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STUDY ON THE HEAVY METALS HAVING EFFECT ON THE WATER BIOCENOSES IN THE BACKWATERS AT ALPÁR AND LAKITELEK

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Abstract

The heavy metals having effect on the water biocenosis were determined monthly during the course of 1982, in the backwaters of Alpár and Lakitelek. The studies involved the determination of the copper-, cadmium-, zinc-, chromium- and mercury-contents in the water. Apart from studying the heavy metals, the organic matter-content in the backwaters was also determined and the development of the ammonium- and nitrateconcentrations was followe a with attention. The pH of the water as well as the sodium- and potassium-contents were determined joint with the studies of the heavy metals. Correlations were observable between the zinc- and copper-contents and the amount of organisms in the waters. It could be determined that the two backwaters have significant mercury-content referring to external pollution.

Introduction

During the past three decades the rapid development of technology called for the increase of the exploitation, processing and utilization of the various heavy metals and this simultaneously meant the concentrated return of the heavy metals into our environment.

Despite the fact that the amount in question is relatively low, the reaction of the environment to the heavy metals appears in an increased degree in many cases. These substances cannot be decomposed, in many occasions they reappear in the environment, incorporated in the aliment-chain, possibly in technical reutilization.

It is also known since several decades that certain heavy metals are necessary for the living world in small amounts. There are also such heavy metals besides those needed for vital processes, the lack of which is not followed by consequences. The heavy metals extraneous for the living organism are definitely toxic (LITERÁTHY 1982).

In general, the various specifications mention the importance of 19 heavy metals in the human environment. From these, nine — boron, zinc, cobalt, chromium, manganese, molybdenum, tin, copper and iron — can be listed among the essential elements. Arsenic, beryllium, silver, mercury, cadmium and lead are explicitly toxic heavy metals (National Research Council 1977).

The heavy metals occurring in surface waters may be present in various forms in the waters and the toxic effects of these forms also vary.

The decomposition and equillibrium with organic matter production (photosynthesis) of the — firstly organic — contamination substances entering into the water is the condition of healthy water life. The heavy metals entering the water may hinder both processes, which may lead to the disintegration of the equillibrium or to the decay of the complete water organisms.

The various forms of heavy metals present in the water may undergo transformation, through which a previously less toxic form might become strongly toxic. Therefore, when studying heavy metals, the chemical parameters influencing the afore-mentioned forms must be taken into account in every case (CAMBLE—SCHNITZER 1973, PICKERING 1980, STUMM—MORGAN 1970).

During the course of our studies the essential heavy metals (copper, zinc, iron, manganese) were divided into a separate group, as were the toxic ones, too (mercury, cadmium, chromium).

Copper is the constituent of the enzymes conducting the important physiological functions. Certain algal species are extremely sensitive against copper, moreover, even a low concentration of copper proves to be toxic in the case of the Spirogyra species (LITERÁTHY 1982, PÉTERFI 1977).

Zinc is an essential element of low toxicity, playing an extremely important role in photosynthesis and respiration. The equillibrium concentration of the bottom sediment and water is highly sensitive to the change in pH.

Iron has an important role in the structure of the respiratory enzymes, the nitrogenase enzymes participating in the photosynthesis and catalyzing the binding of ferrodoxin and the molecular nitrogen (PÉTERFI 1977).

Manganese is of importance regarding the functioning of the oxidases. Its hydroxide, with the binding of other toxic heavy metals, displays significant effect.

Mercury is a typically non-essential element. Due to its strong toxic effect it has become general as germicidal and fungicidal agent in medicine and agriculture. The

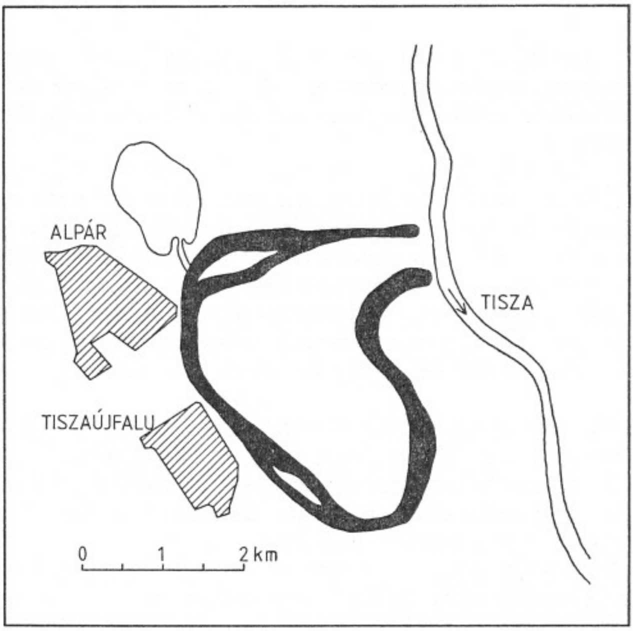

Fig. 1. The backwater at Alpár.

various kinds of mercury compounds firstly accumulate with surface absorption on the algae and other water plants. Fish take up the mercury compounds directly through the alimental chain, at the same time, the transmission of the already bound compounds is very slow (JERNELÖV 1973).

