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HEAVY-METAL INVESTIGATION INTO THE WATER- AND BOTTOM-SEDIMENT SAMPLES OF THE RIVER TISZA

KLÁRA FÜGEDI and E. FEKETE
Water Conservancy of the Lower Tisza Region
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Abstract

The authors determined in Hungary, for the first time, the heavy-metal content of the water and silt of the Tisza along the entire longitudinal section of the river.

Introduction

Among the environment-conservation problems of our days the heavy metals polluting the surface waters come more and more into question. These matters, foreign from the surroundings, mean a great danger because they dont't become harmless in a natural way, inhibit the decomposition of the organic polluting materials, and even they can poison the vegetable and animal kingdom of the living water, as well (KERTAI 1976).

The heavy-metal loading of natural waters is composed of two fundamental factors: the background pollution of geological origin and that of industry and agriculture, which is "foreign from nature". The knowledge of background pollution would be important for investigating into the possible extraordinary pollution, its establishment is, however, a difficult task.

The biological response given to the metals, which got into the water environment, is determined by whether there is present in the water some legandum responding to the water and whether the metal is present in a solution or in the form of colloidal particles.

According to Mancy, the existence of the following forms in water is to be taken into cosideration (MANCY 1972):

Soluble forms:

(a) free hydrated ions
(b) metal complexes formed with inorganic ($^{=}OH$, $CO_3^{2=}$, etc.) and organic ligands (amines, proteins, humic acids, etc.)

Insoluble particles:

(a) aggregates of colloidal metal complexes or hydrated metal oxides
(b) metal complexes, adsorbed on suspended particles.

Both outward forms of heavy metals may be observed both in water phase and in the bottom-sediments of surface waters.

The origin of the heavy-metal pollution, the way of its getting into the living water can be extremely multifarious as depending on the kind of heavy metal.

The main sources of the mercury pollution are: the chloroalkali electrolysis, paper-manufacturing, caustics.

Cadmium comes mainly from galvanization, chemical catalytic processes, metallurgical technologies.

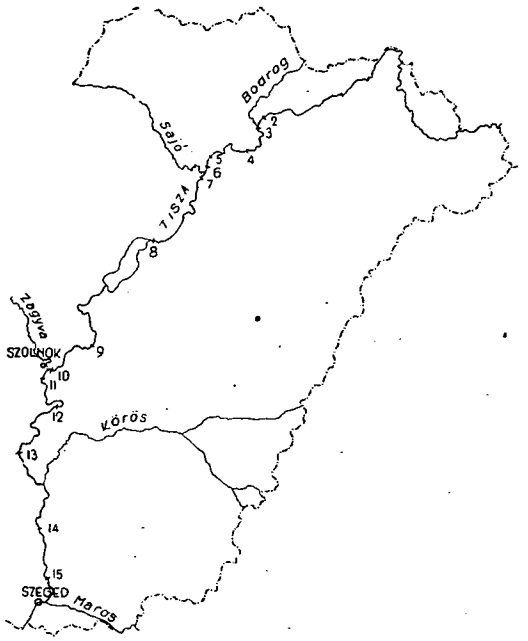

Fig. 1. Numbers used: 1=the Tisza at Dombrád 2=the Tisza above the mouth of the Bodrog 3=the Tisza at Tokaj 4=the Tisza at Tiszalök 5=the Tisza at riv. km 446 6=the Tisza at Leninváros, above the mouth of the Sajó 7=the Tisza at Leninváros, below the mouth of the Sajó 8=the Tisza at riv. km 399 9=the Tisza at Nagykörü 10=the Tisza at Szolnok, above the mouth of the Zagyva 11=the Tisza at Szolnok, below the mouth of the Zagyva 12=the Tisza at Martfü 13=the Tisza at riv. km 268 14=the Tisza at riv. km 213 15=the Tisza at riv. km 199.

A large share of the lead pollution originates from the knock reducers used in petrol. The corrosion of paints, lead-containing things also play some role.

The primary sources of chrome are: metallurgy and galvanic industry. Zinc comes from metallurgy, galvanic and chemical industries, corrosion of structural matters and various metal things.

The main causes of copper pollution are: corrosion of copper-containing things, galvanizing, dye-works, the use of copper-containing pesticides.

The permissible concentration values of the most important metal polluters are summarized in Table 1 (P. LITHERÁTY 1977).

In our investigations, from among the above-mentioned heavy-metals, the investigation of the following was carried out: mercury, lead, cadmium, total chrome, copper, and zink.

