JJC *Jordan Journal of Chemistry* Vol. 13 No.1, 2018, pp. 15-33

Priority Pollutants Present in the Tisza River Hydrographic Basin and their Effects on Living Organisms

Ileana-Andreea Rațiu[a*b], Mihail Simion Beldean-Galea[c], Victor Bocoş-Binţinţan[c], Dorin-Daniel Costea[d]

[a] *Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Str. Arany Janos 11, Cluj-Napoca, RO-400028, Romania.*
[b] *Interdisciplinary Centre of Modern Technologies, Nicolaus Copernicus University, 4 Wileńska Str., 87-100 Torun, Poland.*
[c] *Babeş-Bolyai University, Faculty of Environmental Science & Engineering, Str. Fântânele nr. 30, Cluj-Napoca RO-400294, România.*
[d] *West University Timişoara, Faculty of Chemistry, Biology and Geography, Blvd. V. Pârvan 4, Timişoara, RO-300223, România.*

Received on Dec. 3, 2017 **Accepted on** Jan. 17, 2018

Abstract

Tisza River Basin is the largest sub-basin of the Danube Basin and home for 14 million people from five countries. It has a large diversity of landscapes and provides habitats for many animal and plant life species with protected areas and national parks. Nevertheless, Tisza River has serious pollution problems due to organic substances, nutrients, hazardous substances and hydromorphological alterations. The impacts of pollution are significant and affect human health. Endocrine disruptors are especially worrying as they can interfere with the endocrine systems of living organisms, including humans. A series of heavy metal were introduced by the "Integrated Tisza River Basin Management Plan" on the list of "priority pollutants". This article has the purpose to review the priority pollutants encountered in the Tisza River Basin. Their main effects on living organisms, including people, are discussed as well.

Keywords: *Tisza River; priority substances; heavy metals; toxic effects.*

Introduction

The Tisza River, which drains 157,186 km^2, of which 38,223 km^2 are protected areas, is the largest sub-basin of the Danube Basin. The River Tisza originates in the Zakarpatian Mountains in western; it is formed from the confluence of the Belaya Tisza and the Chiornaya Tisza and flows into the Danube by Slankamen (Serbia)[1].

The Tisza River Basin is home for 14 million people from Ukraine, Romania, Slovakia, Hungary and Serbia, while the diversity of landscapes provides habitats for unique animal and plant life species with a significant number of protected areas and national parks. As well, the Tisza River Basin provides livelihoods for many people through agriculture, forestry, pastures, mining, navigation and energy production. The

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* **Corresponding author:** Ileana-Andreea Rațiu **E-mail:** andreea_ratiu84@yahoo.com

Tisza River Basin socio-geographical characteristics – area, countries and the number of inhabitants are given in Figures 1 and 2 (Source for Figure 1 and 2: Numerical information adopted from "Integrated Tisza River Basin Management Plan" (www.icpdr.org), figures were realized by authors).

Along the time, the Tisza countries have cooperated for the protection of the Tisza. For example, the Tisza countries are all parties to the Danube River Protection Convention (signed in Sofia in 1994 and entered into force in 1998). In addition, all these countries are parties to the Carpathian Convention, which was signed in Kiev, Ukraine in 2003 and entered into force in 2006[1].

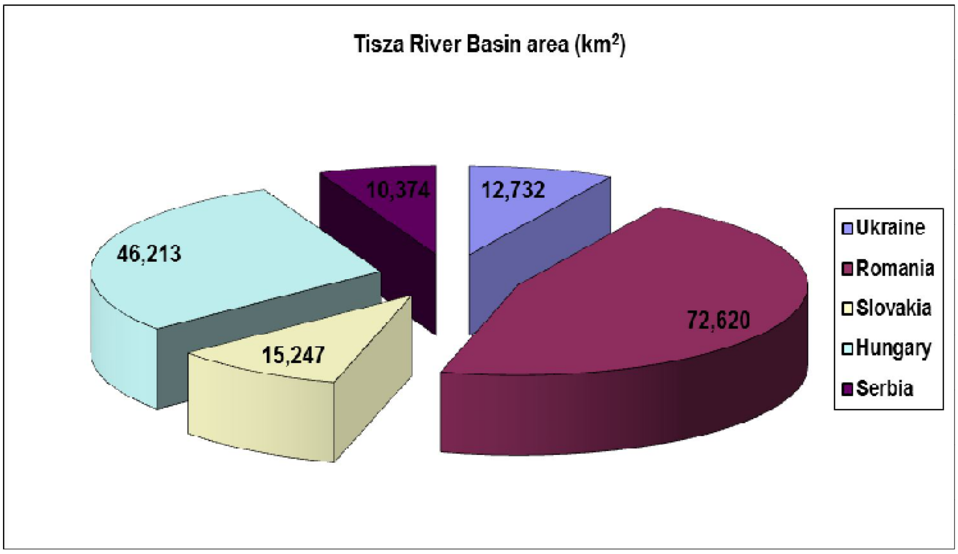

Figure 1: The Tisza River Basin: socio-geographical characteristics – countries corresponding area in km^2.