Cadmium occurs in the natural waters with a value of a few mg/e, generally in the company of other toxic material. Cadmium inhibits the kidney and liver functions in the case of the living beings of higher order and also causes the demineralization of the osseous system (KOWAL 1979).

Chromium is necessary in minimal amount for the living organisms. The biological activity is stricted to the trivalent form of chromium, at the same time, the hexavalent chromiumcompounds are of strongly toxic effect. The tri- and hexavalent forms are harmful to fish in nearly similar concentrations (PICKERING 1966).

In the past year the Water Quality Protection Department of the Water Conservancy Directorate at the Lower Tisza Region has turned particular attention to studies on the backwaters along the Tisza river. Contributing to the research activities of the Tisza Research Committee, the Department has monthly studied the chemical parameters — among them also the occurrence of heavy metals — of the backwaters at Alpár and Lakitelek.

The Alpár backwater (Fig. 1) is situated East from the village Tiszaalpár in the length of about 11,3 km. Its average width is 130 m. It is protected from the overflow

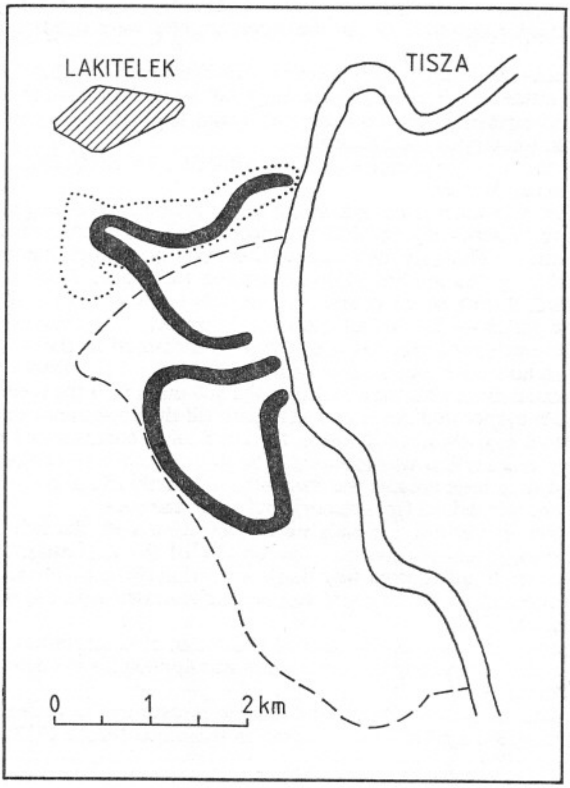

Fig. 2. The backwater at Lakitelek.

of the Tisza by a Summer dam, which provided protection earlier in the case of low and medium water levels. In the meantime, the dam has been heightened, thus no Tisza water enters the backwater even in the case of the moderately high water level of the Tisza river. The filling up of the dead channel is partly accomplished from the Tisza water, when it is at high level, and partly from inland water, as apart from its direct watertank, it can also be filled from the channel at Alpár—Nyárlőrinc. The dead channel is utilized for extensive fishing and extraction for watering.

The backwater at Lakitelek (Fig. 2) is located East from Lakitelek. Its length is 10,5 km, and average width 100 m. Here also a Summer dam protects it from the small and medium floods of the Tisza river. The refilling of the backwater is also possible from the moderate inundations through a lock, apart from the great waters of the Tisza. The water is used for extensive fishing and watering.

Materials and Methods

During the course of our studies, we wished to examine the seasonal changes of the backwaters water quality, with special regard to the heavy metals. For this purpose, water samples were taken ance monthly from the free water surfaces representing the water of the backwaters.

To determine the chemical oxygen demand, the samples were conserved with vitriol in an omount of 5 mg/l. The samples serving for the determination of the ammonium- and nitrate content were stored in cold and these components were determined within 24 hours from the time of sampling. For the determination of the heavy metals the samples were collected in polyethylene flasks, to which 5 ml of concentrated nitric acid and a few crystals of EDTA were added for the purpose of conservation. These samples were processed within 5 days in the laboratory (Batley 1977). The ammonium-ion- and nitrateconcentrations of the water samples were determined with spectrophotometry.

The organic matter-loading of the waters was characterized by the values of the chemical oxygen demand. The latter was determined in acidic medium with potassium-dichromate.

The sodium- and potassium-concentrations essential from the viewpoint of water life were measured by flame photometry in the backwaters.

The pH values of the water samples were determined with electrochemical methods using a Radelkis pH-measuring apparatus.

