae	4	14	12	0	1	56	48	0	4
	Oligonuridae	2	2	2	0	0	4	4	0	0
	Caenidae	7	20	6	0	0	140	42	0	0
Plecoptera (*Stoneflies*)	Chloroperlidae	1	2	2	0	0	2	2	0	0
	Perlodidae	2	42	11	3	4	84	22	6	8
	Capniidae	1	5	1	1	0	5	1	1	0
	Nemouridae	2	7	1	0	2	14	2	0	4
	Leuctridae	0	8	0	0	3	0	0	0	0
	Perlidae	1	1	0	0	0	1	0	0	0
Trichoptera (*Caddisflies*)	Hydropsychidae	4	93	34	64	68	372	136	256	272
	Psychomyiidae	2	4	0	0	0	8	0	0	0
	Rhyacophilidae	0	6	2	0	0	0	0	0	0
	Philopotamidae	3	11	0	1	0	33	0	3	0
	Helicopsychidae	3	3	10	1	0	9	30	3	0
	Total density		1216	235	182	120				
	TV*D						4522	864	702	444
	EPT-Biotic Index [Σ (TV*d)]: D		3.71	3.67	3.9	3.7				

tometric methods by using Shimadzu PC2400 spectrophotometer and following the procedure described by standard analytical methods [APHA, AWWA, WPCF (ed), 1998, EN/ISO standards (1986, 1990, 1999); CEE/CEEA/CE 78/659 (1995)].

Temperature, pH, conductivity, TDS and DO are measured directly using Hach multi-parameter apparatus (Sension 156), TSS is determined after filtering in 0.45 μm glass membrane filter; DO is determined by Winkler method.

Water quality bio-classification of the Mati River is carried out based in some biological parameters like:

a) **EPT - Biotic Index** (E: Ephemeroptera - mayflies, P: Plecoptera - stoneflies and T: Trichoptera - caddisflies).

The link between water quality and the value of the EPT – Biotic Index is proposed by Schmiedt et al. (1998) (table 1). An aquatic environment with a negative impact of outside factors eliminates a lot of species with a low tolerance value.

b) **SWRC - Biotic Index**

The link between water quality and the value of the SWRC - Biotic Index is described and documented by Schmiedt *et al,* 1998; McGonigle J., 2000; SWRC 2003) (table 2).

RESULTS AND DISCUSSION

Water quality classification based on biological indicators

EPT - Biotic Index is calculated for all the sampling stations of the Mati river (table 3) by the following formula (Schmiedt *et al,* 1998; SWRC Bouchard R.W.Jr., 2003; SWRC 2007):

EPT – BIOTIC Index = TV*d/D

Where TV are given tolerance values for the families constituting EPT group (SWRC Bouchard R.W.Jr., 2004; McGonigle J., 2000), *d* is the density of each family and *D*, the total amount of densities.

If we refer to classification by Schmidt et al. (1998), based on the values of EPT - Biotic Index for all the sampling stations, it can be noticed that the water quality of stations 1, 2 and 4 results of no impact, meanwhile for station 3 is of moderate impact.

SWRC - Biotic Index is calculated for all the sampling stations of the Mati River by the following formula (Schmiedt *et al,* 1998; McGonigle J., 2000; SWRC 2007):

SWRC - BIOTIC Index = TV*d/D

Where TV are given tolerance values for all

Table 3. Water bio-classification by Stroud Water Research Center 2007

S.W.R.C. – Biotic Index	0 – 3,75	3,76 – 5,0	5,10 – 6,50	6,60 – 10,00
Water quality	*Excellent*	*Good*	*Fair*	*Poor*

Table 4. SWRC - Biotic Index calculated for all the sampling stations of Mati river

