

Assessment of the environmental situation of Albanian rivers based on physico-chemical analyses

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## Abstract Water quality parameters and heavy metal levels were monitored during 2002–2004 on eight campaigns along the most impacted rivers of the Albanian

along the most impacted rivers of the Albanian Adriatic lowlands: the Mati with its tributary Fani, Ishmi with its tributaries Lana and Tirana. the Shkumbini, and the Semani with its tributaries Gianica and Osumi (Fig. 1). Water samples were analysed for general physico-chemical parameters, concentrations of nutrients, and levels of heavy metals (Pb, Cd, Cu, Zn, Fe, Mn, Cr, Ni, Hg). Several sediments and biota (algae) samples were analysed for heavy metals, too. Assessment of environmental quality of waters is based on two "quality standards": the classification of the Norwegian Institute for Water Research (NIVA 1997) [4] and the European Community Directive (EEC/EEAC/EC 78/659) on "Quality of fresh waters supporting fish life" [5]. Obtained data have been reported recently [1,2,3].

The most critical chemical parameters for nearly all studied rivers found: (a) Total suspended solids (TSS) in excess of 25 mg/L in many sampling points, due to the intensive erosion of the land; (b) High nutrient concentrations in rivers near big towns. Very low dissolved oxygen (eutrophication) was found in the river Ishmi near Tirana city and the river Semani near Fieri city, caused by the discharges of untreated sewage wastewaters. The most polluted rivers for nearly all parameters were the Lana (tributary of the Ishmi) and the Gjanica (tributary of Semani). The conclusions from the chemical analyses are very similar to those found in a parallel study of biological parameters for diatoms in the framework of this study.

Systematic monitoring programs are urgently needed to understand the present environmental state of Albanian rivers and other aquatic ecosystems to characterize the main sources of pollution and to lay the basis for political guidelines to improve the ecological situation. Albania is rich in water resources including lakes, rivers, springs, and lagoons, with a high quantity of available water. The Albanian territory covers about 65% of a total watershed area of 43,905 km<sup>2</sup>. More than 152 torrents and small rivers finally form the eight large rivers: Buna (41 km), Drini (285 km), Mati (115 km), Ishmi (74 km), Erzeni (109 km), Shkumbini (181 km), Semani (281 km), and Viosa (272 km), which run southeast to northwest towards

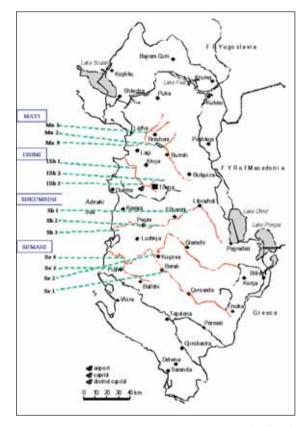


Figure 1 - Map of Albania and monitored rivers

the Adriatic coast [7]. Albanian rivers are characterized by a high flow rate: the total annual mean flow is 1,308 m<sup>3</sup> s<sup>-1</sup>, which corresponds to an annual water volume of 42.25x109 m<sup>3</sup> of which 30% belongs to subterranean waters. This accounts for more than 13,000 m<sup>3</sup> per capita per year [6]. The rivers, fed mainly by precipitation (69%), show a typical Mediterranean regime, with seasonal variation in the flow rate, and high flow from October to May [7].

The transformation of the Albanian economy into an open market during the past decade has caused significant damage to the natural resources of the country, mainly to natural waters, especially the most exposed and unprotected ones. The situation is especially dramatic in the Albanian

western lowlands through which most of the rivers pass. This region has become heavily populated and most urban and industrial waste is discharged directly into the rivers. Many current environmental problems are directly or indirectly linked to aquatic ecosystems, including urban and industrial waste management, water pollution or land erosion. Neither liquid nor solid waste is controlled, nor are samples taken regularly of surface and ground waters [8, 10]. During the past decades, mining, enrichment and metallurgy industries have produced high quantities of solid or liquid waste, often dumped on riverbanks or directly into rivers. Forest mismanagement has given rise to erosion, another increasing problem. The WB report (1997) confirmed that from 1950 to 1995, the naturally forested area in Albania decreased from 46% to 35%. Erosion is not only favored by the mountainous relief and climate, but also by unsuitable human activities [9].