The above studies were carried out according to the methods recommended in the publication "COMECON Uniform Water-Studying Methods; Second Edition, Budapest, 1975".

In the surface waters of Hungary the concentration of the heavy metals does not reach the lowest concentrations definable by the applied atom absorption technique. Therefore, the samples were previously concentrated, during which course attempt was made to extract the possible disturbing components from the water — first of all the organic matter. The degree of concentration was selected so that the lowest concentrations could also be measured in the water, which have been observed by Hungarian authors in our surface waters (Literáthy 1977, Bozsai 1978). 5 ml of vitriol and 25 ml of concentrated nitric acid were added to the 500 ml part of the conserved and homogenized water samples, then evaporated down on water bath till the appearance of sulphuric acid fume. If the residue evaporated dry was not colourless, further 5 ml of concentrated nitric acid was added to it and the drying by evaporation was repeated. The dried samples were raised with 1 ml of 10% hydrochloric acid, and then their volume was amplified to exactly 25 ml in volumetric flask. In such way, 20-fold enrichment was gained from the original water samples.

The concentrations of the heavy metals were determined with the help of Spektromom 190 A-type atomic absorption spectrophotometer. The uptake of the calibration curves regarding the various metals was accomplished in such way that considering the enrichment, the tenth of the end values recommended for surface waters could still be demonstrated with the help of flame-atomization technique (Literáthy 1977).

Acetylene-air flame was used in the case of cadmium, zinc, chromium, manganese, copper and iron; and the so-called cold vaporous atomization was applied for the determination of mercury (*Hungarian Optical Works* 1978).

The analytical data of the calibration and sample measurings were determined on the basis of the literature regarding the applied atom absorption technique (Price 1977).

Results and discussion

1. Figure 3. shows the organic matter loading of the water at the Alpár backwater. It could be determined that the organic matter content of the water was practically the same, with the exception of a high value at early summer and autumn. The ammonia — which is mostly the representative of fresh contamination in the case of surface waters — appeared in relatively constant concentration in the backwater in the Spring and Summer months, and its amount increased in the winter months. The tendency was similar in the case of nitrate. Apart from this, higher nitrateconcentrations were measured also in the months of March and April. It can be concluded from these that the effect of the excessive nutrient solutions washed in from the agricultural areas in the environs of the backwater appeared in the Winter and Spring months (Fig. 4).

Figure 5. demonstrates the changes in the sodium- and potassium-contents of the water. Here, too, the aforementioned tendency prevailed, in so far as the amount of potassium increased in the Winter months. In the case of sodium, there was a Summer (June, July) and an Autumn-Winter maximum, respectively.

The concentrations of the various heavy metals measured in the bottom sediment and the water were in equillibrium with each other (LITERÁTHY 1982).

Figure 6. demonstrates the development of the essential heavy metal concentrations — copper, zinc, iron, and manganese — in the Alpár backwater.

The Content copper showed interesting seasonal change. Increased values were observed in April, and expressedly high values were demonstrable in July—August. It has been mentioned in the fore-goings that the *Spirogyra* algal species are sensitive against copper. In the backwater, *Spirogyra* algae were detected in the spring months, however, the species disappeared from the water at the time of the extremely high copper-concentration in July—August. Studying the development of the zinc-content, it can be determined that the maximal concentrations were measured between the

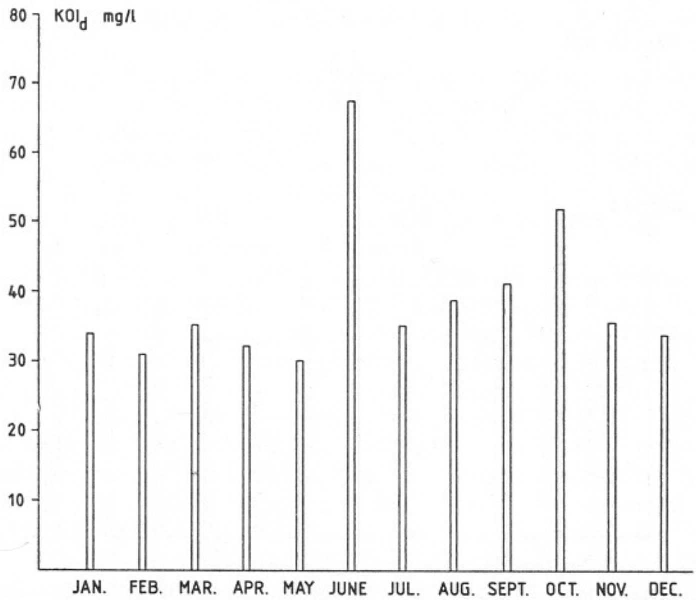

Fig. 3. Organic matter loading of the Alpár backwater on the basis of CODd.