Table 1. *The concentrations of the most important metal-polluters, permissible in surface waters, in mg/l*

Metal pollution	COMECON recommendation, 1963 Class of water quality		
	I	II	III
Toxic:			
mercury	0.005	0.01	0.02
cadmium	0.005	0.03	0.2
lead	0.1	0.1	0.1
chrome (Cr^{3+})	0.5	0.5	0.5
(Cr^{6+})	0.05	0.1	0.1
copper	0.01	0.1	3.0
Organoleptic:			
iron	0.5	1.0	1.5
manganese	0.1	0.3	0.8
zink	0.01	0.1	0.1

Methodological questions

1. Sampling

The processed water and silt samples were taken by young people, taking part in the Tisza-excursion, organized in 1978 by the fourth year undergraduates of the Attila József University, specialized in biology- chemistry. The sampling sites were marked out on the basis of a previous discussion, in some definite places of the longitudinal section of the Tisza, above, resp. below the characteristic inflows (Bodrog, Sajó, Zagyva, etc.). In this way, from the streamline of the river 15 water samples and from the riverside zone 15 sediment samples were carried into our laboratory.

The water samples were collected in 1-litre plastic bottles, without filtering. Previously, preserving matters (EDTA, cc. HNO_3) were put in the bottles.

The silt samples were similarly taken in 1-litre plastic bottles, in the course of sampling. Here was no preservation added.

2. Preparing, processing

Preparing, processing of the water samples

As in the Hungarian surface waters the concentration of the most heavy metals does not achieve the minimum concentration, which can be determined with the applied atomabsorption spectrophotometry, samples were enriched beforehand. Simultaneously, we strove to remove from the water the possibly disturbing components, mainly organic matters. The degree of enrichment was chosen so that even the minimum concentrations, observed by the home authors in our surface waters, can be measured (LITHERÁTY 1977, BOZSAI 1978).

From the preserved, homogenized water samples exactly 500 ml volume was taken out for investigation. To this water quantity 5 ml concentrated sulphuric acid and 25 ml nitric acid were added, then it was evaporated till the appearance of the sulphuric-acid exhalation. Was the dry-evaporated rest not transparent, then a further 5 ml concentrated nitric acid was added and dry evaporation carried out again. The dry-evaporated samples were taken up with a 1-ml 10 p.c. hydrochloric solution, then their volume was completed exactly to 100 ml in a volumetric flask. In this way, from the original water samples a fivefold enrichment was made.

Preparing, processing of sediment samples

The sediment samples carried in were carefully homogenized, then a part of them were carefully dried in an exsiccator, at 105 °C, and pulverized in a porcelain mortar. From the pulverized, repeatedly homogenized sample 5 g was exactly weighed in an assay balance and put in a 100 ml polished round-bottomed flask, and then 20 ml concentrated nitiric acid added. The flask was connected with a reflowing cooling apparatus and the matter boiled for 15 minutes. It was made grow cool for a few minutes, then 10 ml 30 p.c. hydrogen peroxide was added through the cooling apparatus. The matter was repeatedly boiled again for 15 min., then after being cooled, it was filtrated through a previously weighed G4 glass filter into a 100 ml volumetric flask. After leaching the filter with distilled water, the filtrate was poured into the volumetric flask till the mark. The determination of heavy metals was carried out from the filtrate. The residue was submitted to further heating, in order to determine the so-called correlation basis (CB: LITHERÁTY 1975).

This correlation basis is the fraction of bottom-sediment that, in addition to the calcium, magnesium salts of natural origin, contains the polluting matters coming from human activity in an enriched state, namely: the corresponding salts of heavy metals, as well as the organic matters.

3. Analytical methods

The determinations were carried out with an atomabsorption spectrophotometer of Spektromom 190A—type. The calibration curves of the single metals were recorded so that, after taking into consideration the enrichment, on the basis of the calibration curve, one-tenth of the limiting values, contained in Table 1, should still be demonstrable with the technique of atomization in flame, as well.

In case of cadmium, lead, zinc, chrome, and copper air flame was used, for determining mercury, we used the so-called cold-steam atomization (MOM collection of antecedents, 1978).

The analytical data of measurements are contained in Table 2. (PRICE 1977).

