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Heavy Metals Distribution in the Sediment of the Sava Basin in Slovenia

Preliminary investigations 1975—76

Težke kovine v rečni usedlini Save in njenih pritokov

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The sediment samples taken from the Sava and Voglajna river beds in Slovenia proved to be rather abundant in heavy metals. The preliminary investigations indicated a high grade water pollution originating from different industries concentrated in both these river basins. The riverhead of Sava is considered to be unpolluted, while the zinc and lead contents of the sediment samples taken from the reservoir of the Moste Water Power Plant increase up to fifty times, and those of cadmium and mercury nearly twenty times. Another pollution centre is constituted by the Celje industrial district. In the Voglajna sediment chromium and zinc were enriched by a factor of more than 100, copper, lead, and cadmium, however, by a factor of 25—50 compared with the geochemical background.

Kemična analiza je pokazala, da so usedlinski vzorci iz savske in voglajnske struge precej bogati s težkimi kovinami. Po rezultatih preliminarne raziskave gre za visoko stopnjo onesnaževanja vode, ki jo povzročajo industrijske odplake. Napram vrednostim v izvirnem toku Save, ki velja za čistega, se količini cinka v vzorcih usedlin, vzetih v zbiralnem jezeru hidroelektrarne Moste, povečata petdesetkrat, količini kadmija in živega srebra pa približno dvajsetkrat. Še bolj je onesnažena struga Voglajne na celjskem industrijskem območju: vsebnosti kroma in cinka so v njenih usedlinah več kot stokrat večje od naravnega geokemičnega ozadja, količine bakra, svinca in kadmija pa 25 do 50-krat.

Sedimentproben aus den Flüssen Save und Voglajna in Slowenien enthalten stellenweise sehr hohe Schwermetallanteile. Vorläufige Untersuchungen aus dem Zeitraum 1975—1976 deuten darauf hin, daß eine nachhaltige Wasserverschmutzung von Industriebetrieben ausghet, die in diesen beiden Flußgebieten konzentriert sind. Verglichen mit den

Metallgehalten in Sedimentproben aus dem Save-Oberlauf, der als unverschmutzt anzusehen ist, zeigen die Ablagerungen aus dem Stausee des Wasserkraftwerkes von Moste 50-fach höhere Blei- und Zinkanteile sowie nahezu 20-fache größere Cadmium- und Quecksilberwerte. Ein zweites Verschmutzungszentrum bildet der Industrie-Komplex von Celje; Sedimente der Voglajna sind um den Faktor 100 und mehr an Chrom, Zink, sowie um Faktoren zwischen 25 und 50 an Kupfer, Blei und Cadmium gegenüber dem geochemischen »Background« angereichert.

Contents

1. Introduction

The development of modern technology and the associated rapid growth in population of industrial districts have had serious consequences for our rivers and lakes, both as a result of increased removal of water to meet process and drinking water requirements, and because of the growing frequency of pollutants in waste water. During the past decades, the degree of pollution, especially in the industrial centres, has increased exponentially to such an extent that it now poses a threat to drinking water quality and aquatic life.

Among the many kinds of pollutants which reach the water from industrial waste, domestic sewage and agricultural runoff, perhaps the most important are the heavy metals. Spectacular accidents in Japan, caused by mercury and cadmium, have sparked general interest in heavy metals as potential hazards for man: 46 fishermen who had eaten fish from the Minimata Bay died from mercury poisoning; villagers in the Jintsu River Basin were stricken with a skeletal disease known as osteomalacia, caused by elevated cadmium content in drinking water, the source of which was a river polluted by waste material from a closed zinc mine. The particular threat of the heavy metals lies in the fact that they in contrast to many organic pollutants, are not decomposed by microbiological activity. On the contrary, heavy metals can be enriched by organisms and the type of bonding can be converted to more poisonous metal-organic complexes, as observed in the transformation of elementary and divalent ionic mercury into methylmercury (J. M. Wood, 1974).

Public reports on the periodical death of fish and the devastation of certain river areas have long shown that some regions in Slovenia are also endangered by the increasing degree of water pollution. During the past few years, several institutes in Slovenia have been carrying out scientific investigations on problems of water protection. These centred mainly around hydrochemical and biological-limnological studies. In autumn 1974, geological working methods were introduced into water control after evidence showed that the catastrophic pollution of the Sava river, which occured when the dam of the Water Power Plant HE Moste near Jesenice was emptied for repair, was probably caused by eroded deposits from the reservoir bed (M. Ažnik, F. Megušar & J. Štern, 1976 b). In order to solve this complex problem, the Geološki zavod Ljubljana contacted other scientists in other fields of study. The first results of this cooperation have recently been made available (M. Ažnik, F. Megušar, & J. Štern, 1976 a). In particular, a long-term programme of cooperation in the field of environmental geology in Slovenia has been agreed on between the Geološki zavod Ljubljana and the Laboratorium für Sedimentforschung of the University of Heidelberg, which has been looking into this problem for several years (K. Banat et al., 1972; U. Förstner and G. Müller, 1974). The present study of metal contents in sediment from waters of the Sava basin in Slovenia takes the form of a preliminary investigation which is to be extended and intensified during the coming years.