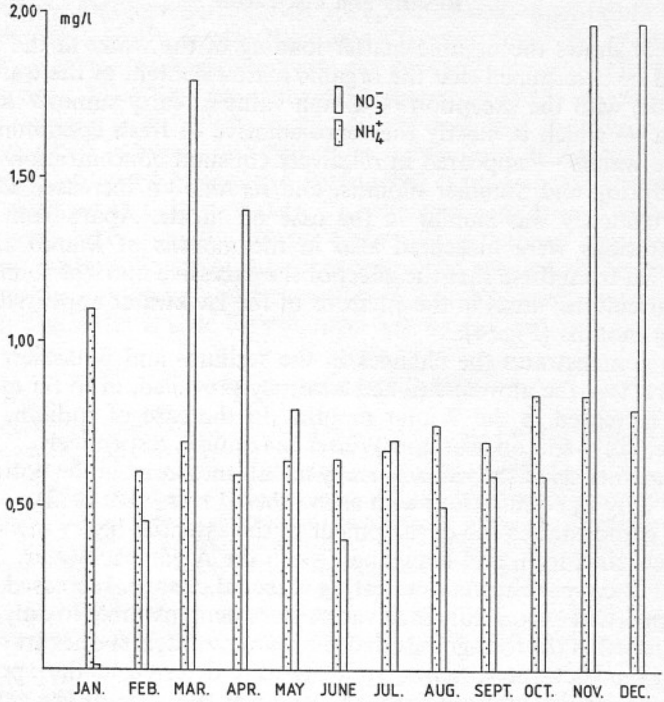

Fig. 4. Changes of ammonia- and nitrate-concentrations in the Alpár backwater.

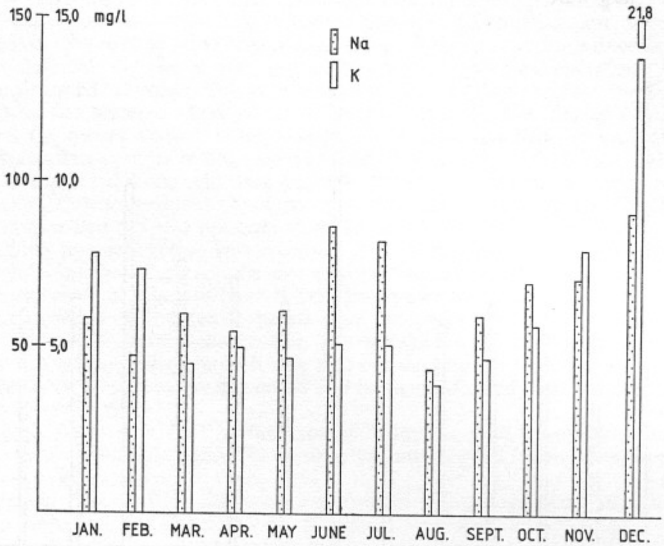

Fig. 5. Seasonal changes of the sodium- and potassium-contents in the Alpár backwater.

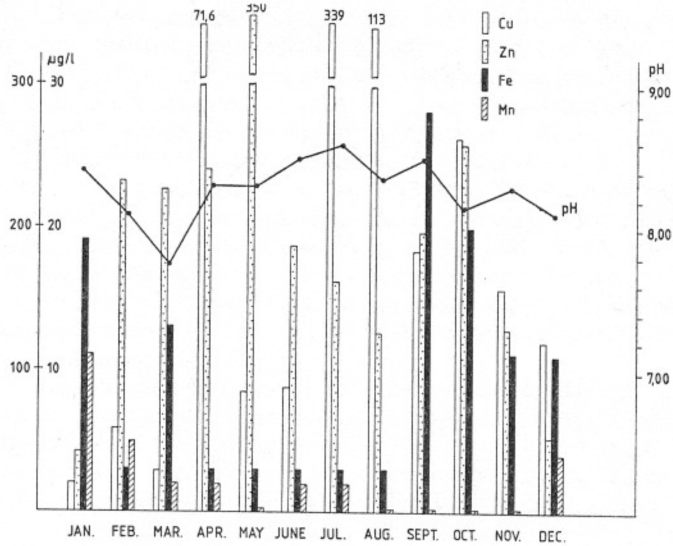

Fig. 6. Changes in the concentrations of the essential heavy metals in the Alpár backwater.

pH 8,2—8,3 values of the water. Both the lower and higher pH values led to the decrease in zinc-content. The prominent zinc-concentration measured in May allows to draw an interesting conclusion. On the basis of the pH value of the water, this should be between the values of 200—250 mg/l. At the same time, it was found that close to 25% of the algae present in the water (2,5 million from 11 million individuals per liter) was the *Chlorella* species, a type of alga markedly fond of zinc; incorporating large quantities of zinc in its organism. According to our opinion the increase in zinc-concentration and the increase in the amount of the *Chlorella* can be brought into correlation.