TAXA	TV	Density				TV*Density			
		St 1	St 2	St 3	St 4	St 1	St 2	St 3	St 4
Ephemeroptera	3.6	1034	174	112	43	3722	626	403.2	154.8
Plecoptera	1	65	15	4	9	65	15	4	9
Trichoptera (Hydropsychidae)	5	93	34	64	68	465	170	320	340
Other Trichoptera	2.8	24	12	2	0	67.2	33.6	5.6	0
Odonata (Anizoptera)	4	18	9	0	0	72	36	0	0
Diptera te tjere	6	250	123	100	57	1500	738	600	342
Diptera(Tipulidae)	3	9	7	2	0	27	21	6	0
Diptera(Anthericidae)	2	5	0	0	0	10	0	0	0
Coleoptera	4.6	31	2	3	0	143	9.2	13.8	0
Oligochaetae (Haplotaxidae)	8	17	4	2	0	136	32	16	0
Molusque	7	48	84	46	7	336	588	679	49
Krustacea (Amphipode)	6	19	5	1	3	114	30	6	18
Nematoda	8	0	6	0	0	0	48	0	0
Total density		1613	475	336	187				
*TV*Density*						6657	2347	912.8	1372.8
SWRC - Biotic Index [Σ (TV*d)]: D		4.1	4.94	5.01	4.89				

the families found during our study (McGonigle J., 2000), *d* is the density of each family and *D*, the total amount of densities.

The values of SWRC - Biotic Index calculated for all the sampling stations of the Mati river are listed in table 4.

Bio – classification of the Mati river, based on SWRC - Biotic Index, shows a good water quality for all the sampling stations.

Water quality classification based on physico - chemical parameters

General statistics of data for physico-chemical parameters, levels of nutrients in water are presented in table 5.

Table 5. Physical-chemical parameters of water samples

Physical-chemical parameters	*Ma1*	*Ma2*	*Ma3*	*Ma4*
pH	8.0	8.13	8.13	8.12
Conductivity (μS/cm)	246.2	256.2	186.8	230.7
DO (mg/L)	8.97	8.55	8.89	8.84
BOD_5 (mg/L)	2.23	2.66	2.84	2.75
TSS (mg/L)	29.3	42.2	33.5	54.9
NO_3^- - N (mg/L)	0.36	0.38	0.40	0.46
NH_4^+ - N (mg/L)	0.031	0.020	0.022	0.027
NO_2^- - N (mg/ L*10^{-3})	8.51	10.19	14.02	12.10
P-PO_4^{3-} (mg/L)	***0.024***	*0.020*	*0.020*	*0.034*
P-PO_4^{3-} (mg/kg ,DW)	280.7	272.1	337.6	374.6
EPT **Total density**	**1216**	**235**	**182**	**120**
EPT **TV*D**	**4522**	**864**	**702**	**444**
EPT-Biotic Index [Σ (TV*d)]: D	**3.71**	**3.67**	**3.9**	**3.7**

(a) Physico - chemical parameters of waters (table 5)

The data of pH values in four stations of our study are between 8 and 8.2 higher than the level for first quality class of NIVA (Heinonen et.al.,1997) classification (pH>6.5). The content of solid matter (TSS) is really a crucial problem. The mean levels of TSS in all stations exceed the guide limit of the CEE Directive and all results are much higher than 10 mg/L, the limit for class 5 (very bad) according the NIVA classification. The main factor is soil erosion caused by several natural factors, like geographical (average slope of the territory is more than 27%), climatic (rainfall 1800-2300 mm/year), hydrological, and as well as of human factors like deforestation. From some studies result that erosion is in average 20 tons/ha/year or 1.6 mm soil layer and about 60 million tons of solid particles discharge into the sea every year [Cullaj, A., Lazo, P., Baraj, B. 2008]. There are no limits for conductivity in watercourses. Relatively high values resulted indicates high content of dissolved matters in water.

Dissolved oxygen (DO) and biological oxygen demand (BOD_5) are very important parameters indicating “health” of water environment. The situation of each site of this study is good; resulting of 1st quality class according NIVA classification and meeting norms of CEE Directive.