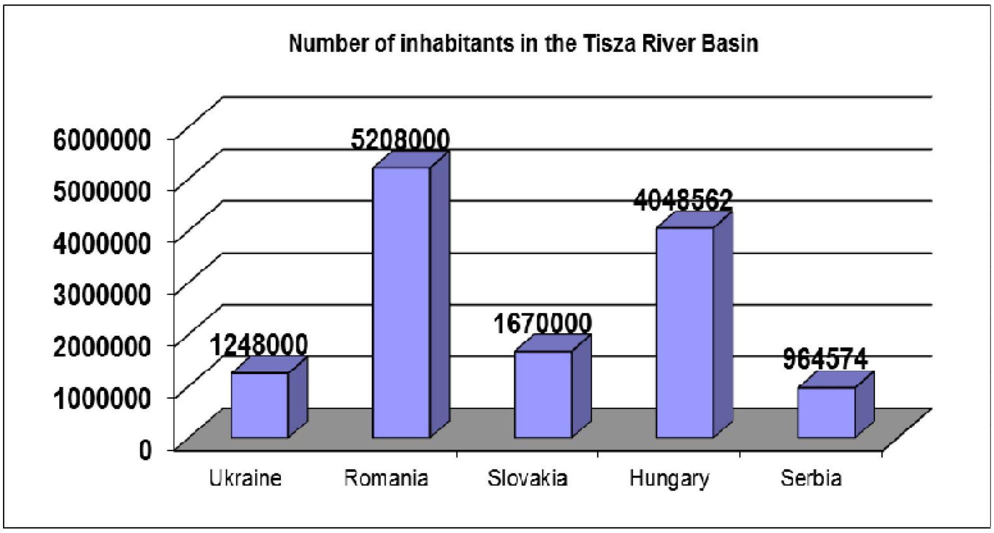

Figure 2: The Tisza River Basin: socio-geographical characteristics – number of inhabitants.

The Tisza Analysis Report realized in 2007 concerning the characterization of surface waters and groundwater concluded that the human influence in the region is major. Activities such as farming, forestry, mining and river engineering (all essential to the livelihoods of the people) have contributed to problems in the form of pollution and changes to the natural composition of the river. The impacts of pollution are significant in the Tisza River Basin and affect human health, the access to healthy fisheries, the safety of settlements and the development of a successful tourism industry. A key conclusion of the analysis report is that water quantity is a relevant water management issue. Integration of water quality and quantity in land and water planning is an essential issue for the ITRBM (Integrated Tisza River Basin Management) Plan[1].

The Tisza Group identified for the Tisza River Basin the following four categories of pollution:

- Pollution by organic substances (from urban wastewater, industry & agriculture);
- Pollution by nutrients (particularly by nitrogen and phosphorus – that can cause eutrophication of surface waters);
- Pollution by hazardous substances (pesticides and other chemicals applied in agriculture; discharges from mining operations; accidental pollution);
- Hydromorphological alterations.

Endocrine disruptors are especially worrying, as they can interfere with the endocrine systems of living organisms, including humans, because they mimic the physiological action of hormones[2]. Although these chemical compounds have been established to disrupt endocrine systems and generate illnesses, the vast majority of them are to date still unregulated and discharged carelessly into the immediate environment, especially in the developing countries where there is no stringent regulatory and legal framework[3]. For example, some of the endocrine disruptor compounds, such as bisphenol A, pesticides, organohalogens (furans, brominated fire retardants, dioxins), phthalates, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) are more frequently found in wastewater treatment plants than in natural environment. Others, such as nonylphenol and octylphenol, are more prominent in surface and groundwater[4]. Heavy metals are of particular concern due to their environmental persistence, biogeochemical recycling and ecological risks. Heavy metals occur in different geochemical forms of distinct mobilities, biological toxicities and chemical behavior[5]. The contaminated sediment serves as a long-term source of toxic elements; mobility and transport in the environment of these elements are strongly influenced by the nature of associated solid phase[6].

Mining is responsible as well for the pollution of Tisza. For example, in 2000, an accidental release of 100,000 cubic meters of heavy metal-laden cyanide solution, used to recover gold from mine tailings, escaped from Baia-Mare gold mine in Romania. An estimated 40 km-long plume flowed into the Tisza River. Concentrations of cyanide in Romania, Hungary, and Serbia were up to 700 times the allowable limit, killing much of the aquatic life and preventing the use of river water by human residents. In addition, large volumes of copper, lead, and zinc were also released into the river[7].

As a direct consequence, the general interest for Tisza River and especially for Tisza protection has increased continuously during the last 22 years. The scientists were also more and more interested in the last two decades in studying the Tisza river pollution. As evidence stands the increasing number of scientific publications in the last 22 years (Figure 3). The literature search was done in four major databases (Springer, Web of Science, Wiley and Science Direct) in February 2017 using the search string "Tisza River".