Table 2. *Analytical data of calibration measurements and sample measurements*

Metal	Wavelength (nm)	Sensitivity (μg/ml)	Limit of demonstration (μg/ml)	Manner of atomization
Hg	253,7	—	0.5	cold steam
Cd	228.8	0.01	0.002	air-acetylene flame
Pb	283.3	0.2	0.03	air-acetylene flame
Cr	357.9	0.05	0.008	air-acetylene flame
Zn	213.9	0.01	0.001	air-acetylene flame
Cu	324.8	0.04	0.002	air-acetylene flame

Results of investigations

The heavy-metal content of water samples is displayed in Table 3, the results of sediment samples in Table 4.

Table 3. *The heavy-metal content of water samples, originating from the longitudinal section of the Tisza, at the single sampling sites*

Sampling site	Heavy-metal content, µg/l					
	Hg	Cd	Pb	Cr	Zn	Cu
1. Dombrád	0.50	7.6	7.2	6.8	288	17.7
2. Above the Bodrog	2.05	2.5	0.5	4.2	100	3.9
3. Tokaj	0.50	3.3	2.4	3.4	42	4.9
4. Tiszalök	1.00	2.8	1.9	3.0	96	3.3
5. riv. km 446	0.50	3.6	2.8	3.4	29	3.9
6. Leninváros, above the Sajó	0.50	2.2	1.7	3.0	40	5.6
7. Leninváros below the Sajó	0.50	3.8	3.3	4.2	34	5.9
8. riv, km 399	0.50	2.2	3.8	3.0	1080	17.4
9. Nagykörü	0.50	1.0	1.0	1.7	29	3.9
10. Szolnok, above the Zagyva	0.80	1.1	1.2	2.2	29	3.9
11. Szolnok, below the Zagyva	1.00	2.6	2.8	4.7	336	5.2
12. Martfü	0.70	8.2	3.5	3.0	1000	7.2
13. riv. km 268	0.50	1.6	1.4	2.2	24	2.9
14. riv. km 213	0.50	3.3	3.8	3.0	78	3.6
15. riv. km 199	0.70	3.8	3.1	2.6	35	4.3
Sajó	0.50	3.3	2.4	4.2	29	4.6

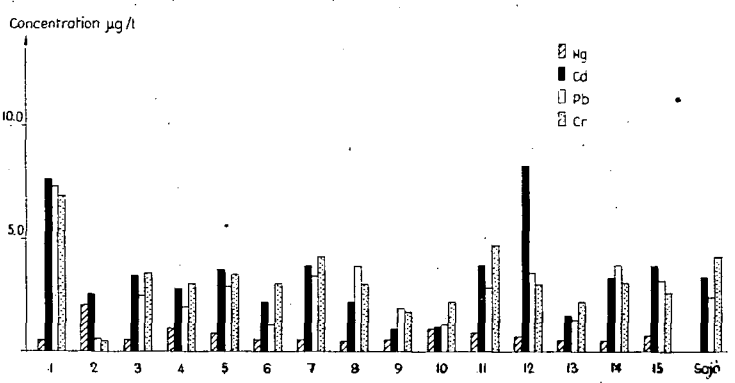

Fig. 2. Hg, Cd, Pb, Cr content of the water of the Tisza

Key to the signs used: Hg, Cd, Pb, Cr

1. Dombrád, 2. above the Bodrog, 3. Tokaj, 4. Tiszalök, 5. riv. km 446, 6. Leninváros, above the Sajó, 7. Leninváros, below the Sajó, 8. riv. km 399, 9. Nagykörü, 10. Szolnok, above the Zagyva, 11. Szolnok, below the Zagyva, 12. Martfú, 13. riv. km 268, 14. riv. km 213, 15. riv. km 199, Sajó, Sampling site.

Taking into consideration that there was only one sampling in the longitudinal section, it is not possible to draw any consequences from these data concerning the permanent pollution.

We may, however, take note of a number of tendencies:

1) The effect of the tributaries carrying the polluting matters of the industrialized area — Bodrog, Sajó, Zagyva — is obvious even from a single measurement datum.