The research project was supported by Sklad Borisa Kidriča (Raziskovalna skupnost Slovenije) and partially financed by the firms Savske elektrarne — TOZD HE Moste, Železarna Jesenice, and Geološki zavod Ljubljana. Some of the sediment and water analyses were carried out in the Laboratorium für Sedimentforschung of the University of Heidelberg.

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2. **Aim of the study**

The variation in trace metal contents of stream sediments can be characterized as a function of potential controlling factors by the following model (E. C. Dahlberg, 1968).

$$T = f\ (L,\ H,\ G,\ C,\ V,\ M,\ e)$$

in which »T« represents the resulting trace metal concentration, »L« the influences of lithological units, »H« the hydrological effects, »G« the geological features, »C« the cultural (man-made) influences, »V« the type of vegetation cover, »M« the effects of mineralized zones and »e« stands for the error plus effects of additional factors not explicitly defined in the model. In mineral exploration, where the method of stream sediment sampling was at first applied with success, the main problem was to maximize the factor »M«, i. e. to eliminate other effects as far as possible. During the last decade, geochemical research on aquatic sediments has acquired new importance as a tool for the investigation of the impact of civilization on natural environments. H. Züllig (1956) described the significance of sediments as »a response to the conditions of an aquatic system«; J. S. Webb (1971), U. Förstner and G. Müller (1973), and S. R. Aston et al. (1974) demonstrated that pollution reconnaissance can be carried out in stream sediments in the same way as in the standard practice of mineral exploration. In this present investigation on heavy metal contents in sediment of waters from the Sava basin in Slovenia, an attempt is made to establish the source and extent of metal pollution. The above mentioned investigation area was selected because the Sava river constitutes the most important inland water artery in the whole of Jugoslavia. Later, we will try, by means of more detailed sampling, to fill in any existing gaps and to answer any unanswered questions.

3. Sampling, Methods, Results

A total of 36 sediment samples were taken in September 1975 after a long dry spell and correspondingly low water levels from the river area of the Sava (see plate 1). Sampling was concentrated on potential »centres« of pollution. 14 samples were taken from the Sava and the tributaries of the Ljubljanica, Kamniška Bistrica and Savinja (into which the Voglajna empties at Celje), 16 samples stem from the HE Moste Dam at Jesenice (MS 1—16), and 6 samples from the Zbiljsko Jezero (Zbilje Artificial Lake) (Z 1—6). A grab sampler was used to collect lake samples from the lake bottom.

In order to reduce the grain size effects as much as possible and compare the different samples, the grain fraction $< 2\,\mu$ was separated, in each case with distilled water in settling tubes. This pelitic fraction was used for the following investigations:

3.1. *Mineral composition*

The carbonate contents and the clay mineral components were measured in some selected samples. The results of the X-ray and gasometric carbonate analyses and the X-ray clay mineral determination of the pelitic fraction are shown in table 1. The highest carbonate contents were measured in the Sava Dolinka and in the tributary of the Kamniška Bistrica. As will be shown, these high carbonate values have a diluting effect on several trace elements, e. g. iron and cobalt. In the upper Sava, relatively high dolomite contents (calcite : dolomite = 1 : 1) were found. In the last Sava sample (S 8), the ratio of calcite : dolomite is approx. 4 : 1. The individual clay components were assessed from the X-ray diagramme. Illite is common in all samples. Below the inflow of coal effluents, the kaolinite contents increase sharply. Expandable clay minerals (smectite) could only be determined with certainty in the Savinja sample.

3.2. *Metal contents of the sediment*

For the metal analyses, the separated pelitic fractions were treated with HNO_3/HCl (1 : 3). The elements iron, manganese, zinc, chromium and copper were determined by conventional (flame-) atomic absorption spectroscopy and the elements nickel, cobalt, lead, cadmium, silver and mercury by means of flameless AAS according to the usual settings used in our Laboratory (U. Förstner + G. Müller, 1974).

Metal data in the sediment are shown in table 2. The order corresponds with the downstream distribution, with the tributary samples being included in each case below the samples from the main river. For the following interpretation, the elements were divided into groups.

3.3. *Water Investigations*

Finally, the data of several water samples were measured. These results can by no means be considered representative; on the one hand, because we are dealing with only one sample, and on the other, because considerably low water levels existed at the time of investigation. These data, however, give an approximate feature of the hydro-chemical conditions in the individual areas of the river basin. The water analyses were carried out according to the usual wetchemical procedures or by means of AAS. The results of the water investigations are summarized in table 3. Remarkable changes can be seen in the main ion contents (data in mg/l) which show an increase in the chloride and magnesium values in the Sava samples situated below the brown coal tributaries. In the case of the trace metals, the water sample from the Voglajna shows distinctly different behaviour from the normal. In the Savinja too, the high cadmium values can remain in solution over long distances. This element, therefore, may represent a particularly serious danger.

