

Heavy Metals in Water, Biological Changes in Aquatic Ecosystems, Economic Damage in R, Kosovo

Adem Dreshaj, Bedri Millaku, Afrim Selimaj, Emine Turkaj, Elit Kukiqi
University of "Haxhi Zeka", Peja, Kosovo

Abstract

Water is the source who apart from its environmental, economic and technological importance, lack of it can have consequences directly to the quality of existence of the living world. Today, the rational usage of water, compared to the past is completely different. If we add to that fact the amount of pollution in urban and industrial origin, then we can say that the potential risk of contamination and loss of water quality directly reflects the health of biocenoses and the degradation of aquatic ecosystems. Scientific studies on different types of fish have shown that different pollutants such as heavy metals, sewage, pesticides, etc. Reflect directly on biochemical parameters of physiological tissue of fish.

Rivers in Kosovo are constantly in pollution, pollution originating from either urban or industrial. The results of our study confirm the contamination of these waters and the tendency for serious changes to their biota, eg Sitnica river.

Sitnica river is contaminated with heavy metals such as: (Pb, Ni, Cd, Cu, Zn, etc.), urban solid waste (sulfate, nitrate), CN, phenol and pollution from power plants while burning lignite from Kosovo.

Research has shown that this river is polluted with polycyclic aromatic hydrocarbons poliklor biphenyl (PCB), are known for their toxic effects (genotoxic, mutagenic, carcinogenic), in living organisms.

Water pollution has a negative impact especially on aquatic organisms, which can absorb pollutants directly from the water through food. In this way, these pollutants bioaccumulate in fish tissues and organs, causing damage to the structure of DNA, and other genotoxic effects of fish.

Keywords: Water, metals, fish, pollution.

INTRODUCTION

According to the World Health Organization (WHO) assessment of water quality is the determination of parameters such as bacteria "Escher Coli", coliforms, total residual chlorine, turbidity, pH, the amount of dissolved oxygen and temperature [4]. Sources of pollution are agricultural pesticide use, discharge of chemicals from industrial activities no chemical treatment, biological wastewater that used for agricultural crops.

Water covers 71% of Earth's surface and the oceans contain 96.5% of water on Earth. Antarctic glaciers contain 61% of all fresh water on Earth [1].

Fish are permanent residents of aquatic ecosystems, which are susceptible to pollutants, negative role in the economy, tourism and public health.

Scientific studies on fish species, which are exposed to pollutants such as heavy metals, sewage, pesticides, etc., directly reflect the physiological biochemical parameters of fish's tissue and blood.

RIVERS AND RIVER BASINS

Hydrograph of water flows of Kosovo is divided in 4 river basins: the "Drini i Bardhë", "Morava e Binçës" and Lepenci. Kosovo rivers flows flowing into three sea basins: the Black Sea, Adriatic Sea and the Aegean Sea [9].

Table 1. Records to the maximum values, minimum and average annual flow of water quantity ($Q = m^3 / s$), Sitnica River.

Name	Length (km) Kosovo	Area(m ²)	Change of the flow
Sitnica	90 km	2.873 m ²	Black sea

The purpose of the study

In this study analyzed aspects of microbiology, eco-physiological -biochemical, physico-chemical parameters, including heavy metals, for impact assessment contaminating water biota of Sitnica with heavy metals such as: (Pb, Ni, Cd, Cu, Zn, As, etc.,). [9].

- Evaluation of microbiological indicators, total coliforms and faecal streptococci, the total number of living bacteria (LB).
- Evaluation of indicators microbiological salmonella spp. and Shigella spp. in the gastrointestinal tract, as well as Helicobacter pylori (Anti H. pylori) in the blood serum of fish Rutilus rutilus and Carassius gibelio in the Sitnica River. [7].
- Assessment of physico-chemical parameters and heavy metals in the water of the river Sitnica.