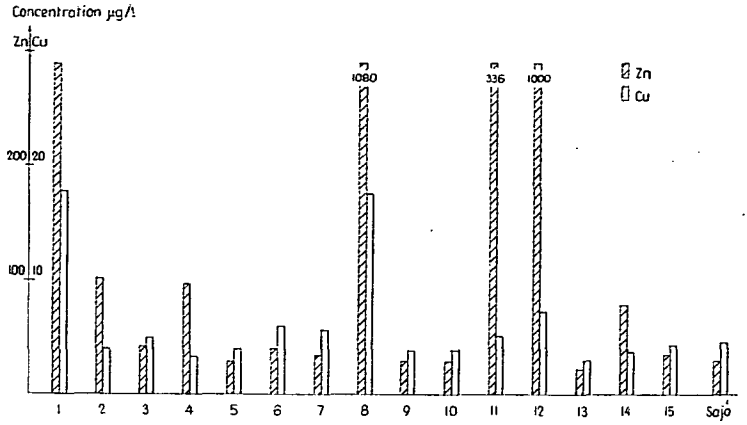

Fig. 3. Zn and Cu content of the water of the Tisza

Key to the signs used: Zn, Cu

1. Dombrád, 2. above the Bodrog, 3. Tokaj, 4. Tiszalök, 5. riv. km 446, 6. Leninváros, above the Sajó, 7. Leninváros, below the Sajó, 8. riv. km 399, 9. Nagykörü, 10. Szolnok, above the Zagyva, 11. Szolnok, below the Zagyva, 12. Martfü, 13. riv. km 268, 14. riv. km 213, 15. riv. km 199, Sajó, Sampling site.

Table 4. *The heavy-metal content of the bottom-sediment samples, originating from the longitudinal section of the Tisza, at the single sampling sites*

Sampling site	Heavy-metal content, mg/kg CB					
	Hg	Cd	Pb	Cr	Zn	Cu
1. Dombrád	0.98	0.90	0.82	4.8	67.2	100.4
2. Above the Bodrog	1.53	1.53	2.35	5.4	189.4	305.5
3. Tokaj	2.87	2.08	2.57	6.7	176.0	315.3
4. Tiszalök	2.42	2.50	3.56	10.0	262.0	375.0
5. riv. km 446	1.76	1.05	2.46	4.9	109.3	131.8
6. Leninváros, above the Sajó	1.28	1.47	1.98	3.2	114.1	179.5
7. Leninváros, below the Sajó	4.90	1.93	3.15	5.5	164.0	235.2
8. riv. km 399	0.14	1.89	2.18	2.6	154.0	259.7
9. Nagykörü	0.53	2.35	3.18	3.6	168.7	299.5
10. Szolnok, above the Zagyva	1.71	2.75	2.08	9.0	150.0	280.0
11. Szolnok, below the Zagyva	2.14	3.08	3.50	16.3	202.8	357.1
12. Martfü	1.42	2.65	2.65	5.5	165.0	305.4
13. riv. km 268	2.50	2.65	3.22	1.8	190.3	260.8
14. riv. km 213	4.80	1.18	1.48	1.6	82.6	116.6
15. riv. km 199	2.85	2.57	2.85	2.1	145.2	262.4

2) There are certain river reaches, which are polluted with heavy metals in a more increased degree. A place like this is the vicinity of Dombrád, Martfü. In these places the concentration of nearly every heavy metal is higher than in other reaches of the river.

3) The polluting effect of the Dongér in our region — riv. km 213 — can also be measured to a certain extent.

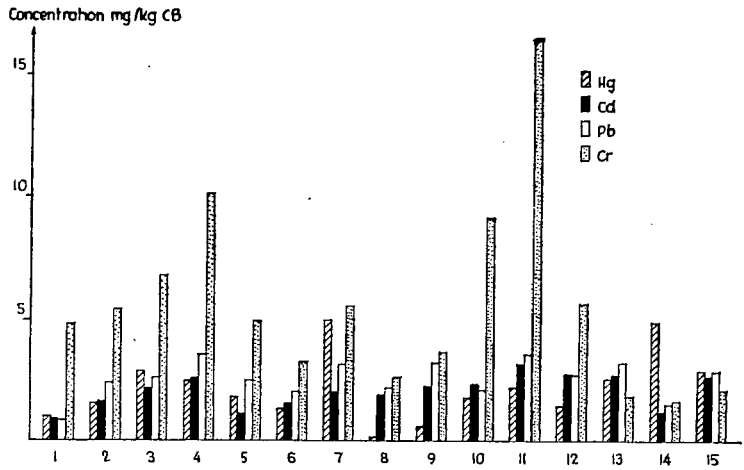

Fig. 4. Hg, Cd, Pb, Cr content of the bottom-sediment samples of the Tisza

Key to the signs used: Hg, Cd, Pb, Cr

1. Dombrád, 2. above the Bodrog, 3. Tokaj, 4. Tiszalök, 5. riv. km 446, 6. Leninváros, above the Sajó, 7. Leninváros, below the Sajó, 8. riv. km 399, 9. Nagykörü, 10. Szolnok, above the Zagyva, 11. Szolnok, below the Zagyva, 12. Martfü, 13. riv. km 268, 14. riv. km 213, 15 riv. km 199, Sajó, Sampling site.