4. **Interpretation of data from the pelitic sediment**

The sediment data from the three investigation areas (a) Moste Dam, (b) Zbilje Artificial Lake (c), and other Sava course with tributaries, will be discussed below. First of all, however, it is necessary to consider the problem of which reference value is to be used for comparison with the individual pollution intensities, i. e. the geochemical »background« for the civilizational metal enrichment. In this case, we are relatively fortunate in that 3 sediment samples (Nos. 17, 18, 19) were taken from the uppermost course of the Sava river from a still relatively unpolluted area. These samples can be used as a basis for comparison in our investigations. A comparison of the average values of these three samples with the corresponding metal contents in shales (after K. K. Turekian + K. H. Wedepohl, 1961) is given in table 4. From this it is evident that in some cases, e. g. with lead, mercury, cadmium and silver, the metal contents in the sediment from the mountain Sava river examined here are still considerably higher than the unpolluted standard values. This finding can be attributed to certain contaminating influences since the enrichment of these elements in pollution zones is particularly strong (see below). On the other hand, some of the samples examined here are poor in iron, manganese, nickel and cobalt. This may possibly be explained by lithologic influences, e. g. elevated carbonate contents. Despite these shortcomings in the internal background of the Sava catchment area, we will use the data from samples 17 to 19 in order to characterize the material contents in the individual samples.

Table 1. **Mineral composition of the pelitic fraction. Clay minerals estimated according to the X-ray diagramme: ($< 2\,\mu$). xxx — very frequent, xx — frequent, x — secondary component, (x) questionable. Quartz contents not given**

	Carbonate %			Clay Minerals			
	Total	Calcite	Dolomite	Smectite	Chlorite	Illite	Kaolinite
Sava S 18	62.5	29.5	33.0	(x)	xx	xxx	(x)
Moste Dam	48.5	27.0	21.5	(x)	x	xxx	x
Zbilje Artificial Lake	30.0	19.5	10.5	(x)	xx	xxx	(x)
Sava S 3	26.5	18.0	8.5	(x)	xx	xxx	-
Ljubljanica	52.5	37.5	15.0	(x)	xx	xxx	x
Sava S 2	31.0	20.5	10.5	(x)	xx	xxx	-
Kamniška Bistrica	78.0	70.0	8.0	-	x	xxx	-
Sava S 6	24.5	20.5	4.0	(x)	x	xx	xxx
Savinja	13.0	13.0	-	x	x	xx	x
Sava S 8	27.0	22.0	5.0	(x)	x	xx	xxx

4.1. *Moste Dam*

Very high contents of zinc and lead were determined in the deposits of the Moste Dam by M. Ažnik, F. Megušar & J. Štern (1976 b). The present investigation of a vertical profile along the dam is mainly aimed at finding the source of the strong metal pollution, as well as answering the question of whether the contamination originates from domestic sewage from Jesenice or from smelting activities of the Javornik factory. In fig. 1 which gives the data of zinc, lead, cadmium and mercury in the vertical profile, a largely uniform distribution of the generally high enrichments of these metals can be seen in the sediment from the different parts of the dam. Three anomalies — in samples MS15, MS11 and MS7 — are particularly of note. Sample MS15 stems from a small island in the immediate vicinity of the industrial discharge point at Javornik and contains zinc and lead concentrations which are enriched by a factor of 50 or more. Cadmium and mercury are enriched twenty times, in each case compared with the corresponding contents in the Sava sediment above Jesenice.

Even before this large-scale pollution, however, which was probably caused by industrial wastes, the contents in the Sava sediment below Jesenice were distinctly enriched compared with the deposits of the uppermost course of the Sava. This increase — copper by a factor of 2 and lead by a factor of almost 3 and zinc by a factor of 3.5 — may be ascribed to the influence of the town of Jesenice and probably originates chiefly from communal effluents.

Table 2. **Metal contents in the pelitic sediment of waters in the Sava basin (Fe in %, all other data in parts per million — ppm)**