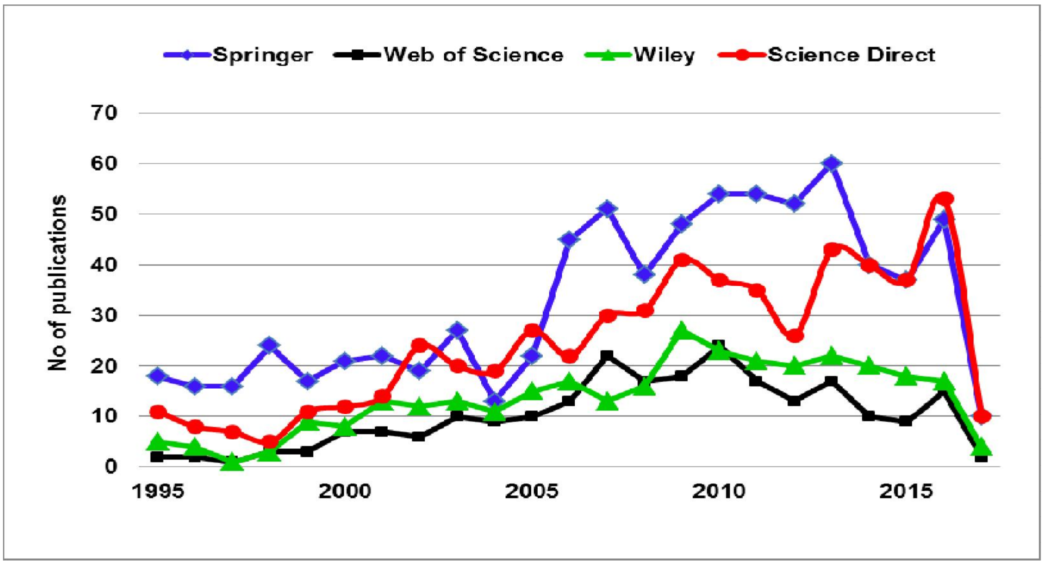

Figure 3: The evolution of scientific publications concerned with the Tisza River in the last twenty-two years.

Priority Substances and their effects on living organisms

The priority pollutants are those chemicals from the category persistent, bioaccumulative and toxic (PCBs). PCBs include two major categories: persistent organic pollution (POPs) and heavy metals. POPs are often called "the dirty dozen" and mentioned in different international conventions (Stockholm Convention - 2001, Aarhus Protocol – 1998, etc.) with the purpose of their reduction and elimination. Persistent organic pollutants are chemical compounds introduced into the environment (air, water, soil, sediments) especially from anthropogenic activities and cause serious adverse effects on human health and ecosystems. The relevant characteristics of persistent organic pollutants are:

(1) Persistence (resistance to degradation) – they can have a long lifetime of the order of years or even decades[8].

(2) Bioaccumulation – they are lipophilic substances; this property determines their concentration in the fatty tissues[9].

(3) Toxicity – poses the ability to harm human and ecosystems' health through acute and chronic effects[8].

(4) Volatility and transport - through the "grasshopper effect" (evaporation – transport by air – condensation – deposition on soil, then the cycle is reinitiated by re-evaporation) they cross long distances and can be therefore found even in the most remote places on Earth (including the polar regions)[10].

(5) Global distribution – due to the properties listed above and because persistent organic pollutants are present everywhere in the environment they represent a serious global problem[10].

The List of Priority Substances for the Danube River Basin and Tisza River Basin included a number of 41 substances or groups of substances[1]. Other countries included on the lists of priority substances the contaminants specific for their zone. For example, in China a priority list of organic compounds was established for preventing groundwater pollution risk; it included 117 organic compounds divided into three groups: high, moderate and low priority organic compounds[11].

Taking into account the above considerations, the Official Journal of the European Communities, L331/4 (15.12.2001) introduced the "List of Priority Substances for the Danube River Basin". This list is valid for the Tisza River Basin as well. Table 1 presents these priority substances and their effects on living organisms including humans.

Most of the studies performed on Tisza River pollution aimed mainly heavy metals and their compounds, and only few articles about PAHs were found. In the following sub-chapter, we will present the pollutants identified in various scientific articles and the concentrations found using different analytical techniques.

Water Framework Directive and Tisza River pollution

The European Parliament issued the Water Framework Directive (WFD) to take action on water quality protection for all European waters. The purpose was to achieve a good ecological and chemical quality status by the year 2015. To reach that goal, necessary measures should be identified and implemented, with the aim of progressively reducing pollution from priority substances. For this purpose, scientists proposed many different solutions. For example, Gevaert *at al.* demonstrated how a dynamic model of the integrated urban wastewater system can be used to test different emission reduction strategies for organic priority pollutants in a semi-hypothetical case study on di(2-ethylhexyl)phthalate[74]. The simulation results revealed that the most effective measure in terms of river water quality improvement and priority pollutants' concentration is reducing the release of this substance into the environment[74]. The issue of priority substances has been so far addressed by many researchers. For instance, the evaluation of occurrence and significance of concentrations and spatial distribution of priority pollutants along the Comunidad Valenciana coastal waters (Spain) was carried out in order to fulfill the European Water Framework Directive[10, 75].

Table 1: Priority substances and their effects on living organisms.

