HEAVY METAL CONTENTS IN RIVER SEDIMENTS

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Abstract. Extensive sample material from river sediments of Carinthia (Austria) was investigated with regard to the contents of heavy metals that are relevant to the environment, Zn, Cd, Pb, Cu, Cr and Ni. The fraction < 20 μm was separated from the total sample to minimize the effect of grain size. The disintegration was done with aqua regia. The results were related to the geochemical data of the geological background. Therefore the amount of anthropogenic pollution due to industry and overcrowded areas was determined. Especially the influence of industrial emissions from Pb-Zn smeltings is shown by extremely high values of Zn (18 400 ppm), Cd (126 ppm) and Pb (7 540 ppm). The contents of Cu, Cr and Ni in the metamorphic rocks from the Central Alps represent the geogenic influences, but the high values from 200 to 300 ppm Cr refer to actions of industries producing highly refrectory materials and chemical industries. The results of the elements zinc and nickel are documented in maps.

1. Introduction

Since 1981 the department 15 U (environment) of the Carinthian government has conducted a survey about the rivers of the country. The results are published in the 'Kärntner Gewässergüteatlas' (Carinthian Atlas of Water Quality) (Honsig-Erlenburg *et al.*., 1990) (Figure 1).

So far the characterization and rating of the various waters and watersystems was done on the basis of biological and chemical-physical analyses (Polzer *et al.*., 1985). The study at hand is the first one to publish investigations of heavy metal contents in river sediments in Carinthia, and to show the results in maps.

Whereas the results of water analyses display only points of time and therefore vary considerably, investigations of sediments record the continuing filling of heavy metal over longer periods of time. It is now possible to determine the accumulative contamination of sediments by pollutants. Thus eventual effects on ecological systems can be measured.

The first basic investigation of this problematic area was concluded by Förstner and Müller (1974). The 'Upper Austrian Atlas of Water Quality' published investigations by Müller and Wimmer in 1987 concerning heavy metals in river sediments in Upper Austria.

In 1989 the 'Geochemical Atlas of Austria' appeared, presenting the results of analyses of river sediments of the Central Zone and the Bohemian Massif. As these samples of sediments were specifically taken from areas without industrial and communal immissions (waste water, sewage sludge, etc.) they reflect the geogenic background; therefore the heavy metal content of sediments represents the geological substratum of catchment areas. For example, high contents of Cr and Ni can be

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found in connection with metamorphic greenschists of the Glocknergruppe in the Hohe Tauern in the Northwest of Carinthia (see Figure 3). When compared to the present data of analyses the dimensions of the anthropogenic intrusions are more easily recognizable now.

Thus the maps show not only the present heavy metal contents of the river sediments but also the values of the geochemical background for each element in three graduations.

To rate the state of rivers the determination of pollutants turned out to be an important and necessary complement to the analysis of the aquatic environment (Müller *et al.*., 1989). Heavy metals, halogenated hydrocarbons, polycyclic aromatic hydrocarbons, radionuclides, and many other substances, partially of anthropogenic origin, are bound adsorptively or chemically in finegrained fractions of sediments. For that reason they are enriched in these fractions respectively detectable. Investigations of sediments therefore present a very good image of dimension and origin of the contamination of waters, but give no evidence of the present toxic contents of the water.

The pollutants are not only accumulated, but under different environmental conditions they can also become mobile again, respectively they can be brought into the food chain by means of benthosorganisms. Thus the sediment itself develops more and more into a source of pollutants.

So far special attention was directed to the heavy metals. On one hand this group of pollutants has already caused serious accidents and deaths which showed the particular danger of heavy metal containing mud. On the other hand investigations of sediments have always been the domain of geochemists and sediment-geologists whose traditional field of activity is more the area of inorganic chemistry.

These inorganic pollutants deserve special attentiveness because – in contrast to most of the organic ones – they cannot be decomposed. By way of mineralogical or organic preconcentration they can get into the food chain again and again.