Higher iron-concentrations were observable in the autumn and winter months, than in the other periods of the year. In January and October practically identical iron-contents were registered (values of 190 and 200 mg/l, respectively), at the same time the saprobity indexes calculated for the water biology qualification were 1,81 and 1,84, resp. Similar relationship could be demonstrated between the months of March and December. It could be concluded from these data that the organisms fond of iron increased in the mentioned periods.

In the Alpár backwater the concentration of manganese decreased to zero value in the spring and autumn months. Maximal values were measured in winter. No relationship similar to those mentioned above was experienced. The concentrations of the expressedly toxic heavy metals — mercury, cadmium, chromium — are shown on Figure 7.

A minimal amount of mercury-content was observed in the first months of the year. In the months of March, April, May and June, however, the mercury-concentration increased by orders. This could be explained by the fact that the Spring inland waters from the surrounding agricultural fields presumably exported a significant amount of mercury to the backwater, which remained in dissolved condition throughout a longer period. Since this relatively high concentration was detectable for a rather short period, its chronic effect on the water organisme could not be demonstrated.

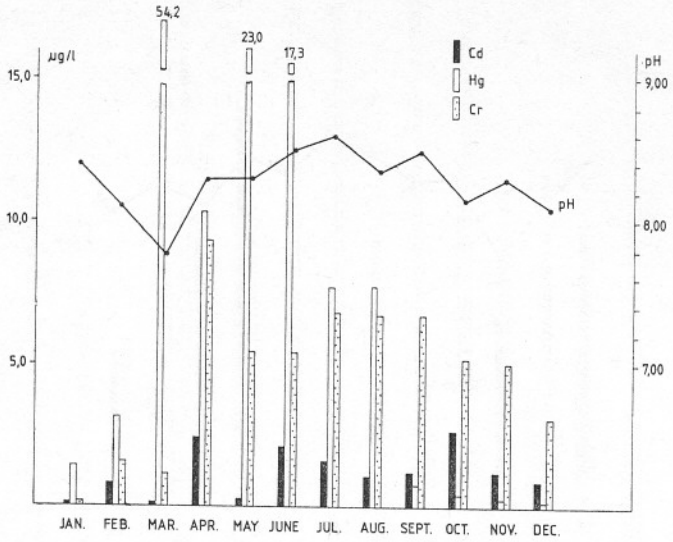

Fig. 7. Changes in the concentrations of three toxic heavy metals — mercury, cadmium, chromium — in the Alpár backwater.

The cadmium-content of the water did not refer to any kind of contamination. The water practically contained this heavy metal in an amount equivalent to the natural cadmiumcontent of surface waters.

The development of the chromium-concentration can also be seen on this figure. It is observable that presumably as the consequence of the sudden change in

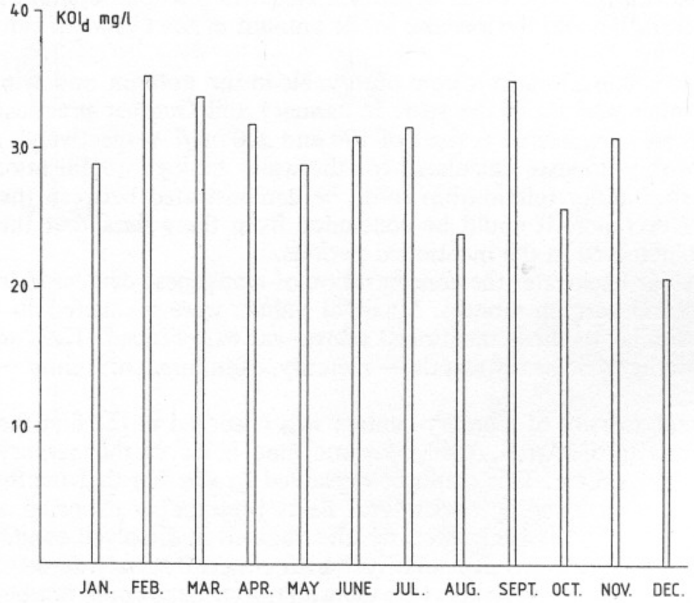

Fig. 8. Organic matter loading of the Lakitelek backwater on the basis of CODd.

pH, the chromium compounds accumulated in the bottom-sediment became mobilized, since their amount increased in the backwater. A balanced condition set in virtually with the settling of the pH-value. The chromium-concentration decreased with that of the pH in the autumn months. Due to the fact that there was an increase in the solubility of the trivalent chromium compounds with the decrease of the pH (PAYNE 1975), it may well be assumed on the basis of the fore-goings that the majority of the total chromium measured by us was present in the form of hexavalent chromium. Studies are in progress regarding the differentiation of these compounds.

