

Geochemical ATLAS

Federal Republic of Germany

Distribution of heavy metals in waters and stream sediments

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Notes on the digital provision of the texts

The texts provided in this document are the original texts from the paper edition of the "Geochemical Atlas of the Federal Republic of Germany" published in 1985 by the Federal Institute for Geosciences and Natural Resources. The content of the texts has not been changed from the original edition. The translation from German into English corresponds to that published in the 1985 paper edition¹. Editorial notes have been added to document and explain the differences between the paper edition of 1985 and the electronic version. These editorial comments are inserted as footnotes in each case.

The digital processing and provision was carried out by U. Rauch, Federal Institute for Geosciences and Natural Resources, Branch Office Berlin, Wilhelmstrasse 25-30, D-13593 Berlin, Email: uwe.rauch@bgr.de. Questions regarding the digital processing and provision of the Geochemical Atlas Federal Republic of Germany as well as questions regarding the content of this atlas should be directed to geochemischeatlanten@bgr.de.

¹ There is no title page translated into English in the paper edition. This was generated retrospectively for the digital provision.

Foreword

The Geochemical Atlas is intended not only to contribute to the protection of the environment but is also to be used for locating new mineral deposits.

Since 1958, the Institute for Geosciences and Natural Resources has been carrying out geochemical prospecting for heavy metals involving analyses of water, stream sediments and soils. The results of these surveys, apart from yielding information about metalliferous mineralization, showed up indications of environmental pollution. In 1977, a systematic multi-element geochemical survey of the entire Federal Republic of Germany (FRG) was started. It covered the prospective areas as well as those areas contaminated with heavy metals. Thus, the current state of heavy-metal contamination is now documented and, for the first time, heavy-metal abundances in waters and stream sediments throughout the FRG can be compared.

The geochemical survey located all the larger areas of natural and historical anthropogenic contamination in the FRG. However, the pollution of very recent origin due to dust, smoke and contaminated precipitation is probably only partially documented by this survey, since this kind of pollution, depending on the local conditions, is initially resorbed, buffered, or accumulated by the soil before it can be detected as an anomaly in stream waters and sediments.

In a country like the FRG, which has a mining tradition going back several centuries and which is relatively well known geologically, it was unlikely that any new deposits of lead, copper, zinc, barite or fluorite would be located by this geochemical survey. In contrast, indications were found, as might have been expected, of accumulations of those rarer elements, such as uranium and tungsten, which have been very actively prospected for during the last several decades. The comprehensive computer-based database GEOMULDAT (GEOchemical MULti-element DATafile), which permits rapid access to extensive detailed information, was established for this project. This can be used to produce lists or maps at any scale and enables statistical analysis of the geochemical data to be carried out, as well as correlation with a wide range of information from mineral exploration, environmental research, public health agencies, and hydrological records. To ensure that optimum use is made of GEOMULDAT data, access will be given to commercial companies, universities, and local government.

Finally, the Atlas is intended to stimulate multidisciplinary research on the factors governing the distribution of trace elements in nature. This is of vital importance in connection with the increasing amount of pollution of our environment, e.g. in the public health field or for improving plant cultivation and animal breeding.

The publication of the Geochemical Atlas was made possible by financial support from the Federal Ministry of Research and Technology. The work was also supported by the Geological Surveys of the Federal States, by local government departments, forestry offices and many other organizations.

I am greatly indebted to all those who have contributed to this project.

A handwritten signature in black ink, appearing to read 'F. Bender'. The signature is written in a cursive style with a large initial 'F'.

(Prof. Dr. F. Bender)

President of Federal Institute for Geosciences and Natural Resources

Hannover, March 1985

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1. Introduction

1.1. General

For the past 60 years geochemical mineral exploration has involved trace-element analysis of rocks, soils, stream sediments, waters and plants with the aim of using elevated concentrations (anomalies) of certain elements to detect mineralized areas. In the early days, geochemical prospecting was usually confined to analysis of a few elements over small areas. In the Federal Republic of Germany, geochemical exploration has been carried out mainly for uranium, lead, copper, zinc, barite, and fluorite. More experience and the introduction of automatic methods of analysis and data processing has now made it possible to carry out exploration for several minerals simultaneously over large areas. Elevated concentrations of chemical elements (anomalies) are not only a reflection of the nature and composition of the ground, but can also give evidence of pollution due to human activity.