In this study, water quality parameters (pH, electrical conductivity, dissolved matter, dissolved oxygen, total suspended solids and nutrients) were monitored in 13 stations along the various rivers. The level of heavy metals (Pb, Cd, Cu, Zn, Mn, Fe, Cr, Ni, and Hg) were measured in water, sediment and algae. Microscopic algae (diatoms Bacillariophyta) were also examined. The trophic state was calculated from chemical and biological data. A complete report is published by Miho *et al.* [2].

### Material and methods

#### Sampling

The sampling stations (13) are shown in figure 1. The stations present various levels of human impact, from near river sources (the least polluted) to near outfall. Eight sampling campaigns were carried out at intervals of 3 to 5 months between May 2002 and March 2004. Sampling was implemented according to standard operation methods [11, 12]

#### Methods of chemical analysis

All analytical methods used are standard ones, recommended by APHA [11], EN/ISO standards [12] and European Community Directives [5]. Temperature, pH, conductivity, TDS and DO were measured directly using Hach multiparameter apparatus (Sension 156), TSS was determined after filtering through a 0.45  $\mu$ m glass membrane filter; DO was measured by the Winkler method. All nutrients were determined by spectrophotometry using a Shimadzu 2401 UV-VIS Spectrophotometer. Heavy metals in the water were determined by Atomic Absorption Spectrometry: Cu, Pb, Cd, Ni, Cr, Mn by Graphite furnace, Fe, Zn, Mn by the flame technique and Hg by CV-AAS.

#### Quality assurance

Quality control was implemented by use of SRM and the standard additions method.

**Results** General data for physico-chemical parameters and levels of nutrients and heavy metals in water are presented in tables 1, 2, 3, 4 and 5. Detailed data for each campaign are reported in [2].

River	PH		Conductivity, µS/cm		TSS, mg/L			DO, mg/L				
	Mean	10%	90%	Mean	10%	90%	Mean	10%	90%	Mean	10%	90%
Mati	8.01	7.78	8.46	261	100	302	38	19	76	9.03	8.1	11.3
Ishmi	7.7	7.41	8.3	550	365	694	89.3	47.3	128	4.04	0.5	9.6
Shkumbin	8.1	7.8	8.46	316	226	412	78.4	45.6	328	9.47	7.9	11.1
Semani	8.01	7.59	8.4	437	230	814	108.9	46.4	351	8.02	2.06	9.3

Table 1 - Physico-chemical parameters of water samples Median; 10% Percentile; 90% Percentile

Table 2 - Nutrient levels in river waters

	N-NO <sub>3</sub> (mg/L)			N-NO <sub>2</sub> (µg/L)			N-NH <sub>4</sub> (mg/L)			P-P0₄(µg/L)		
River	Mean	10%	90%	Mean	10%	90%	Mean	10%	90%	Mean	10%	90%
Mati	0.51	0.21	0.88	13.6	3	30	0.14	0.05	0.39	5.0	3.0	9.0
Ishmi	1.12	0.41	1.57	278.5	7	830	6.64	0.09	13.0	417	5	950
Shkumbin	1.44	0.57	1.85	41.5	4	80	0.24	0.08	0.54	25.5	4.0	28
Semani	1.26	0.31	1.41	108.3	6	136	1.84	0.07	1.70	43.8	4.0	120

Table 3 - Maximum values for heavy metals in river waters (in µg/L except Fe in mg/L)

River	Pb	Cd	Cu	Zn	Ni	Cr	Mn	Fe	Hg
Mati	3.6	1.2	3.7	40	3.5	4.3	60	0.09	0.11
Ishmi	2.9	2.9	9.8	30	7.9	5.2	260	1.05	0.15
Shkumbin	2.5	0.8	3.2	20	13.1	7.6	190	1.37	0.11
Semani	2.9	3.2	2.7	20	16.8	10.0	110	0.83	0.21