No.	Name of compound	CAS number	System affected	Mechanism	Reference
1	Alachlor	15972-60-8	Thyroid	Cytotoxic effects.	[12, 13]
2	Anthracene	120-12-7	Endocrine (estrogen)	Photo-induced toxicity to fish, possibly carcinogenic organic effects in humans.	[14, 15]
3	Arsenic & compounds	7440-38-2	Gluco-corticoid	Co-mutagen, co-carcinogen, and/or tumor promoter.	[16]
4	Atrazine	1912-24-9	Neuro-endocrine – pituitary, reproductive, metabolic.	Inhibits ligand binding to androgen and estrogen receptors; ability to alter endocrine signaling and cause mammary tumors in female, as well as breast cancer; decreases ovarian cell proliferation.	[17- 19]
5	Benzene	71-43-2	Reproductive, nervous, endocrine	Functional aberration of vital systems like reproductive, immune, nervous, endocrine, cardiovascular, and respiratory in humans.	[20]
6	Brominated diphenyl-ethers	N/A	Nervous	Bioaccumulation in liver and muscle of aquatic and terrestrial predatory birds' species; neurotoxic in humans.	[21, 22]
7	Cadmium & compounds	7440-43-9	Hepatic, immunologic, reproductive & estrogenic system	Hepatotoxicity in animal models; affects kidneys, liver and vascular systems in humans; deleterious effects on the reproductive tissues and the developing embryo in humans.	[23]
8	Chlorfenvinphos	470-90-6	Acetylcholine esterase inhibitor	Structural and functional changes in birds' liver; neurobehavioral effects to rats.	[24- 26]
9	Chlorpyrifos	2921-88-2	Nervous system	Neurobehavioral changes in mice; affects the flying ability of birds.	[27- 29]
10	Dichloro-methane	75-09-2	Thyroid	Mutagenesis and carcinogenicity for animals	[30]
11	Di(2-ethylhexyl)-phthalate	117-81-7	Hepatic and reproductive systems	Hepatotoxic, testicular dysgenesis syndrome in humans; cytotoxicity and genotoxicity potential in humans.	[31]
12	Diuron	330-54-1	Reproductive	Embryotoxicity, spermiotoxicity at species of sea urchin (*Paracentrotus lividus*); possible effects on fertility and reproductive performance at rats.	[27, 32, 33]
13	Endosulfan	115-29-7	Estrogenic effect	Cytotoxic effects for hepatocytes.	[34- 36]
14	Fluoranthene	205-912-4	Immune and reproductive	Toxic and genetic damage in marine mussels, possible immunotoxic effects; can affect primary lung epithelial cells in the presence of a pro-inflammatory stimulator in humans.	[37, 38]
15	Hexachloro-benzene	118-74-1	Thyroid, reproductive	Increase in thyroid size, enlargement of follicles, weight loose by depletion of adipose tissue, at male hamsters changes in the cellular ploidy, disturbing in the reproductive system in rats, probable human carcinogen, disruption of human placental function.	[39, 40]
16	Lindane	58-89-9	Estrogen, androgen	Neurotoxicological effect in rats; inhibits ligand binding to androgen and estrogen receptors.	[41]

No.	Name of compound	CAS number	System affected	Mechanism	Refe-rence
17	Isoproturon	34123-59-6	Nervous	Cholinergic hyperactivity and behavioral alterations in rats.	[42]
18	Lead & compounds	7439-92-1	Hematopoietic, nervous, reproductive	Lead as possible human carcinogen (group 2B) and its inorganic compounds as probable human carcinogens (group 2A); potential hepatotoxicity and antagonistic effects on the immune cells in rats; toxic effects on the heart and blood vessels in human populations; childhood neurotoxicity in humans.	[43- 45]
19	Mercury & compounds	7439-97-6	Nervous, thyroid, reproductive	Neurotoxic and endocrine disruptor effects in humans; can cause as well kidney dysfunction, cardiovascular abnormalities, respiratory distress, and neurological impairment in human populations.	[46, 47]
20	Naphthalene	91-20-3	Respiratory	Cancer and necrosis of bronchiolar epithelial cells in mice.	[48]
21	Nickel & compounds	7440-02-0	Nervous, thyroid	Immunological & carcinogenic effects in humans; nickel chloride can affect the redox equilibrium and stimulate apoptosis in oral epithelium cells; cancer risk is related to less soluble oxidic and especially sulfidic nickel species; nickel nanoparticles has significant toxicity for human lung epithelial cells.	[49, 50]
22	Nonyl-phenols & 4-(para)-nonyl-phenol	104-40-5	Estrogen, reproductive	Affect immune system in laboratory animals; there is limited evidence that it affect thyroid function; toxic to aquatic organisms; *Escherichia coli* cell growth inhibition; significantly decrease of sperm production and sperm motility; cytotoxic effect on epididymal sperm at rats; transfer across the human placenta.	[51- 53]
23	4-n-octyl-phenol & 4-tert-octyl-phenol	1806-26-4 & 140-66-9	Estrogen, reproductive, thyroid	Abnormalities in the histology of the testis and epididymis and induced atrophy of prostate gland tubules at rats; decrease of progesterone secretion at mouse; poor male reproductive performance at exposed rats; negative effects on the adrenal, pituitary gland, thyroid & parathyroid and pancreas in rats exposed in fetal period; interference with uterine contractility in rats.	[54- 57]
24	Pentachloro-benzene	608-93-5	Thyroid	Changes in plasma alanine aminotransferase and liver histopathological profiles, presence of protein droplets in tubular epithelial cells, reduction of plasma thyroxine levels in rats; renal lesions, liver weights increased in rats and mice; central nervous system effects, irritation of the eyes and upper respiratory tract, hardening of the skin, and hematological disorders in human; disruption of human placental function.	[40, 58]

No.	Name of compound	CAS number	System affected	Mechanism	Refe-rence
25	Pentachlorophenol	87-86-5	Thyroid	Cytotoxic effects on rats Sertoli cells in vitro; Warburg-like effect on zebrafish embryos during gastrulation & phenotype of developmental delay; potentially disrupts the thyroid endocrine system both in vitro and in vivo in rat.	[59- 61]
26	Benzo-(a)-pyrene	50-32-8	Androgen, hepatic, immune and reproductive	Probable human carcinogen; its metabolites are mutagenic and highly carcinogenic; decreased pulmonary function, chest pain, respiratory irritation, cough, dermatitis, and depressed immune system in human was reported after acute exposure; effects on experimental animals includes affections of the kidney, small intestine, trachea, liver, stomach, and esophagus; endocrine-disrupting effects in marine invertebrates; colon tumors in a subchronic exposure in mice; toxic effect on some immune cells of rainbow trout, causes a decrease in circulating antibody levels.	[62- 66]
27	Benzo-(b)-fluoranthene	205-99-2	Reproductive	Dysfunction in male reproductive function of humans; tumor-initiating activities on mouse skin.	[67, 68]
28	Simazine	122-34-9	Complex effects	Showed deleterious effects on terrestrial invertebrates and on aquatic invertebrates; weight changes; changes in blood composition; damage to testes, kidneys, liver and thyroid; gene mutations.	[69]
29	1,2,4-Trichloro-benzene	120-82-1	Nervous, respiratory	Dilation of smooth endoplasmic reticulum, damage of epicuticle, cuticle layer, and microvilli in *Eisenia fetida* species.	[70]
30	Trichloro-methane	67-66-3	Nervous, liver	Possible adverse health risks such as a small increased incidence of cancers in males and developmental effects on infants.	[71]
31	Trifluralin	1582-09-8	Reproductive, metabolic	Moderately toxic to rats, rabbits; changes in blood & liver weight. Possible carcinogen.	[72, 73]