The mobilization of heavy metals from sediment can be conducted by changes of the water chemistry (pH, redox conditions, etc.). Especially organic substances able to build up complexes are worth mentioning here, e.g. nitrilo-tri-acetic acid, which has recently been used as a substitute for phosphate in detergents. On the other hand, sediments could get onto agriculturally used areas through floods or excavations of reservoirs. At the same time metals that are originally sulphidic or organic bound in sediments free of oxygen are oxidized and thus available for plants.

'If muds containing heavy metal are excavated from reservoirs and brought onto agricultural areas the farmers run the risk of their products becoming garbage' (Müller, 1986).

At the moment there are no laws in Austria regarding permissible concentrations of heavy metals in sediments. For methods of disintegration respectively for the grain size used for analysis there are unfortunately no standardized guidelines, either. Thus the results of various investigations are hardly or only restrictedly comparable. A standardization of the methods as well as directions regarding maximum

TABLE I

Comparison of heavy metal concentration ranges for igneous rocks and sediments in the surveyed region with natural background values and several limiting factors (all values in ppm); after Thalmann, 1987 and ÖWWV-Regelblatt 17, 1984

	Natural occurence			Investigated area		Limits for		
	1	2	3	4	5	6	7	8
Cr	2 -3000	10 -90	5–300	5	330	0.05	0.05	500
Ni	5 -2000	2 -68	50–500	7	256	0.10	0.03	100
Cu	10 -87	4 -45	2–100	17	298	0.10	0.01	500
Zn	6 -19	21 -100	10–300	3	18400	3.00	0.10	2000
Pb	50 -105	7 -20	10	<1	10281	0.05	0.05	500
Cd	0.13–0.22	0.20–0.90	0.06	<1	126	0.005	0.001	10

1 Igneous rocks.
2 Sediments.
3 Soils.
4 Measured values, min.
5 Measured values, max.
6 Drinking water.
7 River water.
8 Sewage sludge.

permissible concentrations of heavy metals in sediments would be desirable. In the future organic pollutants and radionuclides should also be included in this concept.

For this study we analyzed the metals cadmium, lead, zinc, copper, chromium, and nickel. These heavy metals together with mercury are generally seen as relevant to the environment. Because of their frequency and their toxicity, they are taken into consideration in various norms and regulations (e.g. ÖWWV-Regelblatt 17, 1984, U.S. Environment Protection Agency).

2. Materials and Methods

It is already mentioned that the unstandardized treatment of samples at the various investigations causes many problems. At the moment different grain sizes are used for analyses. The use of fraction < 2 μm for pollutant-analyses which was initiated by Müller (1986) in Germany could not prevail. The clay fraction would be appropriate because of the high enrichment with pollutants, however, the problem of getting enough sample material, especially in alpine rivers, and the extensive preparation stand in the way. Especially with large series of samples these efforts seem no longer justifiable. For the work at hand the separation of fraction < 20 μm turned out to be a good compromise. Various concentrations of metals that are due to the use of different grain sizes can at least be compared approximately as there are analyses of the effects of grain size.

More problematic is the use of various disintegrations for the determination of heavy metal contents. Here comparisons of the results can only be seen as estimations. Since analyses of sediments were initiated by sediment geologists and geochemists – as mentioned above –, the complete disintegration was especially obvious and important for the delimitation anthropogenic/geogenic. The crucial question of the