No.		Fe	Mn	Ni	Co	Cr	Cu	Zn	Pb	Cd	Hg	Ag
S19	Sava-	2.1 %	550	36	17	39	44	102	50	1.3	0.5	0.3
S18	Dolinka	1.8 %	450	30	11	38	41	115	35	1.5	0.6	0.2
S17		2.3 %	600	36	10	35	52	145	56	1.5	1.4	0.5
Moste Dam												
MS	(Depth)											
16	(1 m)	3.1 %	417	50	9	83	104	550	145	2.8	2.3	0.42
15	(0 m)	4.4 %	2205	56	15	81	197	8080	2790	29.4	17.7	3.23
14	(2 m)	3.5 %	896	51	13	58	118	2050	575	7.7	4.4	0.67
13	(6 m)	2.6 %	896	31	14	77	119	1540	435	5.1	3.4	0.77
12	(7 m)	3.6 %	835	33	13	59	128	2000	500	6.5	5.7	0.58
11	(7 m)	3.1 %	872	27	14	55	138	3800	1090	10.9	5.5	1.47
10	(11 m)	2.9 %	1024	26	17	64	92	2050	640	7.7	6.2	0.51
9	(11 m)	3.1 %	896	38	12	51	124	1920	510	5.8	5.0	0.61
8	(9 m)	2.2 %	1200	20	14	30	180	4200	1300	8.0	4.0	0.45
7	(10 m)	3.0 %	1920	51	14	90	156	4350	2180	17.4	4.6	2.23
6	(12 m)	3.4 %	763	44	16	60	77	1850	872	6.3	2.6	0.89
5	(18 m)	3.2 %	800	35	14	50	79	2000	650	6.0	4.0	0.60
4	(20 m)	2.9 %	882	59	12	59	95	2650	735	7.1	6.1	0.38
3	(23 m)	3.1 %	714	40	11	51	80	2850	800	6.3	4.0	0.68
2	(32 m)	3.5 %	900	40	15	65	84	3200	1000	7.5	3.8	0.90
1	(32 m)	2.0 %	700	60	16	70	76	2400	700	8.0	4.5	1.00
Zbilje Art. L.												
Z1	(5 m)	3.4 %	375	35	16	68	72	400	67	1.5	1.9	1.13
Z2	(2 m)	2.7 %	266	39	16	60	75	560	108	2.3	1.6	0.80
Z3	(8 m)	3.5 %	450	46	11	55	70	620	125	2.0	1.2	0.90
Z4	(8 m)	3.4 %	300	38	14	50	56	500	85	1.6	1.1	0.72
Z5	(11 m)	4.0 %	400	48	12	50	54	480	76	1.4	0.9	0.60
Z6	(12 m)	3.0 %	900	52	13	60	61	485	82	1.9	1.9	0.60
Sava S3		3.2	750	95	12	70	120	1700	380	2.7	1.5	1.60
Ljubljanica S1		2.1	256	179	14	409	265	1020	290	4.4	2.1	11.30
Sava S2		3.1	366	97	13	610	125	730	120	2.7	1.5	4.70
Kamniška Bistrica S4		0.9	318	48	9	1056	330	1100	85	1.6	31.8	0.50
Sava S5		2.7	475	63	12	1235	145	550	180	2.5	5.2	2.50
Sava S6		1.1	200	65	5	110	45	320	55	1.3	2.5	1.00
Voglajna S11		17.6	920	113	25	3680	1525	15800	1150	65.8	6.1	2.10
Savinja (S10)		5.0	1050	70	17	1490	420	6000	500	25.0	2.7	2.90
Savinja (S9)		4.1	1220	84	16	1280	335	5000	450	14.4	1.9	1.40
Sava S7		1.2	400	45	7	165	65	1100	65	2.9	4.0	1.20
Sava S8		1.4	350	50	8	165	68	1000	75	3.3	4.2	1.20

Table 3. **Results of the water investigations**

	pH	Cl^-	SO_4^{--}	Na^+	K^+	Mg^{++}	Ca^{++}	Fe	Mn	Zn	Cu	Pb	Cd
				mg/l						μg/l			
Sava S3	7.4	10	18	8.5	2.5	15	40	80	30	170	4	2.5	0.5
Ljubljanica S1	7.1	42	15	8.2	3.0	31	52	100	190	150	4	3.8	0.6
Sava S2	7.2	15	15	6.4	3.0	21	46	100	110	50	4	2.8	0.1
Kamniška B. S4	7.0	46	15	12.0	2.5	21	52	80	70	70	18	5.9	1.1
Sava S5	6.9	34	16	11.0	4.0	21	50	100	50	40	7	2.6	0.1
Sava S6	7.1	164	19	9.4	5.0	70	50	240	50	630	4	6.5	0.6
Voglajna S11	6.9	64	48	28.0	6.0	31	130	23.400	1.500	4.100	32	50	8.6
Savinja (S10)	6.7	65	65	13.0	3.0	30	63	400	250	170	6	3.5	2.4
Savinja (S9)	7.1	33	64	14.0	3.0	23	65	440	290	190	5	2.9	0.3
Sava S7	7.1	128	43	12.4	5.0	55	56	140	190	70	4	6.3	0.3
Sava S8	6.9	30	43	7.4	5.0	21	60	1.200	50	50	4	6.6	0.3

Table 4. **Average and maximum values of metals in the clay sediment of the Moste Dam and Zbilje Artificial Lake as well as enrichment factors (compared with clay sediment of the Sava Dolinka)**

	background Ø		Moste Dam Metal content		factor		Zbilje Artificial Lake	
	S17–S19	Shale	Ø	max.	Ø	max.	Ø	f(Ø)
Iron	2.0 %	4.7 %	3.9 %	4.4 %	2.0	2.2	3.3 %	1.7
Manganese	530	850	995	2205	1.9	4.1	449	0.8
Nickel	43	68	41	60	1.0	1.4	43	1.0
Cobalt	13	19	14	17	1.1	1.3	14	1.1
Chromium	37	90	63	90	1.7	2.4	57	1.5
Copper	46	45	116	1200	2.5	4.3	65	1.4
Zinc	121	95	2845	8080	23.6	66.9	507	4.2
Lead	47	20	933	2790	19.8	59.4	91	1.9
Cadmium	1.4	0.3	8.9	29.4	6.4	21.0	1.8	1.3
Mercury	0.8	0.4	5.2	17.7	6.3	21.3	1.4	1.7
Silver	0.33	0.11	0.96	3.23	2.9	9.8	0.76	2.3