(b) Nutrients content in the Mati River (table 5)

Due to agricultural activities and runoff from soil pollution, a distinct pollution by nitrogen compounds was found. Nitrogen and phosphorus are considered as major nutrients whose concentrations in water are affected by anthropogenic activities. The natural levels in nitrogen and phosphorus species are not accurately known in European river systems (Crouzet et.al., 1999).

N-NO_3 mean value of all our data result smaller than 0.5 mg/L, about four times lower than mean concentration 2.63 mg/L for 654 river stations in Europe (Stanners D, Bourdeau Ph, editors. Rivers, reservoirs and lakes. Europe’s environment. Copenhagen 7 European Environment Agency; 1995. p. 73–108). The range of concentrations of nitrate in ecosystems does not pose a toxic risk to aquatic animals (Nixon, 1995). In highly polluted ecosystems, nitrate is reduced and can partially compensate for the lack of oxygen needed to oxidize organic matter.

Table 6 Correlation of Chemical Data

	Ma 1	**Ma 2**	**Ma 3**	**Ma 4**
MA 1	1.000			
MA 2	0.948	1.000		
MA 3	0.907	0.987	1.000	
MA 4	0.731	0.904	0.949	1

Even if relatively high levels of nitrite in the Mati River is an indicator of sewage pollution of waters. Nitrite is a transitional form of nitrogen (between ammonium and nitrate) and is highly toxic even at low levels. The nitrite concentrations found in the stations of Mati River are between 0.01 and 0.03 mg/L NO_2, given in the EC Freshwater Fish Directive 78/659/EEC stipulates guide values of 0.01 and 0.03 mg/L NO_2 - respectively, for salmonids and cyprinids. These recommended values are much lower than the US EPA guideline value of 5 mg/L (Nixon, 1995).

Ammonium average concentration of the Mati River (0.02-0.03 mg/L) results smaller than ammonium limit of 0.16 mg/L N-NH_4 given by ECC Directive for cyprinid waters.

Table 7. Data Correlation

	pH	**Cond**	**DO**	**BOD5**	**TSS**	**NO_3^- - N**	**NH_4^+ - N**	**NO_2^- -N**	**TP**	**P-PO_4^{3-}**	**EPT T. D.**	**EPT TV*D**	**EPT-B.I.**
pH	1.000												
Conductivity	-0.363	1.000											
DO	-0.595	-0.455	1.000										
BOD5	**0.960**	-0.591	-0.346	1.000									
TSS	0.575	0.169	-0.380	0.520	1.000								
NO_3^- - N	0.559	-0.285	0.025	0.645	**0.872**	1.000							
NH_4^+ - N	**-0.845**	0.213	**0.763**	**-0.730**	-0.154	-0.031	1.000						
NO_2^- -N	**0.752**	**-0.874**	0.065	**0.904**	0.268	0.589	-0.500	1.000					
TP	-0.024	0.124	0.280	0.049	**0.742**	**0.794**	0.528	0.037	1.000				
P-PO_4^{3-}	0.436	-0.586	0.347	0.619	0.616	**0.922**	0.083	**0.729**	**0.701**	1.000			
EPT Total density	**-0.987**	0.379	**0.515**	**-0.970**	-0.671	-0.684	**0.750**	**-0.778**	-0.130	-0.563	1.000		
EPT TV*D	**-0.987**	0.372	**0.520**	**-0.968**	-0.675	-0.684	**0.749**	**-0.774**	-0.133	-0.561	1.000	1.000	
EPT-B.I.	0.251	**-0.962**	0.434	0.458	-0.413	0.015	-0.250	**0.757**	-0.371	0.343	-0.229	-0.221	1.000

(c) Assessment of environmental quality

Environmental quality of rivers studied is implemented in two ways: (i) based on chemical data, and (ii) Biotic Index of Benthic Macro-invertebrates.

Based on correlation of parameters presented in table 5, we found very strong positive correlation (r > 0.73) between the distribution of the parameters in each station, resulting in similar environmental condition of the water of these monitory stations.

Strong correlation between each station based on biological and physicho-chemical parameters was found, proving that the situation of these stations do not differ significantly from each other.