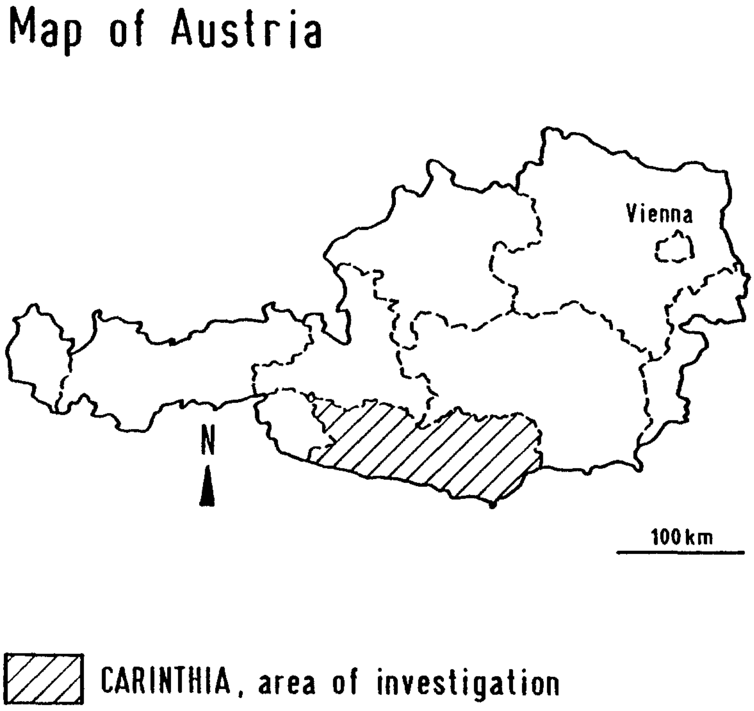

Fig. 1.

relevance to the environment is in which form the pollutants are bound and under which conditions they can be mobilized again. An example is the great difference between mercury sulphide and organic mercury compounds. Sequential steps of leaching (Kralik and Sager, 1986) to determine the mobility are first on the way towards a solution. For routine analyses of large series of samples the disintegration with aqua regio (HCl + HNO_3 3:1) could be a suitable method to record the contamination of rivers with heavy metals. This method is an internationally very common analytical procedure allowing comparisons with results of other investigations (Förstner and Müller, 1974; Förstner and Wittmann, 1983).

The sampling of sediments from the impounded sections of the Drau was part of the project 'Sedimentological and geochemical analyses of sediments in the reservoirs of power plants along the Drau', conducted in the summers of 1987 and 1988. The sampling was done from a drilling platform by means of a piston corer down to the former river bottom respectively to the former valley floor.

For the paper at hand the top 3 to 5 cm of the recent river sediments were analyzed. In addition more samples were taken near the bank with a cutting tube.

The analytical results of reservoir sediments shown in samples 11 - 17 (see Table III and Figures 2 and 3) are average values up to 36 single samples.

The sampling from Carinthian rivers was done in September 1988 corresponding with the sampling places of the expanded net of major measuring places of the