Until were offered some definitions of the term 'biomarker'. These definitions focus on a measurement context (experimentation), which reflects the interaction between a biological system and a potential danger, which may be chemical, physical or biological.

Pisces, as markers bio-accumulative, can be applied to demonstrate the effects of contaminants environmental and answer biota to them, as well as bio-concentrating to identify micro-certain substances, which have an impact on aquatic organisms, even in small amounts of water [6].

Most markers bioaccumulation in the body of the fish, assimilate from contaminants organic, as bisphenol polychloride (PCBs), then polychlorides dibenzofurans (PCDD) and dibenzo-dioxins (PCDF) and furthermore

compounds biodegradable as well as polycyclic aromatic hydrocarbons (PAH).

Exploitation of waters for fishing and Kosovo's aquaculture

In most of Kosovo's rivers and lakes, fishing is applied mainly as a recreational sports activity and touristic. Contamination of rivers and riverbeds demolitions have resulted in reducing the quality and quantity of fish. [9].

Fish meat consumption in Kosovo is estimated 0.8 kg / per capita. Compared with the countries of the region is below the average level of consumption. According to the Chamber of Commerce of the Republic of Kosovo due to the river pollution, about 10% of fish import was increased for consumption, consequently the economy of Kosovo losses approximately a million euro for a year. [5].

Agriculture yields started to decline because in this pond used for irrigation of agricultural crops. In 2000 a hectare planted with wheat yield has sheep to 6 kg in 2016 and decreased productivity 2500-3000kg wheat as a result of the use of polluted water and climate change [9].

In the rivers basin of mentioned rivers this year (2016) appeared the animal disease "tubercular" and consequently were destroyed 3000 animals and again due to environmental pollution. Escheria Coli and fecal coliforms are an indicator bacteria, whose presence indicates that the water may be contaminated with animal waste. The bacteria present in the water can cause acute effects in humans such as diarrhea, cramps, nausea, headaches, or other symptoms [9].

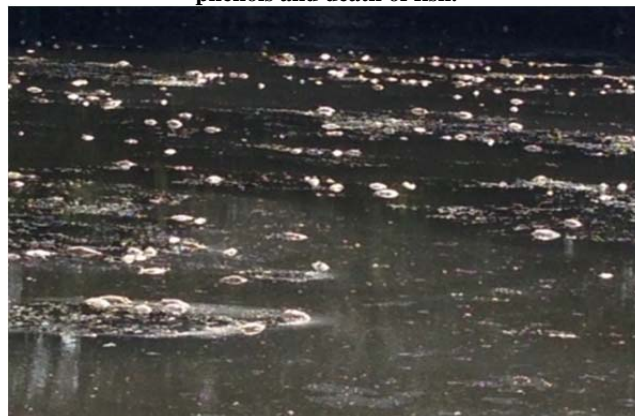
Drinking water is considered clean and without risk to human health, when there is the presence of fecal coliforms (0 CFU / 100 mL water) and standard level of fecal coliform in surface waters is (100 CFU / 1000 mL water). Most of them are originated from faeces and people's faces, blood, and animals. All types have anti gene by Lancefield group D, belonging sexes and Streptococcus Enterococcus [5]. Most of them are from the faecal origin and can be used as an indicator of pollution, furthermore, they just breed by fecal contamination. To determine the total number of bacteria and fecal streptococci caliform we hagar feeder in 1 ml water at 37 0C for the second day, pollution of human origin presents the high (> 4) FC / FS while the lowest ratio (<07) shows no contamination with human origin.

Phenols - Phenol and their derivatives are used as dyes, polymers, pharmaceuticals and other organic substances.

Table 2. Pollution reports Fc/Fs

The initial report FC / FS	Report during time FC/FS	Potential source of fecal contamination
< 4	Grows	Unsure
	Lessen	Human
>07	Grows	Not-Human
	Lessen	Unsure

Fig 1. Water pollution in the river Sitnica high amounts of phenols and death of fish.