The Geochemical Atlas of the Federal Republic of Germany, which contains 62 maps, can be used both for environmental problems and in the search for mineral deposits. Compilation of the maps necessitated the collection and analysis of about 80,000 stream sediment and water samples. The water samples were analysed for 10 different parameters in a mobile laboratory in the field; the stream sediments were sent to the BGR laboratory in Hannover, where they were analysed for 30 elements using various methods.

All the data is stored on magnetic tape or discs and can be recalled in the form of computerized lists, maps (black-and-white or coloured) and statistical plots. This means that detailed data can be obtained that is not contained explicitly in the Geochemical Atlas.

For reasons of format, the geochemical maps in the atlas have been printed at the scale of 1:2,000,000 and consequently it was not possible to depict the individual results¹. The entire area of the Federal Republic of Germany has therefore been subdivided on the basis of a 3 x 3 km grid. For each grid square, the median and/or maximum¹ value for all the samples in the square was calculated and plotted. Normally, the values were arranged into six empirical classes. As a rule, elements with a smaller number of classes show a large proportion of values below the limits of detection.

¹ Due to the digital provision of zoomable maps via GIS as well as the further development of printing technology compared to 1985, it was now possible to present the measured values individually for the digital provision of the Geochemical Atlas of the Federal Republic of Germany. Therefore, the calculation of the maximum values of the grid cells as well as their three-dimensional columnar representation has been omitted in the digital edition. They were replaced by point maps of the individual values, from which the maximum values are also recognisable. In addition, the digital edition contains colour shaded contour maps with 72 classes, from which both the levelling of the geochemical background and the distribution of elevated and anomalous contents are recognisable in more detail than from the maps of the 1985 print edition.

The results are depicted firstly using colours on a map. In addition, maximum values are plotted using a three-dimensional columnar representation on the map¹. Use of both these maps together with the median and maximum values permits them to be employed to their best advantage for further geochemical prospecting and/or for environmental problems.

To obtain truly natural concentrations, the upper reaches of streams, as well as wells and springs were sampled since they were less likely to have anthropogenic contamination. Samples collected from polluted rivers permit the amount and nature of pollution to be assessed.

1.2. Sampling and sample preparation

The samples were collected between May and September from 1977 to 1983. As a rule, the weather was not taken into consideration. Only during extreme weather conditions such as severe gales or thunderstorms was sample collecting interrupted. In the upper reaches of streams the water became clear relatively quickly after heavy rainstorms and no significant changes in the composition of the water were detected. The sampling sites were chosen using 1:25,000 topographic maps. The sites were selected to be as random as possible so that no one geological unit would be given preference. Industrial and residential areas (e.g. the Ruhr District, the Rhine-Main area, and Berlin) were not sampled.

Three field units were involved in sample collecting. At each sample site, one litre of stream, well or spring water was collected in a polyethylene bottle and about 500 g stream sediment in a kraft paper envelope. If the stream sediment was too coarse, it was sieved on site and the < 2-mm fraction retained as a sample.

At each site the width, depth and flow velocity of the stream were entered on a field-data card; any evidence that local contamination might be present was noted. The conductivity and pH of the water were also measured on the same day the samples were taken.

The water samples were analysed in a mobile laboratory, parked in each case in the middle of a 3000 - 4 000 km² working area. The stream sediment samples were dried in a drying cabinet at 90°C.

In Hannover, the sediment samples were split; one half was kept for reference and the other sieved to < 0.200 mm (80 mesh). About 2 g of the fine fraction was then ground to < 0.03 mm in an agate microgrinder.

After sieving and grinding, some of the material was kept for reference, although in some cases (about 5 % of all samples) the material was completely used up for repeat analyses.

At 6000 of the sites, two more samples were taken as a check; these duplicate samples were subjected to the same preparation procedure as described above.

¹ See footnote on previous page.

1.3. Analytical methods

In 1976, the analytical equipment available to carry out the large number of analyses envisaged were an optical emission spectrometer (Jarrell-Ash Atomcomp 750) as the main instrument, an atomic absorption spectrometer (IL 751), a photometer, and a fluorimeter.