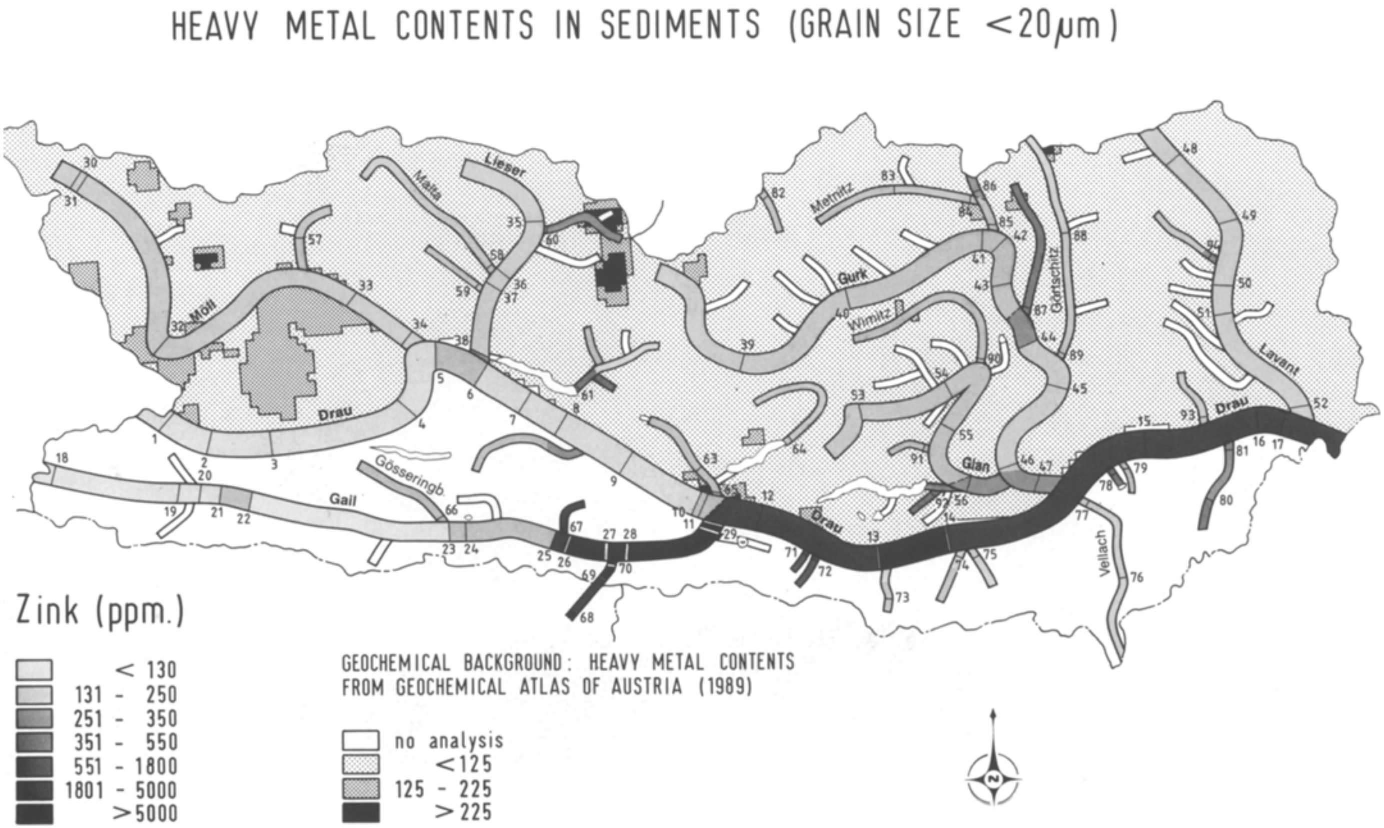
HEAVY METAL CONTENTS IN SEDIMENTS (GRAIN SIZE <20μm)
Möll
Malta
Lieser
Drau
Gail
Gösseringb.
Metnitz
Gurk
Wimitz
Glan
Görtschitz
Lavant
Drau
Vellach
Zink (ppm.)
< 130
131 - 250
251 - 350
351 - 550
551 - 1800
1801 - 5000
>5000
GEOCHEMICAL BACKGROUND: HEAVY METAL CONTENTS
FROM GEOCHEMICAL ATLAS OF AUSTRIA (1989)
no analysis
<125
125 - 225
>225

Fig. 2.