Wei He *et al.* developed a novel platform, named “the Bayesian matbugs calculator”; a friendly, accessible, efficient tool to select the best model, calculate relevant indicators, assess ecological risks with uncertainty and sets the priority of toxic substances[76]. Robles-Molina *et al*. reported the development and validation of an analytical method for the trace level determination of 14 selected priority chemicals. Most of the compounds targeted were detected in the ng L^{-1} range at concentrations ranging from 0.19 to 135 ng L^{-1} [77]. The contamination in the Upper Tisza Region, along the upper reach of the Tisza and the lower reach of the Somes, based on the trace element concentrations of the Gomphus flavipes larvae was studied by E. Simon el al. in 2016[78].

In the Tisza River Basin, human activity is affecting both the channel morphology as well as fluvial processes, which can be quite varied. Indirect influences, including land-use and management, changes to the catchment, urbanization and land drainage, alter run-off and sediment yield. A wide range of direct impacts influences ultimately the river channel, such as dam construction, reservoirs and grade-control structures, channelization, artificial cut-offs and rectification, in-stream mining, installation of groynes, etc[79]. Moreover, in the Tisza River Basin, numerous human activities, including municipal, industrial, commercial and agricultural operations, release a variety of toxic and potentially toxic pollutants into the environment.[1] In Table 2 we can observe the major categories of pollutants that may be present in the Tisza waters. Mining has been responsible for heavy trans-boundary pollution events on Tisza River for many years as was the case mentioned above in 2000 of the accidental escape of cyanide solutions from the Baia-Mare gold mine in Romania[7,80].

Table 2: Major categories of pollutants that may be found in Tisza.

No.	Category	Provenience
1	Household product ingredient	Appliances, vehicles, building materials, electronics, crafts, textiles, furniture, household cleaning products
2	Personal care product / cosmetics	Cosmetics: shampoos, lotions, soaps, deodorants, fragrances, and shaving products
3	Food additive	Antioxidants, dyes, compounds used in food processing and as components in food packaging
4	Flame retardant	Chemicals used to prevent & inhibit fires
5	Plastic and rubber	Components, reactants, or additives used in the manufacturing of rubbers or plastics
6	Pesticide ingredient	Insecticides, acaricides, herbicides, fungicides, rodenticides, and other biocides
7	Antimicrobial	Chemicals that prevent the growth of and/or destroy microorganisms
8	Biogenic compound	Naturally occurring or biologically derived chemicals such as phytoestrogens, flavonoids, monophenols, mycochemicals and phenolic acids
9	Industrial additive	Preservatives, antioxidants, and surfactants used as glue, plastic, rubber, paint, and wood products
10	Solvent	Chemicals used to dissolve other chemicals
11	Metal / metallurgy	Elements & chemicals used in the extraction, processing, or manufacturing of a metal or metal-containing product, including welding
12	By-product / intermediate / reactant	Chemicals used in the synthesis of other compounds and/or unwanted byproducts such as impurities and contaminants, including combustion byproducts
13	Medical / veterinary / research	Chemicals used in hospitals, medical supplies and equipment, in laboratories or as reagents, and pharmaceuticals
14	Metabolite / degradation product	Breakdown of chemicals

Sources: Information adopted and summarized from "Integrated Tisza River Basin Management Plan" www.icpdr.org.

Fortunately, although cyanide is highly toxic, it does not persist very long in the environment. In addition, large volumes of heavy metals were also released into the rivers. Unfortunately, the long history of environmental contamination of the rivers made it difficult to isolate the specific damage induced by the Baia-Mare incident[81].

Investigations of water and sediment at selected sampling points from a longitudinal profile in 2000 showed substantial heavy metal loads (e.g. Cd, Pb, Cu and Zn) in several sediments of Someş and Tisza rivers[81]. This enhanced metal content might have been bioaccumulated in benthic organisms during the following years[82]. We have summarized in Table 3 the concentration of different metals found in Tisza river and some important tributaries, which were analyzed using different analytical techniques.

Table 3: The principal pollutants of Tisza River and its tributaries.