In the further course of the metal values within the dam, a distribution can be seen which is characterized by relatively high contents in the shallow places (widening of the valley), e. g. samples MS11 and MS7, and by relatively low metal contents in the narrow parts. This is probably representative of varying erosion and sedimentation behaviour whereby, in the shallow areas, the sediment particles originating from industrial effluents are preferentially deposited while in the narrow parts, more Sava suspended load is sedimented. It can also be due to a certain grain size effect whereby — despite separation of the pelitic fraction — a large amount of fine material still occurs in these samples of sediments from the shallower parts of the lake, which also contains relatively elevated metal contents. A grain size effect of this kind is indicated in the lower part of the dam sample MS6 where, according to M. Ažnik, F. Megušar & J. Štern (1976 b), the deposits become progressively finer-grained downstream in the direction of the dam and exhibit continually increasing metal contents (Zn, Pb).

In addition to the median and maximum metal contents in the dam sediment, table 4 also gives the individual enrichment factors. It is evident that on the whole, it is zinc and lead (by a factor of 20 compared with the Sava background) as well as cadmium and mercury (by a factor of 6) which are the most strongly enriched. Copper and silver also exhibit a significant increase. All these metals are distinctly positively correlated (table 5) and originate predominantly from the same source. The enrichment of manganese is probably attributable to syndiagenetic effects: as has since been observed in very many stagnant waters (e. g. U. Tessenow, 1975), manganese in

Fig. 1. Distribution of zinc, lead, cadmium and mercury in the pelitic sediments of the Sava Dolinka, the Moste Dam, and the Zbilje Artificial Lake (Zbilje Dam). (Above: Water depth of the dams. Data in meters).

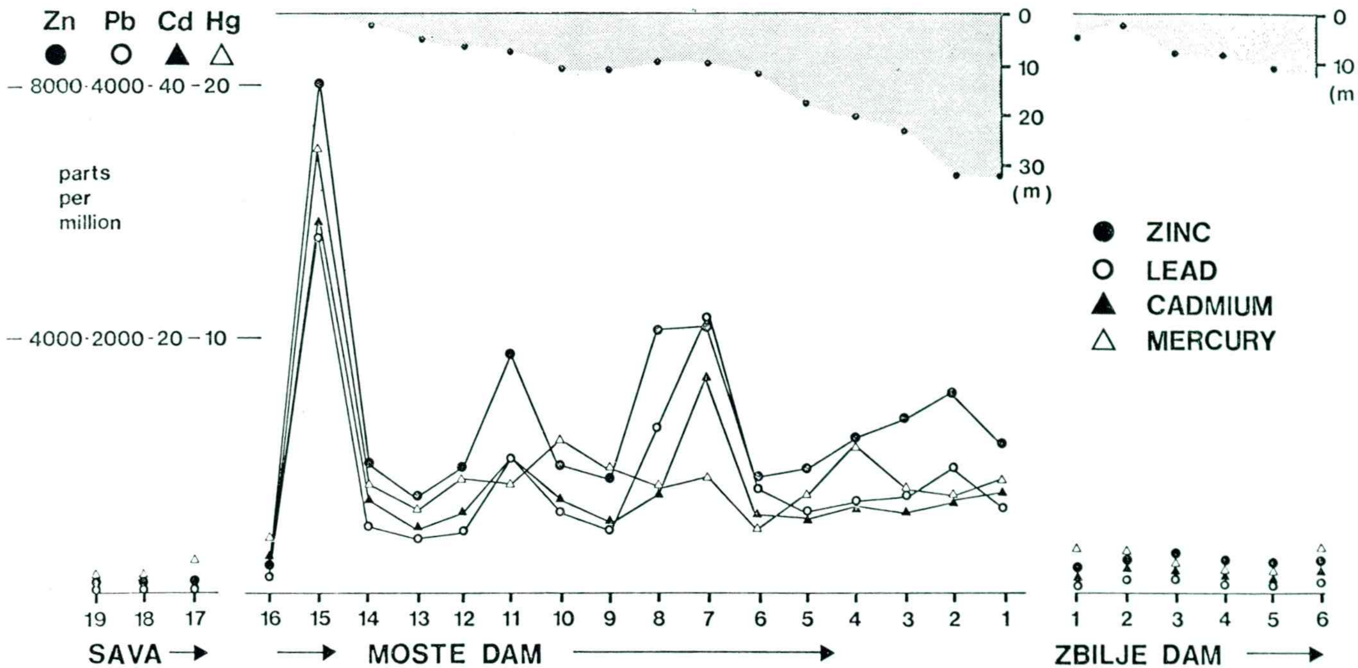

Table 5. **Correlation coefficients for the metal contents in the clay sediment of the Moste Dam (Underlined: > 99 % probability).**