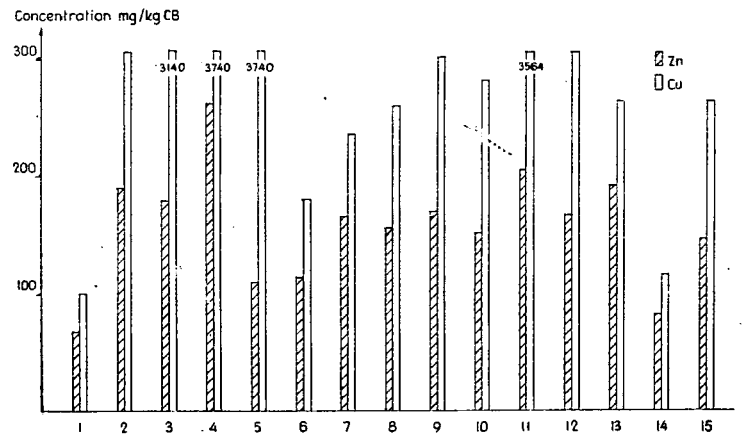

Fig. 5. Zn and Cu content of the bottom-sediment samples of the Tisza

Key to the signs used: Zn, Cu

1. Dombrád, 2. above the Bodrog, 3. Tokaj, 4. Tiszalök, 5. riv. km 446, 6. Leninváros, above the Sajó, 7. Leninváros, below the Sajó, 8. riv. km 399, 9. Nagykörü, 10. Szolnok, above the Zagyva 11. Szolnok, below the Zagyva, 12. Martfü, 13. riv. km 268, 14. riv. km 213, 15. riv. km 199, Sajó, Sampling site.

As the tendencies are known, it is very important to repeat this task in the future by means of manifold samplings and to make a survey in our area of the polluting foci of heavy metals, water-courses, having an effect on the Tisza.

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A Tisza folyó víz- és fenéküledék mintáinak nehézfém vizsgálata

FÜGEDI KLÁRA és FEKETE E.
Alsó-Tiszavidéki Vízügyi Igazgatóság Szeged

Kivonat

A szerzők Magyarországon először határozták meg a Tisza vizének és iszapjának nehézfém tartalmát, a folyó teljes hossz-szelvénye mentén. Megállapításaik szerint vannak a folyónak olyan szakaszai, melyek fokozottabb mértékben szennyezettek nehézfémekkel. Ilyen pl. Dombrád és Martfű térsége. Ezeken a helyeken majd minden nehézfém koncentrációja magasabb, mint más folyószakaszokon. Az iparvidékek szennyező anyagait szállító mellékfolyások, mint a Bodrog, Sajó, Zagyva hatása nyilvánvaló.

АНАЛИЗ ОБРАЗЦОВ ПРОТОЧНОЙ ВОДЫ И ОТЛОЖЕНИЙ ДНА Р. ТИСЫ НА СОДЕРЖАНИЕ ТЯЖЁЛЫХ МЕТАЛЛОВ

К. Фюгеди—Е. Фекете
Управление водного хозяйства Нижне-тисайских районов

Резюме

Авторы впервые производили определение содержания тяжёлых металлов в воде и иле реки Тисы на протяжении всей длины реки. Ими установлено, что река имеет участки, отличающиеся значительной загрязнённостью тяжёлыми металлами. Таковы, например, пространства Домбрад и Мартфю. На этих участках наблюдается повышенная по сравнению с другими участками реки концентрация почти всех тяжёлых металлов. Здесь очевидно влияние таких приточных вод, как Бодрог, Шайо и Задьва, несущих загрязняющие материалы промышленных районов.

Ispitivanje teških metala u uzorcima vode i mulja reke Tise

Fügedi Klára i Fekete E.
Vodoprivredna uprava donjeg područja Tise Szeged

Abstrakt

Sadržaj teških metala uzdužnog profila vode i mulja Tise prvi put su odredjivali autori u Madjarskoj. Prema dobijenim rezultatima autori su utvrdili da reka ima deonice koje su znatnije zagadjene teškim metalima. Takva su područja na pr. Dombrád-a i Martfü-a. Na navedenim područjima je koncentracija skoro svih teških metala veća u odnosu na druge deonice reke. Očigledan je uticaj pritoka kao što su Bodrog, Sajó, Zagyva koje donose industrijske otpadne vode.