No	Pollutant	Concentration	Found in	Technique	Reference
1	Arsenic	2.7 [μg L^{-1}]	Dissolved in Someş water	X-ray fluorescence spectrometry	[82]
		9.3 [g kg^{-1}] ^{d}	Tisza sediments		
		34.1 [g kg^{-1}] ^{d}	Someş sediments		
		7 – 148 [μg g^{-1}] ^{b}	Tisza sediments	X-ray analytical methods	[83]
		17 – 52 [μg g^{-1}] ^{c}	Someş sediments		
		8 – 26 [μg g^{-1}] ^{c}	Tur sediments		
		18 [mg kg^{-1}]	Tisza surface sediment	Inductively coupled plasma – mass spectrometry	[84]
		37 [mg kg^{-1}]	Someş surface sediment		
		54 [mg kg^{-1}]	Lăpuş surface sediment (0 – 96 km)		
		32 [mg kg^{-1}]	Lăpuş surface sediment (20 – 96 km)		
		77 & 99 [μg g^{-1}]	Someş (2000 & 2002) – biofilm	X-ray fluorescence	[85]
		18.3 & 31.8 [μg g^{-1}]	Tisza (2000 & 2002) – biofilm		
2	Cadmium	1.3 [mg kg^{-1}]	Tisza surface sediment	Inductively coupled plasma – mass spectrometry	[84]
		9 [mg kg^{-1}]	Someş surface sediment		
		21 [mg kg^{-1}]	Lăpuş surface sediment (0 – 96 km)		
		4 [mg kg^{-1}]	Lăpuş surface sediment (20 – 96 km)		
3	Copper	32-162 [mg kg^{-1}] ^{a}	Tisza sediments	Flame atomic absorption spectrometry	[86]
		42–1250 [μg g^{-1}] ^{b}	Tisza sediments	X-ray analytical methods	[83]
		87 – 189 [μg g^{-1}] ^{c}	Someş sediments		
		51 – 73 [μg g^{-1}] ^{c}	Tur sediments		
		1.3 [μg L^{-1}]	Dissolved in Tisza water	X-ray fluorescence spectrometry	[82]
		3.5 [μg L^{-1}]	Dissolved in Someş water		
		4.7 [μg L^{-1}]	Dissolved in Mureş water		
		16.3 [g kg^{-1}] ^{d}	Tisza sediments		
		95.8 [g kg^{-1}] ^{d}	Someş sediments		
		101 [g kg^{-1}] ^{d}	Mureş sediments		

No	Pollutant	Concentration	Found in	Technique	Reference
3	Copper	54 [mg kg^{-1}]	Tisza surface sediment	Inductively coupled plasma – mass spectrometry	[84]
		220 [mg kg^{-1}]	Someş surface sediment		
		4850 [mg kg^{-1}]	Lăpuş surface sediment (0 – 96 km)		
		240 [mg kg^{-1}]	Lăpuş surface sediment (20 – 96 km)		
		261 & 228 [μg g^{-1}]	Someş (2000 & 2002) – biofilm	X-ray fluorescence	[85]
		118 & 63 [μg g^{-1}]	Tisza (2000 & 2002) – biofilm		
4	Chromium	7 – 24 [mg kg^{-1}] [a]	Tisza sediments	Flame atomic absorption spectrometry	[86]
		70 – 157 [μg g^{-1}] [b]	Tisza sediments	X-ray analytical methods	[83]
		108 – 143 [μg g^{-1}] [c]	Someş sediments		
		59 – 137 [μg g^{-1}] [c]	Tur sediments		
		78 & 34.7 [μg g^{-1}]	Someş (2000 & 2002) – biofilm	X-ray fluorescence	[85]
		10.3 & 56 [μg g^{-1}]	Tisza (2000 & 2002) – biofilm		
5	Zinc	54 – 567 [mg kg^{-1}] [a]	Tisza sediments	Flame atomic absorption spectrometry	[86]
		133 – 3200 [μg g^{-1}] [b]	Tisza sediments	X-ray analytical methods	[83]
		397 – 1260 [μg g^{-1}] [c]	Someş sediments		
		1640 – 2500 [μg g^{-1}] [c]	Tur sediments		
		2.4 [μg L^{-1}]	Dissolved in Tisza water	X-ray fluorescence spectrometry	[82]
		9.1 [μg L^{-1}]	Dissolved in Someş water		
		5 [μg L^{-1}]	Dissolved in Mureş water		
		90.1 [g kg^{-1}] [d]	Tisza sediments		
		1270 [g kg^{-1}] [d]	Someş sediments		
		426 [g kg^{-1}] [d]	Mureş sediments		
		200 [mg kg^{-1}	Tisza surface sediment	Inductively coupled plasma–mass spectrometry	[84]
		1200 [mg kg^{-1}]	Someş surface sediment		
		3890 [mg kg^{-1}]	Lăpuş surface sediment (0 – 96 km)		
		770 [mg kg^{-1}]	Lăpuş surface sediment (20 – 96 km)		
		1.5 & 2.4 [μg g^{-1}]	Someş (2000 & 2002) – biofilm	X-ray fluorescence	[85]
		195 & 4 [μg g^{-1}]	Tisza (2000 & 2002) – biofilm		
6	Lead	11–123 [mg kg^{-1}] [a]	Tisza sediments	Flame atomic absorption spectrometry	[86]
		20 – 2100 [μg g^{-1}] [b]	Tisza sediments	X-ray analytical methods	[83]
		35 – 190 [μg g^{-1}] [c]	Someş sediments		
		33 – 53 [μg g^{-1}] [c]	Tur sediments		