	Fe	Mn	Zn	Cr	Ni	Cu	Pb	Co	Hg	Cd	Ag
Fe	x	.38	.40	.24	.20	.23	.39	-.11	.58	.51	.49
Mn	.38	x	.87	.34	.17	.76	.94	.34	.74	.93	.86
Zn	.40	.87	x	.12	.15	.72	.95	.30	.83	.94	.85
Cr	.24	.34	.12	x	.54	.08	.28	.03	.24	.39	.53
Ni	.20	.17	.15	.54	x	-.13	.22	-.16	.27	.31	.34
Cu	.23	.76	.72	.08	-.13	x	.69	.04	.60	.69	.61
Pb	.39	.94	.95	.28	.22	.69	x	.34	.73	.95	.91
Co	-.11	.34	.30	.03	-.16	.04	.34	x	.22	.32	.31
Hg	.58	.74	.83	.24	.27	.60	.73	.22	x	.88	.76
Cd	.51	.93	.94	.39	.31	.69	.95	.32	.88	x	.95
Ag	.49	.86	.85	.53	.34	.61	.91	.31	.76	.95	x

Table 6. **Metal enrichment factors in sediment of the Sava and its tributaries**

	Sava					Tributaries			
	S17–S19	S3	S2	S5	S8	Ljublja-nica S1	Kamniška Bistrica S4	Voglajna S11	Savinja S9–10
Iron	2.0% = 1	1.6	1.6	1.4	0.7	1.0	0.5	8.8	2.0
Manganese	530 = 1	1.4	0.7	0.9	0.6	0.5	0.6	1.7	2.3
Nickel	43 = 1	2.2	2.3	1.5	1.2	4.2	1.1	2.6	2.0
Cobalt	13 = 1	1.0	1.0	1.0	0.6	1.1	0.7	1.9	1.2
Chromium	37 = 1	2.0	16.5	33.4	4.5	11.0	28.5	100	34.6
Copper	46 = 1	2.6	2.7	3.1	1.5	5.8	7.2	33	7.3
Zinc	121 = 1	14.0	6.1	4.6	8.3	8.4	9.1	130	41.2
Lead	47 = 1	8.0	2.5	3.8	1.6	6.2	1.8	25	9.6
Cadmium	1.4 = 1	1.9	1.9	1.8	2.3	3.1	1.2	47	10.3
Mercury	0.8 = 1	1.9	1.9	6.5	5.2	2.6	39.5	7.6	2.4
Silver	0.33 = 1	4.8	13.8	7.6	3.6	34.2	1.2	6.4	4.2

particular is mobilized under anoxic conditions in the deeper sediment layers, diffused upwards in the sediment column and then re-precipitated — provided there is enough oxygen present — at the sediment/water interface. There is still difference of opinion concerning the question of to what extent this affects the distribution of other metals (cf. D. Reinhard + U. Förstner, 1976).

4.2. *Zbilje Artificial Lake*

The metal contents in the sediment of the Zbiljsko jezero are much more evenly distributed than in the Moste Dam described above. Only zinc, lead and silver exhibit a characteristic enrichment by a factor of 4 and 2, respectively, compared with the Sava-background (fig. 1 — table 4). This »recovery« of the Sava, as demonstrated by the sediment data, may be due to the introduction of suspended particles which are polluted to a lesser extent; it il also possibly due to the fact that a large amount of the polluted Moste sediment is held back in the water reservoir. A characteristic correlation between water depth and elevated manganese contents can be observed which provides a further indication of the effect described above of a diagenetic redistribution of this metal.

4.3. *Sava and tributaries*

The development of the metal contents in the sediments of the Sava and its most important tributaries below the Zbilje Artificial Lake is shown in table 6 by the individual enrichment (or derichment) factors. In addition, the sequence of data of zinc, lead, cadmium, copper and chromium is given in fig. 2. Sample S3 which was taken at *Črnuče,* represents the metal contamination in the *Sava region above Ljubljana* with elevated concentrations of zinc, lead and silver. These originate predominantly from the domestic sources and from small industry. One sediment sample from the *Ljubljanica* (S1), which was taken just before the point where it flows into the Sava, contains, in addition to Fe, Mn and Co, all trace elements in considerably enriched quantities. The composition of the sample represents the large *industrial district from Ljubljana to Vrhnika,* with very high concentrations of silver (possibly from photochemical factories) as well as of zinc, lead, copper and (unusually!) of nickel. The effects on the sediments of the Sava can be traced in Sample S2, several 100 m below the mouth of the Ljubljanica into the Sava. All the metal components which were strongly enriched in the Ljubljanica decrease sharply, with the exception of chromium which is only changed to a relatively small degree. Significant enrichments can be seen in the case of silver, zinc and chromium compared with the Sava background. The sediment sample from the *Kamniška Bistrica* (S4) was taken immediately before the point where it flows into the Sava. It represents the influences of the predominantly *chemical industry of the towns Kamnik to Domžale* on the metal composition. Very strong enrichments of mercury (32 ppm) and chromium were measured, the latter originating from the neighbouring tanning industry. The zinc and copper values are also relatively high. A high Cr content is characteristic of the sample S5 on the right bank of the *Sava below Litija*; this can also be ascribed to the tanning industry. In the sample from *Zalog,* there is a distinct enrich-