River		Pb	Cd	Cu	Zn	Ni	Cr	Mn	Fe	Hg
Mati	Min.	1.5	$\leftarrow$	96.5	33.7	103	184	577	3.32	0.12
			0.02							
	Max.	10.8	0.13	575	98.4	194	584	1627	4.43	0.28
Ishmi	Min.	2.94	0.03	106	32.8	73.3	86.6	273	2.21	0.12
	Max.	16.4	0.15	223	133	162	214	1165	3.98	0.20
Shkumbin	Min.	1.9	0.03	41.5	20	181	195	533	3.21	0.08
	Max.	13.6	0.11	163	75	328	504	1079	4.21	0.16
Semani	Min.	1.03	0.02	38.4	17.9	131	101	556	2.37	0.08
	Max.	9.46	0.06	144	47.4	289	429	990	3.82	0.17

Table 4 - Values ranges for heavy metal concentrations in river sediments (in mg/kg DW, except Fe in g/kg DW)

Table 5 - Maximum heavy meta	l concentrations in Chladophor	a alaae (in ma/ka DW	except Ha in ua/kal

River	Pb	Cd	Cu	Zn	Ni	Cr	Mn	Fe	Hg
Mati	3.6	1.2	3.7	40	3.5	4.3	60	0.09	0.11
Ishmi	2.9	2.9	9.8	30	7.9	5.2	260	1.05	0.15
Shkumbin	2.5	0.8	3.2	20	13.1	7.6	190	1.37	0.11
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#### Discussions

Assessment of the environmental quality of waters is based on two "quality standards": the Classification of the Norwegian Institute for Water Research (NIVA 1997) [4], and the European Community Directive (CEE/CEEA/CE 78/659) regarding "Quality of fresh waters supporting fish life" [5]. The NIVA classification is more complete, because it is based not only on the levels of the usual physico-chemical parameters and nutrients, but also on the content of heavy metals in water, sediments and fish. Under this scheme, natural freshwater bodies are classified into five quality status levels, from very good (class 1) to very bad (class 5).

(a) Physico-chemical parameters of waters (Tab. 1) There is no problem concerning the pH values of the studied rivers: all data are between 6 and 9 (the limits of the EU Directive), and higher than the level for the best quality class of the NIVA classification (pH=6.5). There are no limits for conductivity in watercourses, but relatively higher values were observed in the Semani and the Ishmi, indicating higher content of dissolved substances in their waters.

Solid matter (TSS) in all the studied rivers is really a crucial problem. Median and mean levels of TSS in all

rivers exceed limits. Only about 4% of all our samples had TSS levels below 25 mg/L, the guide limit of the EU Directive, and all results were much higher than 10 mg/L, the limit for class 5 (very bad) according to the NIVA classification. Particularly high TSS values were recorded on the Semani (max. 436 mg/L) and the Shkumbini (max. 521 mg/L). The primary cause is soil erosion, caused by several natural factors, geographical (average slope of all territory is more than 27%), pedological, climatic (rainfall 1800-2300 mm/year) and hydrological, and some human factors such as deforestation, poor maintenance of the hillside terraces, etc.). Some studies estimate erosion at 20 tons/ha/year or 1.6 mm soil layer on average, and about 60 million tons of solid particles are discharged into the sea every year [13].

Dissolved oxygen (DO) is a very important quality parameter indicating the "health" of the water environment. A critical situation was observed at the two last stations of the Ishmi and Semani (most of the values were below 2 mg/L, which means "very bad" status according to the NIVA classes). Untreated sewage discharged from the cities of Tirana (700,000 inhabitants) and Fieri (60,000 inhabitants) leads to rapid and severe deoxygenating of the water and hence to the disappearance of aquatic invertebrates, "killing" the rivers in these sites. For the other rivers (sites), the situation is relatively good, in the 2nd or even 1st quality class according to the NIVA classification, and meeting the norms of the EU Directive. The same conclusions derive from the oxygen saturation of waters (data not shown).