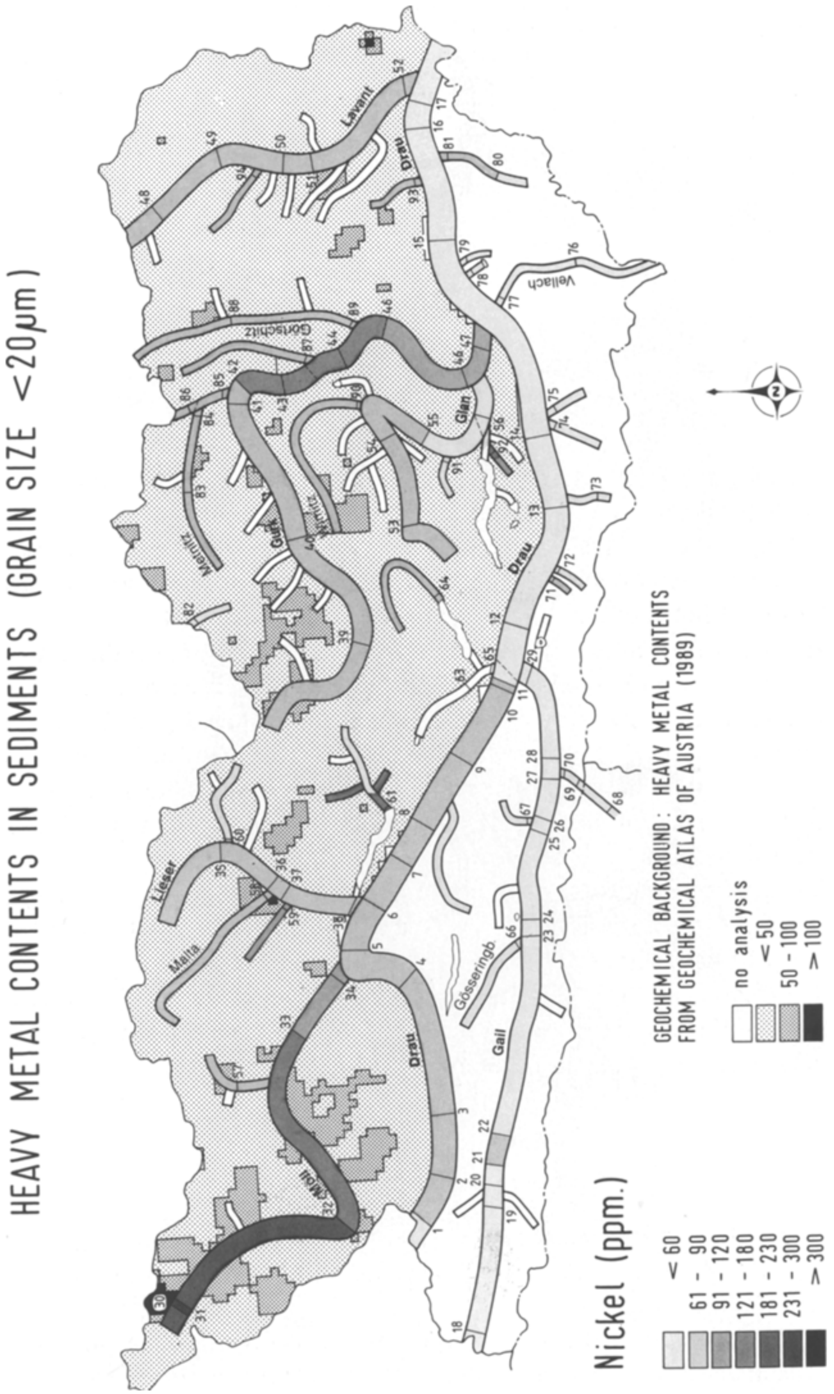
HEAVY METAL CONTENTS IN SEDIMENTS (GRAIN SIZE <20 μm)
Nickel (ppm.)
< 60
61 - 90
91 - 120
121 - 180
181 - 230
231 - 300
> 300
GEOCHEMICAL BACKGROUND: HEAVY METAL CONTENTS
FROM GEOCHEMICAL ATLAS OF AUSTRIA (1989)
no analysis
< 50
50 - 100
> 100
Drau
Gail
Möll
Lieser
Malta
Gurk
Glan
Lavant
Görtschitz
Vellach
Metnitz

Fig. 3.

TABLE II

Reference samples, mean and reproducibility

		Zn	Cd	Pb	Cu	Cr	Ni
Labor stadard 171							
Number of determinations	n	73	70	73	73	73	43
Mean	x	2168±115	14.18±0.85	845.8±57.9	67.9±4.7	108.6±8.15	48.0±3.82
Reproducibylity	%	±5.3	±6.0	±6.85	±6.9	±7.5	±7.95
Labor stadard D4							
Number of determinations	n	65	25	42	60	60	60
Mean	x	82.02±14.08	0.87±0.44	30.02±2.68	42.1±1.86	40.11±1.6	41.1±2.07
Reproducibylity	%	±17.2	±50.6	±8.9	±4.42	±4.0	±5.04

Carinthian institute for lake research. Additional sampling was conducted in September 1989 (samples No. 95-106, not numbered in the maps).