No	Pollutant	Concentration	Found in	Technique	Reference
6	Lead	1.3 [μg L^{-1}]	Dissolved in Tisza water	X-ray fluorescence spectrometry	[82]
		3.9 [μg L^{-1}]	Dissolved in Someş water		
		0.5 [μg L^{-1}]	Dissolved in Mureş water		
		12.3 [g kg^{-1}] [d]	Tisza sediments		
		93.8 [g kg^{-1}] [d]	Someş sediments		
		74.6 [g kg^{-1}] [d]	Mureş sediments		
		38 [mg kg^{-1}]	Tisza surface sediment	Inductively coupled plasma–mass spectrometry	[84]
		97 [mg kg^{-1}]	Someş surface sediment		
		3630 [mg kg^{-1}]	Lăpuş surface sediment (0 – 96 km)		
		200 [mg kg^{-1}]	Lăpuş surface sediment (20 – 96 km)		
		68 & 72.6 [μg g^{-1}]	Someş (2000 & 2002) – biofilm	X-ray fluorescence	[85]
		10.1 & 46.9 [μg g^{-1}]	Tisza (2000 & 2002) – biofilm		
7	Nickel	17 – 55 [mg kg^{-1}] [a]	Tisza sediments	Flame atomic absorption spectrometry	[86]
		20 – 48 [μg g^{-1}] [b]	Tisza sediments	X-ray analytical methods	[83]
		19 – 41 [μg g^{-1}] [c]	Someş sediments		
		21 - 27 [μg g^{-1}] [c]	Tur sediments		
		3 [μg L^{-1}]	Dissolved in Tisza water	X-ray fluorescence spectrometry	[82]
		1.4 [μg L^{-1}]	Dissolved in Someş water		
		10.1 [μg L^{-1}]	Dissolved in Mureş water		
		32.3 [g kg^{-1}] [d]	Tisza sediments		
		22.7 [g kg^{-1}] [d]	Someş sediments		
		50.5 [g kg^{-1}] [d]	Mureş sediments		
		59 & 75.1 [μg g^{-1}]	Someş (2000 & 2002) – biofilm	X-ray fluorescence	[85]
		17.5&36.9 [μg g^{-1}]	Tisza (2000 & 2002) – biofilm		
8	PAHs	1.22 – 260.26 ng L^{-1}	Vișeu River	HPLC	[87]
		11.34 – 197.02 ngL^{-1}	Iza River		
		2.23 – 71.4 ng L^{-1}	Tisza River		

[a] Values measured in different points along the Tisza River, expressed in dry weight.
[b] Values measured between 2000 and 2003.
[c] Value measured between 2001 and 2003.
[d] 0–3 cm sediment layer in the rivers Someş, Tisza and Mureş in 2003.

Concluding discussions

The accumulation of heavy metals in aquatic ecosystems can lead to hazards on human and wildlife. Anthropogenic activities, particularly mining, have been greatly influencing the quality of Tisza waters, as well as the local and global geochemical cycles of heavy metals. Without any doubt, the pollution with heavy metals on Tisza River and its principal tributaries represent a problem which needs a stringent proper resolution. The principal heavy metals found in Tisza and its tributaries are discussed further[88].

Arsenic

Chronic human exposure to arsenic is associated with an increased risk of cancer. Although arsenic does not directly cause DNA damage or mutations, it is thought to act principally as a co-mutagen, co-carcinogen, and/or tumor promoter. Arsenic is present in high concentrations at many toxic waste sites containing compounds from industrial and mining practices. In addition, arsenic can accumulate in groundwater and well water from natural sources. Certain geological formations contain high levels of arsenic that can leach into groundwater and find their way into wells and other public water supplies[16].

Different researchers determined arsenic in Tisza river and its tributaries, Someş, Tur and Lăpuş, using X-ray fluorescence spectrometry and inductively coupled plasma – mass spectrometry of sediments and biofilm samples. The concentrations varied from 7 to 148 $\mu g\ g^{-1}$ in Tisza sediments in different periods of time (between 2000 and 2003) and between 18.3 and 31.8 $\mu g\ g^{-1}$ in biofilm samples. Very low concentration of dissolved arsenic (2.7 $\mu g\ L^{-1}$) was found in Someş, while between 17 and 52 $\mu g\ g^{-1}$ were found in sediment samples and 77 to 99 $\mu g\ g^{-1}$ in biofilm samples. In Tur river, the arsenic concentration was lower than in Someş, from 8 to 26 $\mu g\ g^{-1}$, while in Lăpuş sediments the concentrations reached values of 32 to 54 $\mu g\ g^{-1}$.[81-84] Unfortunately these values exceed the maximum allowable concentration (7.2 $\mu g\ L^{-1}$) of arsenic in surface waters, according to the Romanian government decision no. 1038 from 13/10/2010[89].

Cadmium

This is a pollutant associated with modern industrial processes, which can also be absorbed in significant quantities from cigarette smoke. It is known to have numerous undesirable effects on health of test animals and humans, targeting the kidneys, liver and vascular systems in particular. However, a wide spectrum of deleterious effects on the reproductive tissues and the developing embryo has also been described by Thompson *et al*; they concluded that in the testis, changes due to the disruption of the blood–testis barrier and oxidative stress have been occurred, with onset of widespread necrosis at higher dosage exposures[23].

Due to its extremely high toxicity, the maximum allowable concentration of cadmium is 0.2 $\mu g\ L^{-1}$.[89] Higher concentrations were found in Tisza sediments (1.3 $\mu g\ g^{-1}$), Someş sediments (9 $\mu g\ g^{-1}$) and Lăpuş sediments (between 4 and 21 $\mu g\ g^{-1}$). The analytical technique used was inductively coupled plasma – mass spectrometry[84].

Chromium

Chromium is considered an essential nutrient and a health hazard. This is possible because chromium exists in more than one oxidation state. Specifically, while Cr(VI) chromium is considered harmful even in small intake quantities, Cr(III) is considered essential for good health in moderate intake.[90] Health effects are categorized as: mutagenic, reproductive, hematological, cardiovascular, gastrointestinal, hepatic, renal, carcinogenic, respiratory and skin effects[90].