During the course of routine analysis with the optical emission spectrometer, however, it became apparent that due to matrix effects (the matrix of the sediment was difficult to evaluate), overlapping of lines, deflagration, and formation of carbides, the reproducibility was inadequate for the following trace elements Ag, As, B, Be, Bi, Cd, Ce, Ga, Ge, La, Li, Mo, Mn, Nb, Sb, Sc, Sn, W, Y, Zn, and Zr. Only the Ba, Co, Cr, Cu, Ni, Pb, Sr, and V analyses were sufficiently accurate.

It was then decided to carry out the bulk of the analyses with the atomic absorption spectrometer since this produced considerably more reliable results for Cd, Cu, Co, Ni, Pb, Zn, and Li dissolved by acid digestion, and for Sn using a special method of digestion. These AA analyses were used for the compilation of this Atlas; the optical emission data were used only for the elements Ba, Cr, Sr, and V.

F, U and W were determined using potentiometric, fluorimetric, and photometric methods, respectively.

All the methods were employed throughout the entire 7-year duration of the program in spite of the fact that improved techniques became available (e.g. ICP).

The detection limits and errors for the individual elements are given in Figures 1 - 3.

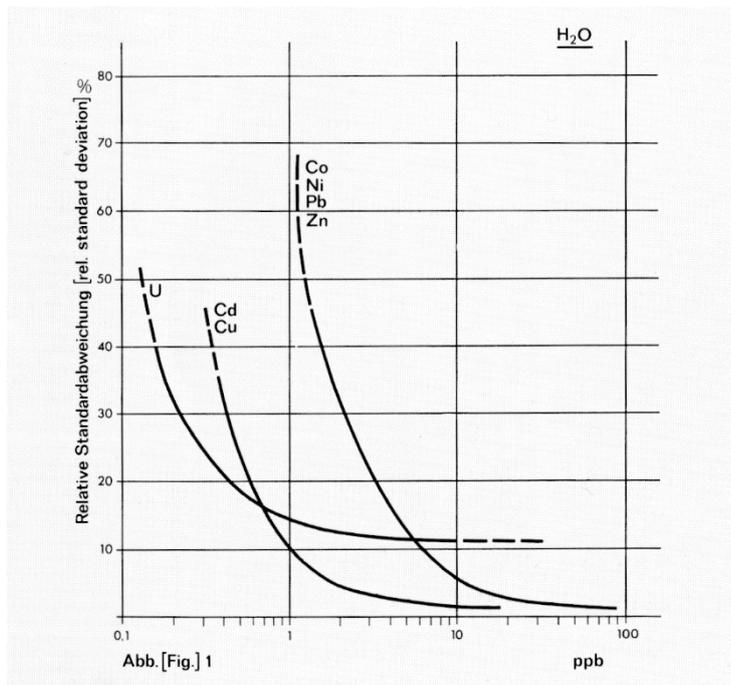


Figure 1. Analytical error (% rel. standard deviation in relation to the value), water

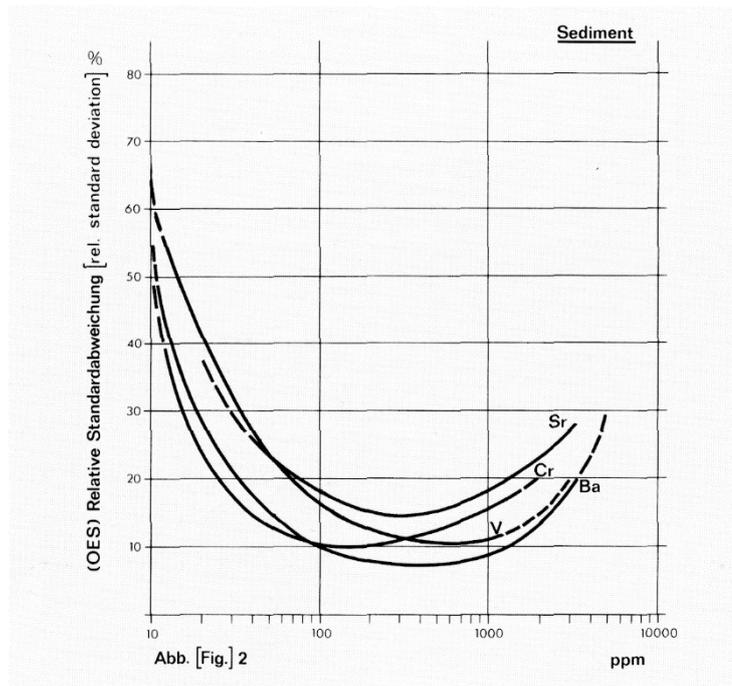


Figure 2. Analytical error (% rel. standard deviation in relation to the value), sediment, OES