Biological parameters like EPT Total density and EPT TV*D had very strong negative correlation (r > 0.7) with pH, BOD_5 and NO_2-N; negative correlation (0.7<r>0.55) with TSS, NO_3-N and PO_4-P, proofs that Benthic Macro-invertebrates can not live in dirty environment. It was found that nitrogen levels did not decrease as water traveled in the distribution system, indicating that it was not consumed by the microorganisms to support growth (EPA, Office of Water (4601M) Office of Ground Water and Drinking Water Total Coliform Rule Issue Paper). In contrary, the same biological parameters were found to have positive correlation with DO and strong positive correlation with NH_4^+ - N.

As for EPT - BI parameter, it appears very strong negative correlation with conductivity and positive correlation with NO_2^- -N. If we see TN:TP ratio, which is a good variable to study changes in rivers and is inversely related with the trophic status. This ratio can be influenced by a complex set of interrelated biochemical mechanisms and depends also from discharges which are rich with nitrogen. The importance of epilimnetic nitrogen to phosphorus (N:P) ratio is important for evaluation of limiting nutrient. This ratio is lower than the mass Redfield Ratio relative to molar stechiometric ratio 16:1 required for balanced algal growth at two stations (St1 and St2) and higher this value for rest of two stations, where was proved that phosphorus is a limiting nutrient.

Based on mean concentration of four nutrients and four physico-chemical parameters (pH, TSS, DO and BOD_5) the "average" quality class was calculated by the formula:

$$Average..class = \frac{\Sigma(QC)}{N}$$

Where QC mean Quality Class and N mean the number of parameters. The results are presented in the table 6.

The same class of quality classification results from chemical and SWRC bio-classification.

If we observe the values of EPT – Biotic Index for all sampling stations, the water quality of three stations have no impact and in one station has moderate impact. Meanwhile, values of SWRC – Biotic Index show a "good" water quality for all the four sampling stations.

A possible explanation for the different results for station no 3, may be the fact that when calculating the EPT – Biotic Index we consider all the insects EPT including those with low tolerance to the pollution. While for the SWRC –Biotic Index, we consider even taxones with high tolerance to pollution.

The assessment of water quality of the Mati river, during the period 2009 – 2010, based on the use of benthic insects as bio-indicators and of some physico-chemical parameters of water quality show still a good quality. Similar results are obtained even from the study of the Mati river water quality during the period of 2003 – 2005 (A.Cullaj, P.Lazo, B.Baraj, 2008).

Conclusion

Bio-assessment of macro-invertebrates was conducted at four sites within the year 2010 along, the Mati River during 4 field campaign. Assessment of each site included physicochemical parameters, habitat score, and the following indices: EPT - Biotic Index and Biotic Index *of family/sequence* level, as well as Biotic Index parameter (Stroud Water Research Center), used for water quality bio-classi-

Table 8. Quality evaluation of Mati River according NIVA, UNECE : "Surface water quality parameters" and Biotic Index classification

Station	Average class	Quality evaluation	EPT - Biotic Index	Schmidt classification	S.W.R.C. – Biotic Index	S.W.R.C bio-classification
MA 1	2.0	*Good*	3.71	*No impact*	4.1	*Good*
MA 2	2.0	*Good*	3.67	*No impact*	4.94	*Good*
MA 3	2.0	*Good*	3.90	*Low Moderate impact*	5.01	*Good*
MA 4	2.0	*Good*	3.70	*No impact*	4.89	*Good*

fication.

This study illustrates the importance of biological data in conjunction with physicochemical data to assess water quality and to characterize impacts from urban runoff. Sites located upstream of urban activity showed high diversity and richness of aquatic communities and overall good water quality. However, the condition of biotic communities was directly related to habitat and water chemistry. Habitat is degraded in urban areas due to dredging, channelization, and impaired riparian buffer zones that contribute to poor species diversity. The results of our bioassessment monitoring lead us to the conclusion that physical and chemical data of storm events going in reasonable accordance with biological parameters and demonstrate the same water conditions

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