Phenols affect in oxidative capacity, they are hem toxic and hepatotoxic, provoke mutagenesis and cancer at humans, fishes and other organisms.

The first doubts speak for a poisoning of fishes with the organic substance Phenol which is a substance that is mostly used by power plants in Obiliq and no doubt that this substance poisoned fishes, this will be confirmed from analysis of samples received at: 6/15/2016. Then they were sent to the toxicology laboratory in Pristina.

From Table :3. can be seen the high value of phenol. The results indicate that the fishes had died as a result of the high amount of phenol released from Kosovo power plants and mining activities of "Trepca" Mitrovica [5].

Cyanides—Cyanides are compounds with high potential toxic. When their presence in drinking water results higher than 0.2 ppm / L, then the water is not considered clean (according to the Agency for Environmental Protection-EPA) [3] . To reduce the pollution of the rivers from cyanide, microbial sensors are designed to measure oxygen consumption in micro-concentrations of cyanide to the amount 0.3-150 ppm / L. [4].

Table 3.The value of samples of phenol in Sitnica River.

Sitnica river	Standard methods	Unit	Standard value	January	April	June	September
Phenols	SMWW5530-B	mg/L	0.5	0.60	0.60	0.70	0.60

Table 4. Measured values of cyanides in Sitnca River

Sitnica river	Standard methods	Unit	Standard values	January	April	June	September
Cianuret	SMWW4500CN	mg/L	0.5-1.0	≤0.020	≤0.025	≤0.025	≤0.035

Table 5. Isolated heavy metals in fish liver

Metals mg/L	Locations of samples					
	D1	D2	D3	D4	D5	D6
Zn	0.1672	0.3625	0.379	0.370	0.381	0.383
Cu	0.023	0.063	0.0587	0.063	0.064	0.0689
Cd	0.014	0.014	0.014	0.015	0.016	0.017
Pb	0.048	0.048	0.048	0.049	0.049	0.049

Table 6. Determination of heavy metals in the Sitnica river

Nr	Element's name	Allowed value mg/L	March	May	September	November
1	Pb	0.05	≤0.047	≤0.049	≤0.050	≤0.050
2	Ni	1.5-5	≤0.018	≤0.020	≤0.019	≤0.019
3	Cd	0.05	≤0.018	≤0.017	≤0.018	≤0.019
4	Cu	0.0005-1.0	≤0.017	≤0.019	≤0.018	≤0.019
5	Zn	5	0.036	0.037	0.038	0.037
7	CN ⁻	0.5-1.0	≤0.002	≤0.0022	≤0.0025	≤0.0030

MATERIALS AND METHODS

Blood taking was performed by drilling below the lateral line of the fish, straight into the caudal vein and bronchial veins, blood is taken using a sterile hypodermic syringes (2ml size, with dimensions: 0.8x38mm). Maintaining the blood analysis is done in a special section tubes EDTA as anti-coagulant. Bio-indicator organisms taken in this study were the fishes. Using the technique of electro fishing, at six sampling points across the river Sitnica, were caught in total 60 individual fish, or D1, D2, D3, D4, D5, D6, (n = 10), Fishes belong to the family Cyprinus carpio.

To assess the degree of bioaccumulation of heavy metals in fishes tissue, we measured the concentration of heavy metals in the liver tissue of the caught fishes in six site-sampling.

The study period of heavy metals in the river Sitnica (Spring / Fall 2016), concentrations of heavy metals were carried out (Pb, Ni, Cd, Cu and Zn), determined by the technique of induction (ICP OES, Inductively Coupled Plasma-Optical Emission Spectrometry, Perkin-Elmer Optima). All analyzes were analyzed by ICP OES Laboratory licensed "Agrovet" in Fushë Kosovë.