2. Samplings were achieved also monthly from the backwater at Lakitelek, and analyses were performed similarly to those described above. Figure 8 illustrates the organic matter-loading of the backwater on the basis of the chemical oxygen demand calculated with potassium dichromate. The values of this varied between 21—36 mg/l, practically meaning a constant value.

Figure 9. demonstrates the annual change in the ammonia- and nitrate-contents at the backwater. The concentration of ammonia was relatively constant in the backwater, increased values were only measured in January and April. Studying the nitrate-concentration it can be seen that it increased in the autumn — winter months. To a certain degree, this is also in correlation with the effect of the inland waters.

Figure 10. shows the changes in the water's sodium- and potassium-content. The concentration of sodium slightly rose by the autumn months, that of potassium practically remained constant.

On the basis of the above water quality indexes it can be determined that the water quality of the backwater at Lakitelek is more stable than that of the above reviewed Alpár backwater.

The concentrations of the essential heavy metals at the Lakitelek backwater are demonstrated on Figure 11. The concentration of copper in the backwater slightly

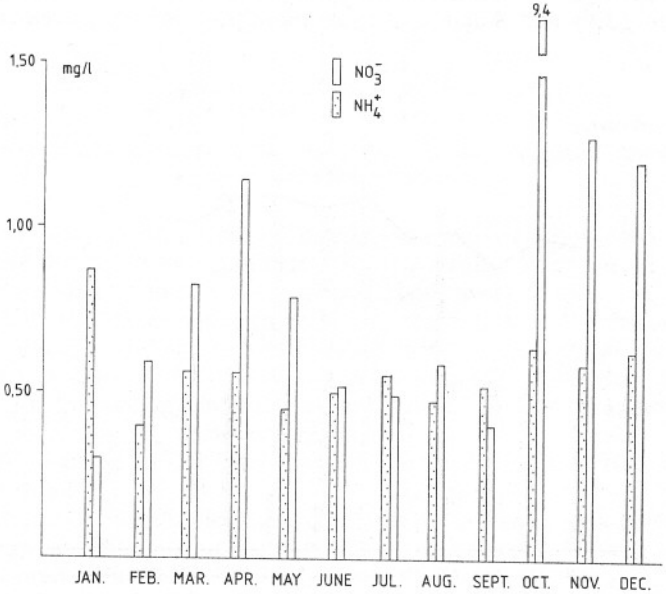

Fig. 9. Changes in the ammonia- and nitrate-concentrations in the Lakitelek backwater.

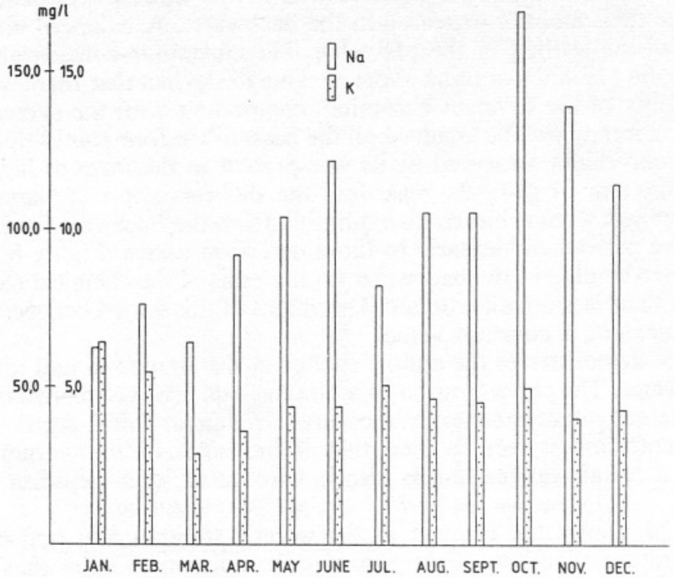

Fig. 10. Seasonal changes of the sodium- and potassium-contents in the Lakitelek backwater.

increased in the Spring and Autumn months. Nevertheless, this increase is not of such degree that it would lead to the decrease in the amount of the organisms sensitive to copper.

Determinations similar to the fore-goings could be made in the case of the zinc-content. Rather high zinc-concentration was registered from the backwater in the months of June, July and August. In these months, relatively increased amounts of

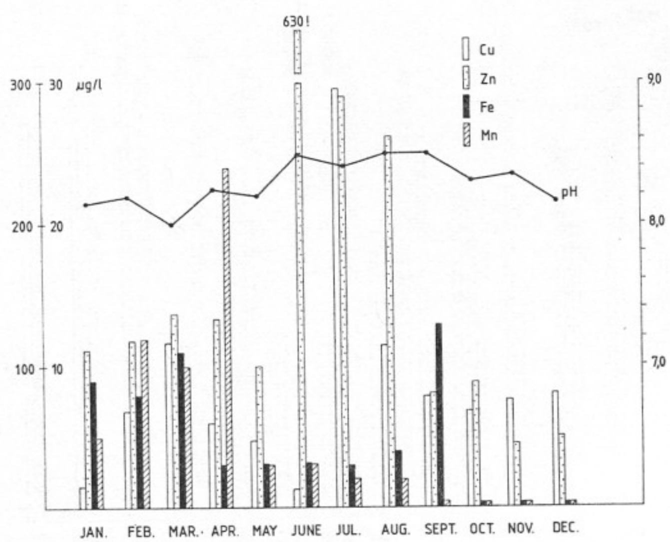

Fig. 11. Changes in the concentrations of the essential heavy metals in the Lakitelek backwater.