#### (b) Nutrient levels in river water (Tab.2)

Most of our rivers have "bad" or "very bad" status according to the NIVA classification. This means that there is distinct pollution from nitrogen compounds, largely due to agricultural activities and runoff from soil pollution. The mean value of all our data is 1.1 mg/L N-N03, less than half the mean concentration of 2.63 mg/L for 654 river stations in Europe [6]. The best situation is seen in the river Mati, with nitrate levels about half those of other rivers.

The presence of nitrite is an indicator of sewage pollution of waters, but there are no limits for nitrite content in fresh waters. Very high levels were observed especially in the two last sampling stations of the Ishmi and the Mati, caused by sewage discharges from large towns.

Except the river Mati (average concentration 0.144 mg/L) all rivers exceed the ammonium limit of 0.16 mg/L N-NH<sub>4</sub> of the EU Directive for cyprinid waters. The mean value of all our samples is 1.84 mg/L, nearly three times higher than the average concentration of 0.66 mg/L reported for 580 European river stations [6]. The main contribution to this is from the rivers Ishmi and Semani, particularly their tributaries, respectively Lana and Gjanica. The former collects urban effluent from Tirana, including untreated sewage, and the latter collects urban discharges from the city of Fieri and a large oil refinery and oilfield. It is well-known that levels as high as 1 to 5 mg N/L when converted to ammonia may be very toxic to fish and other river fauna. This is the case of the Lana (av. 14.1 and max. 32.7 mg/L) and Gjanica (av. 2.2 and max. 4.3 mq N/L).

Generally, the majority of phosphate measurements are very low, much lower than the limit of 65.3 µg/L P-PO4 of the EU Directive for salmonid waters. Important exceptions are the Ishmi and Gjanica (tributary of Semani), which are heavily polluted by urban effluent. Especially low phosphate concentrations were found in samples from the Mati due to the limited human activity (including agriculture). According to the NIVA classification, most of our rivers belong to quality class 3 or 4, whereas the Ishmi and Gjanica are in class 5 ("very bad").

#### (c) Heavy metals in water

General assessment of the state of HM pollution of rivers is difficult, primarily because measurement of metals is rarely included in monitoring programmes, but also because concentration levels are usually so low that problems arise with sample preparation and the precision of analytical results. Comparison and assessment of the state of HM in rivers is therefore more difficult than for most of the other water quality variables. The following evaluation of HM in rivers must be looked at with these reservations in mind.

Based on the NIVA classification, nearly all our data relative to HM levels belong to quality class 2 ("moderately polluted"). Relatively higher HM content was found in samples collected in the Lana and Gjanica, which are "markedly polluted" (class 3) with Pb, Cd and Cu. No evident pollution was observed in the waters of the Mati and Shkumbini.

#### (d) Heavy metals in sediments and algae

It is relatively easy to determine HM content in sediments and algae compared to water, but it is very difficult to use the data for environmental quality assessment. Total metal content in sediments does not reflect the bioavailable fraction, and it is not possible to find everywhere the same species of alga and in a similar biological state. For this reason, the evaluation of HM levels in sediments and the biota is only very rarely included in river monitoring programs of.

Our evaluation of HM in sediments is based on the NIVA classification [4]. The majority of our data place our rivers in the 1st ("slightly polluted") and 2nd ("moderately polluted") quality classes, belonging to the "high diffuse background level". Relatively high concentrations of copper in the sediments and algae of the river Mati reflect the natural pollution from copper-containing minerals found in this area and also pollution from dumping of solid wastes from mines and former metallurgical plants.

#### (e) Assessment of environmental quality

The environmental quality of the rivers studied is assessed in two ways: (i) based on chemical data, and (ii) based on biological data for diatoms.