CONCLUSIONS

The state of waters in Sitnica river, considering the dimensions of "natural health" is not good. The fact that water resources are in shortage and on the other hand the systematic contamination and degradation in the absence of an effective system of management and protection. Heavy metals in the river Sitnica have not resulted in international standard limits, almost all isolated heavy metals in fishes results above the standards.

The results of the microbiological indicators of river water as; Fecal streptococci (SF) *Pseudomonas aeruginosa* (BP), while the total number of live bacteria (LB) resulted in slightly increased values. Lack of microbiological indicators, despite the presence of untreated water collectors, could be influenced by heavy metals, especially Cd and Pb, who demolished the bacterial flora in the respective rivers.

By bacteriological analysis in the gastrointestinal tract of fishes, *Carassius gibelio* and *Rutilus Rutilus* in Sitnica rivers, in addition bacterias such as: *Salmonella* and *Shigella* spp Spp were not isolated.

The absence of bacteria in the gastrointestinal tract of fish does not justify cleanliness of fish by microbiological aspect, since the impact of heavy metals, may have contributed to their bacterial flora.

RECOMMENDATIONS

It is recommended to advance the methods and the dynamic of monitoring of water pollution in rivers: Sitnica and their biota, especially fish as bio-indicators organisms.

We recommend institutional studies of water biota (fish), as well as their impact on the human aspect. Analysis of fish metabolically (metabolomics and proteomics) genetic and histopathological (micro nucleuses) wich provides a more complete picture about metabolism and their genetic profile, influenced by the stress of pollution.

Critical fall in the number of fish in the Sitnica rivers requires institutional caution towards this natural resource. Such studies provide concrete examples of awareness, to improve the situation of the respective river waters and their biota. All will affect the development of economic activities, especially tourism and recreational activities would increase their effect.

REFERENCES

1. Dakonta. 2009. Consulting services for Environmental Assessment and Remedial Action Plan for Mitrovica Industrial Park, Kosovo, UNDP.
2. Damek-Poprawa, M. and Sawicka- Kapusta, K., 2003. Damage to the liver, kidney, and testis with reference to burden of heavy metals in yellow-necked mice from areas around steelworks and zinc smelters in poland. *Toxicology*, 186(1-2), 1-10.
3. Davis Jr, K. B. &McEntire, M. E. 2006. Comparison of the cortisol and glucose stress response to acute confinement and resting insulinlike growth factor- concentrations among white bass, striped bass and sunshine bass. *Aquaculture America Book of Abstracts* p 79.
4. Di Giulio, R. T., Benson, W. H., Sanders, B. M. and Van Veld, P. A. (1995). *Biochemical mechanisms: Metabolisem, adaptation and toxicity*. In: G. M. Rand (Eds.), *Fundamentals of aquatic toxicology*:

- Effects, environmental fate and risk assessment, 2nd ed. Taylor & Francis, Washington, D.C., pp. 523-561.
5. Dreshaj, A. (2014). Product Quality Management and Environmental Impacts in Business, Pristina. Olymp; ISBN, 978-9951-635-32-5.
 6. Ferguson HW. 1989. Systemic pathology of fish: a text and atlas of comparative tissue responses in diseases of teleosts. Iowa State University Press, Ames, IA, 263p.
 7. Filho, D.E., Torris, M.A., Tribes, T.B., Pedrosa., R.C., and Soares, C.H.L. 2001. Influence of season and pollution on the antioxidant defences of the cichlid fish acara (*Geophagusbrasiliensis*). Brazilian Journal of Medicinal and Biological Research. 34: 719-726.
 8. Furhan Iqbal, Irfan Zia Qureshi and Muhammad Ali, 2005. Histopathological Changes in the Liver of a Farmed Cyprinid Fish, *Cyprinus carpio*, Following Exposure to Nitrate. Pakistan J. Zool., vol. 37(4), pp. 297-300, 2005.
 9. Dreshaj, A. (2013). Doctorate: Study chemical - environmental watershed White Drin and Ibar in Kosovo. University Tirana www.fshn.edu.al.