the *Chlorella* alga species' individuals were observable in the water during the course of the biological studies. As mentioned earlier, these algae are particularly fond of zinc. There was also a relationship between the increased zinc-concentration and the increase in *Chlorella* in the case of this backwater.

The amount of iron increased in the Spring and Autumn months, and was unchanged in Summer. In the months of January—February, when the iron-concentration at the backwater was virtually the same, the saprobity indexes also showed values of 1,97 and 1,93, respectively. The same could be observed in the period between April and August, when the amount of iron was constant and the S-index values ranged between 2,02—2,10.

The manganese-concentration in the backwater was high in the months at the end of Winter—Summer, then it gradually decreased and could not be demonstrated from the water in the Autumn months.

Figure 12. shows the concentrations of the toxic heavy metals observed in the backwater.

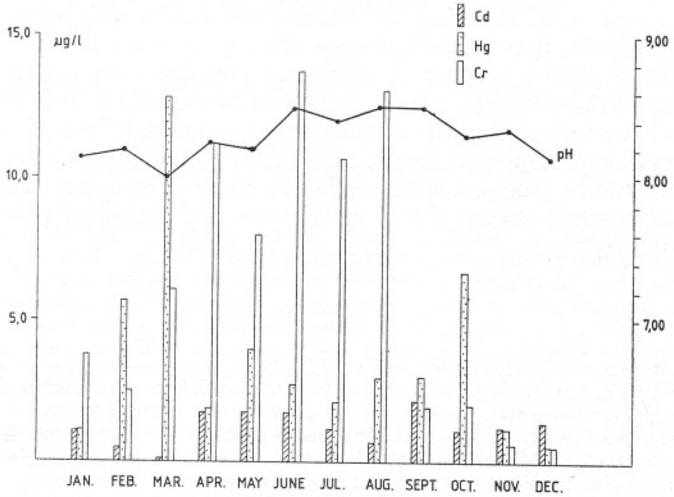

Fig. 12. Changes in the concentrations of three toxic heavy metals — mercury, cadmium, chromium — in the Lakitelek backwater.

In February and March increased mercury-content was registered in the water, which gradually decreased to a minimal value (to a value which could be registered as a natural background in the water of the Tisza river). Higher mercury content was measured in the water again in October, decreasing in the following month. Therefore, the effect of the Spring and Autumn inland waters coming from the agricultural fields was also demonstrable in the backwater et Lakitelek. The effect of mercury was not long-lasting in this case either, thus no chronic alterations could be observed concerning the water organisms.

Cadmium occurred in the backwater in a concentration corresponding to the natural background.

Among the toxic metals, the concentration of chromium was particularly high in the Spring-Summer months at the backwater. Nevertheless, it did not surpass the recommended limit-value (MSZ 12 750).

Regarding the development of the chromium-concentration, the same tendency could be observed as in the case of the Alpár backwater; with the decrease of pH, there was also a decrease in the amount of chromium in the Autumn months. On the basis of this it is assumable that the majority of chromium is present in hexavalent form in this backwater, too.

Considering the experiences gained last year, the followings can be determined:

1. Studies on the essential metals should be continued in the Alpár and Lakitelek backwaters, with particular regard to the zinc- and copper-contents, which showed relationship with the life of the waters. The studies are also wished to be expanded to the bottom sediments so that further basic knowledge could be gained on the conditions of the equillibrium. It is also expedient to perform biochemical studies related to the heavy metals, for which purpose cooperation is necessary on behalf of several teams taking part in the research.

2. Due to the intensive agricultural production going on in our environment, the water and living world in the backwaters are still loaded with mercury, from the toxic heavy metals. It is unambiguously striking from the studies on cadmium that this metal does not occur in significant concentration in the backwaters, therefore its further studying is not thought to be expedient. It is of importance to decide what proportion of the total chromium-content measured by us is given by the hexavalent chromium compounds. The samples originating from the bottom sediments should be included in the studies on the toxic heavy metals, to obtain a complete as possible image of the equillibrium and transport processes taking place in the backwaters.

References

BATLEY, G. E.—GARDNER, D. (1977): Water Res. *11*, 745.

BOZSAI, G.—KÖVES, L. (1978): A Dunából nyert ivóvizek nehézfém szennyezettségének vizsgálata atomabszorpciós módszerrel. (Studies on the heavy metal contamination of drinking water gained from the Danube using atom-absorption method) — Hidrológiai Közl. 468—472.