An environmental quality evaluation for each river station was performed, calculating the "average" quality class using mean concentrations of four nutrients, three physico-chemical parameters (pH, TSS and DO) and seven HMs (maximum content) in water samples by using the formula:

Average class= $\Sigma$ (Quality class)/no. of parameters

Results are presented in table 6.

		Evaluation based on								
River	Station	Physico-cl	nemical parameters	Heavy metal concentrations						
		Av. class	Evaluation	Av. class	Evaluation					
	Ma 1	2.0	Good	2.2	moderately polluted					
Mati	Ma 2	2.2	Good-Fair	2.7	moderately polluted					
	Ma 3	2.3	Good-Fair	2.2	moderately polluted					
	lsh 1	2.7	Good-Fair	3.1	markedly polluted					
Ishmi	lsh 2	4.5	Bad-Very Bad	3.4	markedly polluted					
	lsh 3	4.2	Bad-Very Bad	3.4	markedly polluted					
	Sh 1	2.7	Good-Fair	3.0	markedly polluted					
Shkumbini	Sh 2	2.8	Good-Fair	3.0	markedly polluted					
	Sh 3	2.7	Good-Fair	2.9	moderately polluted					
	Se 1	2.2	Good-Fair	2.6	moderately polluted					
Semani	Se 2	2.5	Good-Fair	3.0	markedly polluted					
	Se 3	4.3	Bad-Very Bad	3.6	markedly polluted					
	Se 4	3.0	Fair	3.1	markedly polluted					

Table 6 - Quality evaluation of rivers according to the NIVA classification

#### Conclusions

 The most critical general physico-chemical parameters for the studied rivers are:

 total particulate content (TSS) exceeds all environmental limits in all rivers, caused by very high erosion rates;

 very low dissolved oxygen concentration in some stations of the Ishmi and Semani, caused by discharge of untreated liquid urban waste from big cities (Tirana and Fieri).

- Levels of nutrients are relatively high in most rivers, especially near the inhabited areas, caused mostly by urban waste and agricultural effluent.
- Heavy metals content in the water is relatively low and generally does not present a threat to the biota.
- 4) The chemical and biological data support the evaluation of the trophic state of our rivers in various stations, as presented in table 6. The situation is critical for the two last stations of the Ishmi and Semani. The main cause is discharge of untreated sewage from large towns.
- Eutrophication of the rivers may strongly influence their deltas, nearby lagoons (Patoku and Karavasta) and the Eastern Adriatic seacoast.

In summary, Albania is in a lucky situation to have so many water resources, but the responsibility to protect and use them properly must be taken extremely seriously, because the present state of water pollution in Albania is a real risk for the economy and human health. Taking the appropriate measures in important and sensitive watershed areas will help to prevent further damage to biodiversity and humans, and will help regain the original beauty of the landscape. The Albanian territory is also important for the supply of water to the Eastern Adriatic coast. Sustainable watershed management guarantees the fulfillment of these tasks on regional and international levels.

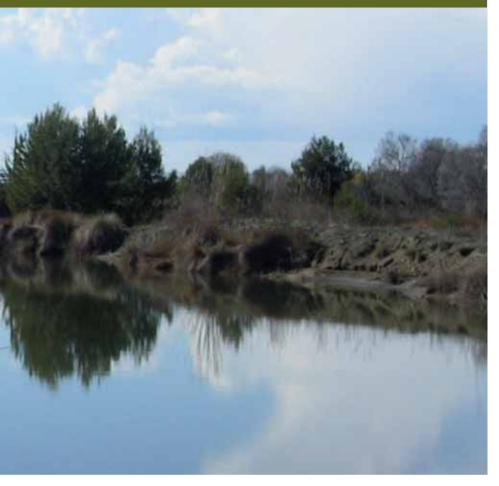
#### Acknowledgement

The authors are grateful to their Swiss partners from Zurich University, especially Profs. R. Bachofen, F. Schanz and H. Brandl, for their collaboration in this study, implemented in the framework of the SCOPES program (Scientific Cooperation between Eastern Europe and Switzerland, project 7ALJ065583).



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