The sampling of recent fine-grain sediments was done with a cutting tube respectively with a plastic spoon. Subsequently the sample material was put into leakproof bottles of polyethylene and kept cool until it was analyzed.

In the laboratory the samples were wet-sieved through a 20 μm synthetic sieve with bi-deinonized water. The run 20 μm was dried in the drying box at 105 °C and then homogenized in an agate bowl. For the disintegration 1 g of the sample was moistened with 2–3 mL water, then mixed 15 mL HCl and 5 mL HNO_3 and left over night. After a warming period of half an hour the disintegration was done at 105 °C. It lasted for an hour. In each series 18 samples and tow reference samples were disintegrated.

After cooling the sample solutions with their residues were transferred into a 100-mL-measuring flask and filled up to 100 mL with 2 n HNO_3. After filtration the measuring of heavy metals was conducted with a plasma emission instrument (DCP by Spectrometrics). The reproducibility of the disintegration and the measurements was confirmed through reference samples. The elements Pb, Zn, Cu, Cr, Ni were measured by the multi-element-method, the element Cd by single measurement.

3. Results and Discussion

The complete results of the survey are listed in the following tabulation.

As examples the heavy metals zinc and nickel are presented in maps, seven steps of concentration can be distinguished.

To record the relations to the geogenic background with regard to the region the data of the analysis acquired within this study, they were compared with those from the Geochemical Atlas of Austria (Thalmann, 1987). As these data are at

TABLE III

Heavy Metal Contents in River sediments (ppm). The sample numbers correspond to the locations cited in the maps

No.	Zn	Cd	Pb	Cu	Cr	Ni
1	109	<1	29	62	55	56
2	129	<1	49	111	56	79
3	110	<1	40	85	57	65
4	117	<1	37	85	66	72
5	122	<1	38	96	70	80
6	162	<1	54	90	64	75
7	119	<1	37	98	81	89
8	108	<1	30	78	78	76
9	99	<1	32	62	63	63
10	123	<1	41	79	60	73
11	227	11	73	93	78	78
12	2528	29	1526	72	58	43
13	2538	21	1600	68	51	48
14	5070	25	1850	69	54	48
15	2417	15	1021	70	89	49
16	4130	14	1480	80	79	50
17	2315	16	566	71	127	54
18	49	<1	2	48	38	46
19	121	1	31	49	57	56
20	35	<1	<1	51	33	45
21	130	2	38	48	32	49
22	184	2	56	70	36	67
23	3	<1	<1	29	22	29
24	164	1	64	75	47	60
25	151	1	52	62	39	54
26	3240	13	3910	116	49	37
27	7760	25	1780	82	36	22
28	8630	34	2520	83	35	20
29	7290	31	5130	108	30	15
30	156	1	58	133	136	227
31	151	1	65	148	144	256
32	232	1	91	162	107	215
33	206	1	83	117	82	121
34	202	<1	77	110	81	107
35	217	1	75	85	59	76
36	198	2	65	80	49	68
37	200	<1	77	70	50	61
38	253	1	88	79	60	73
39	159	1	49	60	80	74
40	156	1	52	60	68	66
41	188	<1	62	71	77	69
42	203	1	93	89	77	81
43	219	1	84	83	202	133
44	266	2	132	90	220	157

Table III (Continued)