GAMBLE, D. S.—SCHNITZER, M. (1979): In: SINGER, P. C., Ed., Trace Metals and Metal — Organic Interactions in Natural Waters. Ann Arbor, Ann Arbor Science Publ. 1973.

JERNELÖV, A.—LANN, H. (1973): Studies in Sweden on feasibility of some methods for restoration of mercury- — contaminated bodies of Water. — Environmental Science and Technology 7, 712—718.

KOWAL, A. L.—SWIDERSKA—BRÓZ, M. (1979): Gaz, Woda i Technika Sanitarna, *53*. 50—53.

LITERÁTHY, P. (1977): A Sajó fenéküledékében felhalmozódó biorezisztens anyagok vizsgálata (Study of the bioresistant substances accumulating in the bottom sedimentation of the Sajó). — Hidrológiai Közl. *1*. 45—54.

LITERÁTHY, P. (1982): Felszíni vizek nahézfém szennyezései (Contaminations of surface waters by heavy metals). — Budapest *Magyar Optikai Művek:* Spektromom 190 A előiratgyűjtemény (*Hungarian Optical Works:* Spectromom 190 A Antecedents Collection). Hung. Opt. Works. Bp. 1978.

PAYNE, K.—PICKERING, W. F.: (1975): Water, Air, Soil Poll. *5*.

PICKERING, W. F.—HENDERSON, C. (1966): Int. Jour. Air. Water Pollution. *10*, 453.

PICKERING, W. F. (1980): Cadmium retention by clays and other soil or sediment components. In: J. O. NRIAGU, Ed., Cadmium in the environment. — New York, Wiley Interscience, 1980.

PRICE, W. J. (1972): Atomabszorpciós spektrometria. Budapest.

SHEPHARD, B. K.—MCINTOSH, A. W. (1980): Water Research, *14*, 1061—1066.

STUMM, W.—MORGAN, J. J. (1970): Aquatic Chemistry New York, Wiley Interscience, 1970.

A vízi biocönózisokra hatást gyakorló nehézfémek vizsgálata az Alpári és Lakitelki holtágak vizében

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Kivonat

1982. évben az Alpári és Lakitelki holtágak vizében havi gyakorisággal meghatároztuk azokat a nehézfémeket, amelyek hatást gyakorolnak a vízi élővilágra. Vizsgálataink a víz réz-, kadmium-, cink-, króm- és higanytartalmának meghatározására irányultak. A nehézfémek vizsgálata mellett meghatároztuk a holtágak vizében a szervesanyag-tartalmat. figyelemmel kísértük az ammónia- és nitrátkoncentráció alakulását. A nehézfémvizsgálatokhoz kapcsolódóan határoztuk meg a víz pH-ját, valamint nátrium- és káliumtartalmát, A vizek cink- és réztartalma, valamint a vízi szervezetek száma között összefüggéseket figyeltünk meg. Megállapítottuk, hogy a két holtág vizének jelentős a higanytartalma, amely külső szennyezésre utal.

Анализ тяжёлых металлов, влияющих на водные биоценозы, в воде мёртвых русел Алпар и Лакителек

Е. Фекете

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Резюме

В 1982 годы мы ежемесячно проводили определение тяжёлых металлов, влияющих на водный живой мир, в воде мёртвых русел Алпар и Лакителек. Наши анализы были направлены на определение содержания в воде меди, кадмия, цинка, хрома и ртути. Наряду с определением тяжёлых металлов, в воде мёртвых русел мы определяли также содержание органического вещества, а также наблюдали формирование концентрации аммиака и нитрата. Параллельно с анализом тяжёлых металлов, мы определяли также содержание рн воды и содержание натрия и калия. Нами наблюдалась зависимость между содержанием цинка и меди, с одной стороны, и количеством водных организмов — с другой.

Установили, что вода обоих мёртвых русел содержит значительное количество ртути, что свидетельствует о внешнем загрязнении.

Ispitivanje uticaja teških metala na biocenoze mrtvaja Alpár i Lakitelek

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Abstrakt

U 1982. godini odredjivani su u mesečnim intervalima u vodama mrtvaja Alpár i Lakitelek oni teški metali koji utiču na živi svet voda. Ispitivanja su bila usmerena na odredjivanje bakra, kadmijuma, cinka, hroma i žive u vodi. Pored ispitivanja teških metala odredjivan je i sadržaj organskih materija. Praćena je koncentracija amonijaka i nitrata u mrtvajama. Takodje je utvrdjivan i pH, te sadržaj natrijuma i kalijuma. Uočena je uslovljenost izmedju sadržaja cinka i broja vodenih organizama. Konstatovana je značajna količina žive, koja upućuje na zagadjenje mrtvaja.