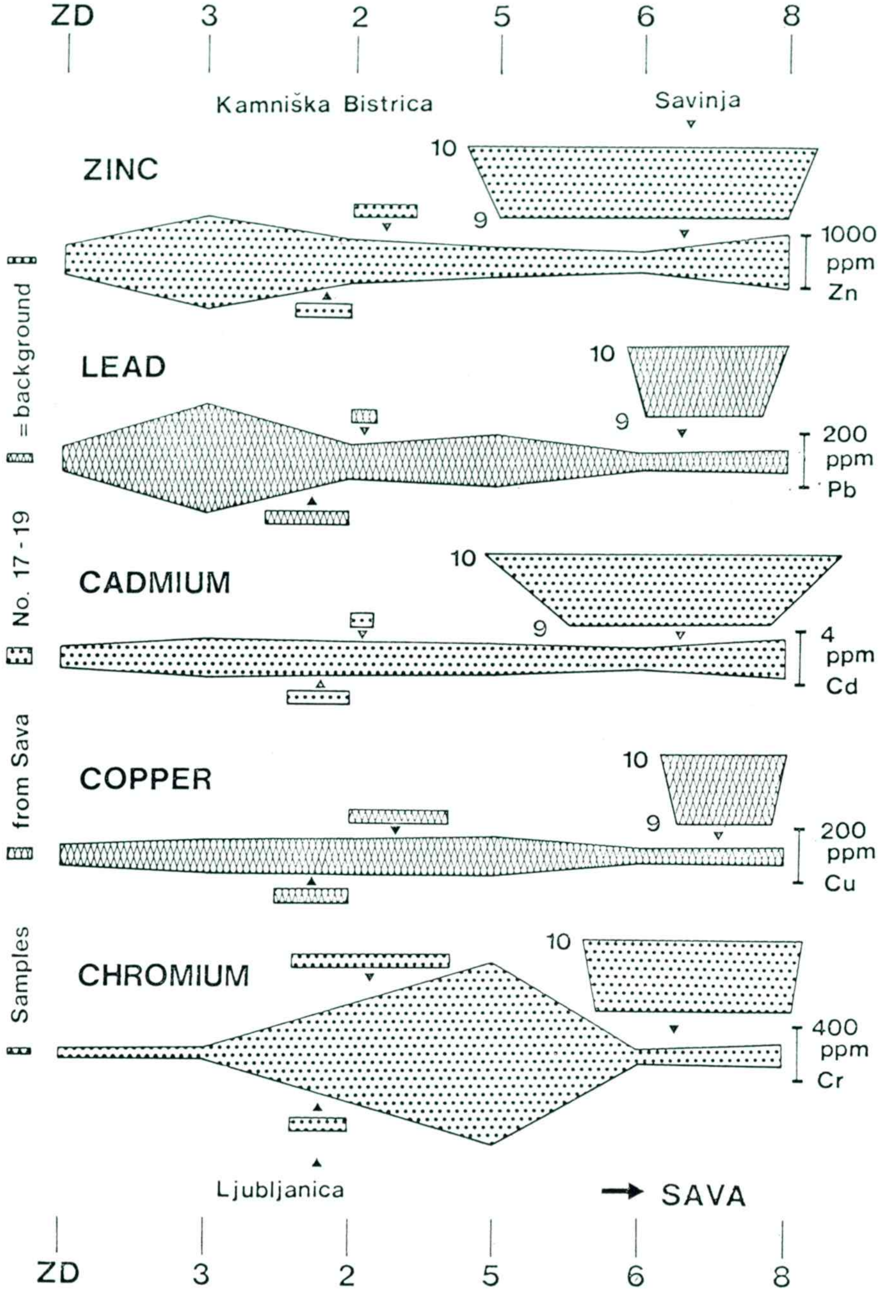

Fig. 2. Distribution of zinc, lead, cadmium, copper, and chromium in the pelitic sediments of the upper Sava and its most important tributaries

ment of the mercury content. This can probably be explained by the influence of the Kamniška Bistrica. The next sample, also from the Sava about 20 km downstream, stems from the right bank near the new bridge at *Hrastnik*. A strong »pollution« by brown coal components from the processing waters from the coal district of Zagorje—Trbovlje is typical for this section of the river. Instead of the expected enrichment, a characteristic »dilution« of the metal contents takes place, in the case of most metals — even those which are less exposed to pollution influences, such as iron, manganese and cobalt — of 50 to 70 %. Whether this is due to a mobilizing effect of the dispersed coal components on the sediments or due to dilution by lower metal contents in the coal particles, can not be determined here. The influence of an inaccurate separation of the pelitic fraction must also be taken into account since the specific weight of these particles is much less than that of the mineral substances. In the samples taken further downstream below the mouth of the Savinja at *Zidani Most* (S7) and *Radeče* (S8), a mixing of coal-containing sediment of the Sava with the heavily polluted sediment of the Savinja can be seen. Both samples exhibit very similar metal contents; only zinc, chromium, mercury and silver are significantly enriched.