No.	Zn	Cd	Pb	Cu	Cr	Ni
45	246	2	103	88	160	126
46	202	1	85	77	125	106
47	293	1	97	80	159	101
48	176	1	70	76	74	86
49	155	1	65	72	70	75
50	187	<1	139	101	66	79
51	173	1	128	89	85	73
52	171	1	81	79	84	70
53	243	<1	75	73	93	69
54	204	1	62	79	132	85
55	217	<1	55	64	108	68
56	290	1	106	86	148	58
57	182	1	112	95	32	72
58	149	1	52	79	60	58
59	178	2	67	56	107	157
60	340	4	198	51	34	47
61	460	2	475	77	330	67
62	256	1	83	29	22	24
63	207	2	64	88	63	80
64	216	1	71	70	56	61
65	198	1	63	79	66	77
66	227	2	98	59	42	48
67	4800	13	4770	37	21	11
68	18400	36	7540	286	5	7
69	3600	7	911	34	35	23
70	17600	126	7190	148	41	31
71	699	1	48	33	69	75
72	773	<1	21	24	51	43
73	93	<1	28	20	50	43
74	129	1	105	18	17	16
75	109	1	31	17	25	23
76	140	1	53	34	24	36
77	160	1	96	35	26	40
78	408	3	61	78	43	30
79	174	<1	65	33	55	30
80	394	2	301	52	61	47
81	255	1	186	56	72	64
82	143	1	58	29	36	45
83	162	1	46	85	59	82
84	174	1	67	90	66	80
85	208	<1	77	83	75	81
86	281	1	112	96	91	88
87	391	2	254	90	130	87
88	239	1	124	94	76	88
89	216	1	88	90	68	85
90	205	1	123	65	79	76

Table III (Continued)

No.	Zn	Cd	Pb	Cu	Cr	Ni
91	249	1	74	70	73	57
92	280	2	621	68	61	41
93	157	1	51	69	95	74
94	251	2	93	113	69	88
95	459	0.89	209	298	71	134
96	189	0.92	<1	33	50	53
97	454	1.27	117	132	295	145
98	129	0.59	3	35	37	37
99	249	1.25	104	107	94	124
100	385	1.69	48	108	94	125
101	515	1.55	229	106	82	101
102	485	2.12	155	134	201	132
103	344	1.09	83	78	63	72
104	151	<0.1	<1	49	53	68
105	215	0.46	10281	58	73	43
106	173	0.57	181	18	55	26

present only from the Central Zone north of the Drau only those areas could be included into the graphic representation.

The data normally used as standards for the geogenic background (Turekian and Wedepol, 1961) for most of the analyses of river sediments published so far (by Förstner and Müller, 1974; Förstner and Wittman, 1983) are hardly suitable for alpine river systems. Even in small parts the corresponding catchment areas are extreaordinarily heterogenous with regard to their geochemical compound. It would be necessary to find out specific background values for the different river sections (Steffen, 1989).

Due the the lack of regional geochemical data in previous studies only the results of Turekian and Wedepol (1961) were available. For the present study it was possible to compare directly the real heavy metal contents of the river sediments with the existing background data of the Geochemical Atlas of Austria (Thalmann, 1987) and to present these results in maps.

The following results of analyses by other authors are only relatively comparable due to the use of different grain fractions.

3.1. Zinc (Figure 2)

The high concentrations of zinc (up to 18 400 ppm) in the sediments of river Gail and tributaries refer to geogenic and anthropogenic influences. The geogenic burdens originate from Pb – Zn mineralizations of the immediate surrounding, while the anthropogenic from ore dressings and smeltings. Also for sample 60 a geogenic attribution is proved definitely.

If compared with international analytical values (Rhine 2000 ppm at maximum, Elbe up to 2450 ppm; Förstner and Müller, 1974) no similarly high concentrations could be found anywhere except in an Upperaustrian river (33 200 ppm; Müller and Wimmer, 1987).

3.2. Cadmium

The highest burdens of Cd were proved in the lower section of river Gail and tributaries (up to 126 ppm) continuing in the river Drau down to the border of Austria. The reasons of these high concentrations are also geogenic and anthropogenic influences. The content of 4 ppm in sample 60 is relating to mineralizations in the catchment area.