The maximum allowable concentration of chromium in surface waters is 2.5 μg L^{-1}.[89] In Tisza river, concentrations between 7 and 157 μg g^{-1} were found in sediments samples[83-86] and between 10.3 and 56 μg g^{-1} in biofilm samples[85]. The concentrations in sediments samples were comparable in the tributaries Someş (108–143 μg g^{-1}) and Tur (59–137 μg g^{-1})[83]. In Someş river, the concentration in biofilm samples were from 34.7 to 78 μg g^{-1} [84]. The analytical techniques used were flame atomic absorption spectrometry, X-ray analytical methods and biofilm samples were analyzed using X-ray fluorescence[83, 85, 86].

Copper

Copper, together with chromium and zinc, was not considered a "priority pollutant", but they were all found often in Tisza and its tributaries waters. Because it is known that the exposure to copper, chromium and zinc can cause health problem, and because they were found in large amounts in the studies[82-86], we decided to include the data in this review paper. Copper is a reddish metal that occurs naturally in rock, soil, water, sediment, and, at low levels, in air. Its average concentration in the earth's crust is about 50 parts copper per million parts soil (ppm). Copper also occurs naturally in all plants and animals. It is an essential element for all known living organisms including humans and other animals at low levels of intake. At much higher levels, toxic effects such as acne, allergies, hair loss, anemia, anxiety, chronic candida, depression, diabetes, infections, inflammation, insomnia, panic attacks, and premenstrual syndrome can occur[91].

Quantities between 16.3 μg g^{-1} and up to huge amount of 4850 μg g^{-1} (in March of 2000, after the accident from Baia Mare) were found in Tisza River and its tributaries: Someş, Tur, Mureş and Lăpuş (see Table 3 for details). The maximum allowable concentration for copper in water is 1.3 μg L^{-1} [89]. Relatively small amounts of copper dissolved (1.3 in Tisza, 3.5 in Someş and 4.7 in Mureş) were found[82]. For copper detection in Tisza and tributaries, the analytical techniques used were flame atomic absorption spectrometry, X-ray fluorescence spectrometry and inductively coupled plasma – mass spectrometry while the samples used were sediments, surface sediments and biofilm samples[82-86].

Lead

Lead and its organic compounds were classified as possible human carcinogens (group 2B), while its inorganic compounds are probable human carcinogens (group 2A). They have potential hepatotoxicity and antagonistic effects on the immune cells in rats, toxic effects on the heart and blood vessels in human populations and can initiate childhood neurotoxicity in humans[43-45]. The maximum allowable concentration in water of rivers is 7.2 μg L^{-1} [89].

In Tisza river and the tributaries (Someş, Lăpuş, Mureş and Tur), the researchers found different amounts of lead in sediments, surface sediments and biofilm samples using various analytical techniques: flame atomic absorption spectrometry, inductively coupled plasma – mass spectrometry and X-ray fluorescence spectrometry[82-86]. Dissolved lead was measured in water of Tisza, Someş and Mureş, but insignificant concentrations were found, which did not exceed the allowable concentration[82]. while the maximum concentration of 3630 μg g^{-1} has been detected in Lăpuş river immediately after the accident of Baia Mare occurred in March of 2000. Apart of that period, concentrations of several tens of μg g^{-1} were currently recorded in Tisza and the tributaries; in Table 3, all these concentrations values are given.

Nickel

Nickel is another heavy metal introduced on “The List of Priority Substances”. It was found that immunological and carcinogenic effects in humans can occur after a chronic exposure of nickel and some of its compounds. Nickel chloride can affect the redox equilibrium and stimulate apoptosis in oral epithelium cells, while cancer risk is related to less soluble oxidic and especially sulfidic nickel species. Nickel nanoparticles have a significant toxicity for human lung epithelial cells[49,50]. The maximum allowable concentration for nickel in river water is 20 μg L^{-1} [89].

Relatively low concentrations of nickel, up to dozens of μg g^{-1}, were found in sediments or in biofilm samples from Tisza and tributaries, while insignificant amounts of dissolved nickel were detected[82,83,85,86]. The analytical techniques used were flame atomic absorption spectrometry and X-ray analytical methods.

Zinc

Zinc is an essential nutrient in humans and animals that is necessary for the correct functioning of a large number of metalloenzymes. Zinc deficiency has been associated with dermatitis, anorexia, retardation increasing, poor wound healing, impaired reproductive capacity, impaired immune function and depressed mental function. Increased incidence of congenital malformations in infants has also been associated with zinc deficiency in the mothers[92]. Just as zinc deficiency has been associated with adverse effects in humans and animals, overexposures to zinc also have been associated with toxic effects such us: gastrointestinal, ocular, cardiovascular, pulmonary, hepatic, toxicity; nephrotoxicity, neurotoxicity, hepatotoxicity and hemotoxicity[92].

Using different analytical techniques (flame atomic absorption spectrometry, X-ray analytical methods, inductively coupled plasma–mass spectrometry), the researchers found in Tisza river and the tributaries large amounts of zinc, which exceeded by far the maximum allowable concentration of 100 μg L^{-1} (Table 3)[89].

Conclusions

In Tisza River Basin and the basins of its principal tributaries, human populations and economic development have significantly contributed to the current deterioration in water quality, including accumulation of heavy metals in the aquatic environment and sediments. Heavy metals are among the most harmful pollutants in aquatic ecosystems under natural conditions.

Acknowledgements

This work was supported by NATO Project SfP 984440 *„A model to predict and prevent possible disastrous effects of toxic pollution in the Tisza River"*. For Dorin-Daniel Costea, financial support was provided from the POSDRU /159/1.5/S/133391 Project.

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