One of the most heavily polluted waters in Slovenia is undoubtedly the *Voglajna,* which is the recipient of the total effluent from the metal-manufacturing and -processing industries as well as from the chemical industry of Celje. No life has been observed in this little river for several decades. The effluents from the old waste dumps of a zinc-works, from an iron-works near Štore, from a TiO_2-factory and an enamel pottery factory are assumed to be among the main contributors to the unusually high metal contamination in the Voglajna. A sediment sample (S11) was taken at the *Skalna Klet* site, just before the point where it empties into the Savinja, from the left bank of the industrial stream. Compared with the Sava background, the contents of zinc and chromium are enriched by a factor of 25 to 50. Only the zinc contents in the pelitic fraction reach 1.5 %. The increase of iron is also of note: the red mud contains 17.6 % Fe. Although there is a distinct decrease in the extreme metal contents, metal enrichments can still be observed in the samples from *Laško* (S10) and *Rimske Toplice* (S9) (the latter approx. 20 km below Celje) which are 10 (lead, cadmium) to 40 times (chromium, zinc) higher than the normal values.

5. Conclusions

Three groups of metals can be differentiated according to their mode of occurrence. (a) In the first instance are those which are influenced to a very small extent or not at all by civilizational influences. These include — with the exception of the example of the Voglajna sediment — the heavy metals iron, mangenese, nickel and cobalt. In some cases, a decrease of these contents can even be observed, particularly in the case of elevated carbonate contents in the samples. (b) The second group of metals, according to our data, is significantly enriched to a more or less large extent in all samples. Moderate rates of increase can be seen in the case of copper. Lead and cadmium are for the most part strongly enriched and relatively high enrichments can always be


Plate 1
LOCALITIES OF THE SAMPLING SITES
IN THE SAVA BASIN
10 5 0 10 20km
S1-11
S17-19 SAVA
1-16 MOSTE (MS)
Z1-Z6 ZBILJE
Sampling points
and sample Nb.
MOSTE DAM
Sampling points
0 500m
Artificial Lake
ZBILJE
Sampling points
0 500m
LOCATION
MAP
0 75 150 km
AUSTRIA
ITALY
HUNGARY
YUGOSLAVIA
KLAGENFURT
MARIBOR
CELJE
LJUBLJANA
ZAGREB
SPLIT
SARAJEVO
Drava
Sava
Javornik
Valjarna
Javornik
Lipce
Potoki
Moste
Završnica
Sava Dolinka
Zbilje
Zbiljsko jezero
Verje
Dovje
Hrušica
JESENICE
MOSTE DAM
Bled
Blejsko jez.
Bovec
Tržič
Kokra
Bohinjsko jez.
Sava Bohinjka
Bohinjska
Bistrica
Kobarid
Tolmin
Soča
Bača
Idrijca
Radovna
KRANJ
Kamnik
Kamniška Bistrica
Škofja
Loka
Sora
Polj. Sora
ZBILJE
Črnuče
Zalog
LJUBLJANA
Gradaščica
Šujica
Ljubljanica
Vrhnika
Borovnica
Iška
Ižčica
Grosuplje
Reka
Litija
Radomlja
Zagorje
Hrastnik
Laško
Rimske Toplice
Zidani most
Radeče
Sopota
Sevnica
Sevnična
Mirna
Temenica
Krško
Brežice
Sotla
Bistrica
Savinja
Ložnica
Žalec
Hudinja
CELJE
Štore
Voglajna
Dravinja
Mežica
Meža
Ravne na
Koroškem
Črna
SAVA
S1 S2 S3 S4 S5 S6 S7 S8 S9 S10 S11 S17 S18 S19
Z1 Z2 Z3 Z4 Z5 Z6

observed in the case of zinc. The evenly elevated contents of zinc may be attributed mainly to the influence of communal effluents (corrosion of the household pipe network). However, the effluents from the metal manufacturing and textile industries can also introduce high zinc concentrations into the water. (c) In the third group, which among other metals includes chromium, mercury, and silver, unusually strong enrichenmts can be observed in some places, whereas in most samples — particulary in the case of chromium — the concentrations are similar or even below the background level. This indicates the influence of industrial effluents, whereby the elevated chromium contents originate predominantly from the tanning industry.

Very high metal enrichments, particularly of zinc, lead, cadmium and mercury were found in the sediment of the Moste Dam, our primary investigation target. As had been expected, the present investigations were unable to determine to what extent these metals were responsible for the catastrophic biotope poisoning which occurred after the emptying of the Dam in autumn 1974 (and even on earlier occasions). Further investigations, especially on sediment cores and the corresponding pore water solutions would be necessary. Nevertheless, it is assumed that the interstitial water of the dam sediments, when suddenly released, can present a danger for the surface water not only because of its strong oxygen consumption but also due to its high proportion of soluble complexed heavy metals. Moreover, under changed physical-chemical conditions during the emptying of the dam, a release of metals from the sediments must also be expected. In reverse, however, the Moste Dam, if it did not need to be emptied periodically, would form a very effective means of protection against pollutants originating from the industrial region of Jesenice which are discharged into the downstream sections of the Sava river.

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