Similarly high values as in river Gail were found only in sediments of river Neckar (88 ppm; Förstner and Müller, 1974).

3.3. Lead

The high concentrations of lead (up to 10 281 ppm) in the sediments of the lower Gail and the Drau downstream of Villach (where river Gail flows into river Drau) are due to the mining industry and to ore smelting. The majority of this heavy metal appears as lead sulphide (PbS) and as lead carbonate ($PbCO_3$) in the river sediments; these minerals could be proved by means of x-ray analyses.

Similarly high results could not be found in any other European river. Normal values in the Austrian part of the Danube are maximum 171 ppm; in the Rhine they are maximum about 500 ppm (Förstner and Müller, 1974).

Higher contaminations in other Carinthian rivers are mostly due to geogenic sources. The samples 80 and 81 refer to Pb-mineralizations in the Karawanken mountains in the south of Carinthia, samples 60 and 87 to mineralizations in the Central Alps. The vast majority of river sediments shows values of lead below 100 ppm.

The conditions for zinc and cadmium are very similar to those for lead.

3.4. Copper

The Cu-concentrations of river sediments are corresponding mainly due to geogenic influence. The highest values are found in the catchment area of river Möll with 198 ppm originating from the geochemical composition of the metamorphic greenschists of the Hohe Tauern (samples 30 – 33, 95).

Higher anthropogenic burdens (tributary of river Gail with 286 ppm) are frequently exceeded in other European rivers (Elbe 1 250 ppm, Rhone 700 ppm, Rhine 400 ppm after Förstner and Müller, 1974).

3.5. Chromium

Also the higher Cr-contaminations in the sediments of river Möll (samples 30, 31) refer to the chemical composition of the metamorphic rocks of Hohe Tauern.

The highest Cr-values of 295 and 300 ppm (samples 61 and 97) are connected with industries producing highly refractory materials, the higher loads of Cr in the samples 43 and 44 (202, 220 ppm) are related to chemical industries.

Essentially higher Cr-contaminations are found in the sediments of river Rhine with 1195 ppm, of river Neckarwith 790 ppm and of river Elbe with 770 ppm (Förstner and Müller, 1974).

3.6. Nickel (Figure 3)

The larger part of the Carinthian river sediments shows low contents of nickel with values below 90 ppm. In a few areas there are higher loads of nickel because of the geological substratum, e.g. green metamorphic rocks of the Großglockner area (Möll valley) with values up to 256 ppm. Higher geogenic and anthropogenic fillings up to 157 ppm are found in the sediments of river Gurk.

Average values of Danube-sediments in Austria are between 46 and 83 ppm, extremely high values are found in the rivers Wupper - 883 ppm - and Rhine - 416 ppm (Förstner and Müller, 1974).

More details and results of analyses regarding the contamination of rivers in Carinthia can be found in the Kärntner Fließgewässergüteatlas 1987 - 1989.

4. Conclusion

Six heavy metals relevant to the environment were analysed in sediments of rivers and impoundments in Carinthia. The aim of these investigations was the attribution of more highly contaminated sediments to anthropogenic pollutions. Higher levelled values not corresponding with such emittents were referred to geogenic influences from parent rocks of the catchment areas.

Data from the Geochemical Atlas of Austria (Thalmann, 1987) could be used as a basis for interpreting the results of the present study. Therefore it was possible to distinguish regionally adjacent areas with different contents of heavy metals. This method has proved successful in alpine investigation regions to find out essential emittents. Extremely high contaminations with Zn, Cd and Pb refer to smelting industries in the lower part of Gail valley and these pollutants could be proved hundred of kilometers downstream. The high values of Cr (partly also Cu and Pb) of samples 61 and 97 are due to industries producing highly refractory materials, Cr- and Ni-values in the sediments of river Gurk to chemical industries.

Acknowledgement

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