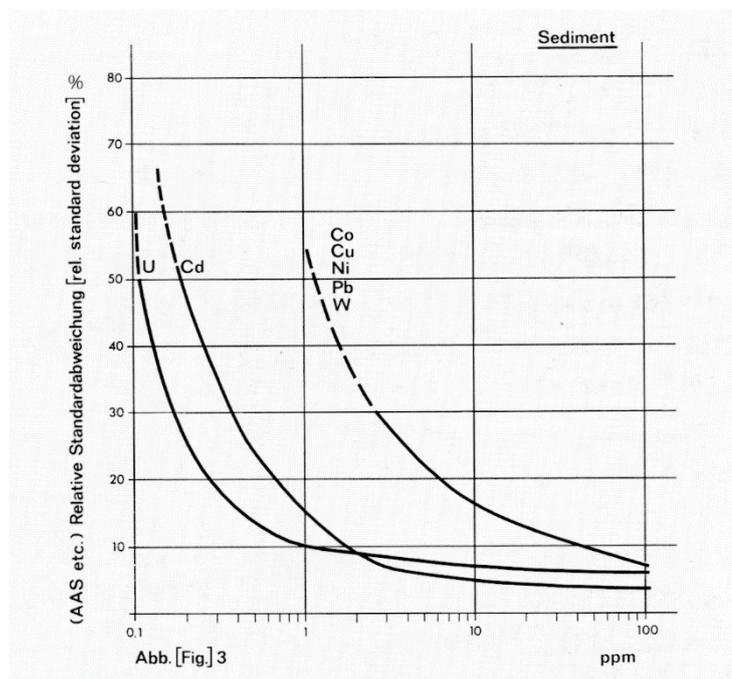


Figure 3. Analytical error (% rel. standard deviation in relation to the value), sediment, AAS e.t.c.

Trace elements in water

Cd, Cu, Co, Ni, Pb, and Zn ions were extracted from 400 ml water with dithizone/butyl acetate and determined by atomic absorption spectroscopy. Uranium was extracted from 100 ml water with tri-n-octylphosphinic oxide/cyclohexane and determined by fluorimetric analysis. Fluoride was analysed in 10 ml water using an ion selective electrode.

Trace elements in stream sediments

Ba, Cr, Sr, and V were determined using an optical emission spectroscopy quantometer on the lines 455.4, 424.5, 460.7 and 437.9 nm, respectively.

For Cd, Co, Cu, Ni, Pb, and Zn, the sample was first digested in 7 N HNO₃ (for Sn the sample was sub-limed with NH₄I) and then analysed by atomic absorption spectroscopy.

After acid digestion, U and F were determined in the same way as for the water samples.

For W, the sample was digested using HCl-HClO₄ and determined as a dithiol complex by photometry.

In most cases, the analytical measurements were stored by an online computer.

1.4. Statistical analysis

1.4.1. Statistical parameters for the stream sediments and waters

The huge amount of data (about 3 million single pieces of data) which was used for the geochemical atlas was subjected to statistical analysis.

Table 1 shows the statistical parameters such as the maximum and minimum values, geometric mean, median, and the number of samples. The median is the value that separates a spread of values into two parts of 50 % each. In comparison with the arithmetic mean, the median is not influenced by extreme values.

The geometric mean is often used for the interpretation of geochemical data. These values are listed in Table 1.

The values less than the analytical detection limit were treated statistically as if they were equal to half the detection limit (e.g. fluoride values < 100 ppb in water samples were set to 50 ppb).

These statistical parameters were calculated for the whole of the Federal Republic of Germany and for subareas defined on the basis of the geology. But only 60 % of the samples could be assigned to a specific source area on the basis of the geological maps.

In addition, statistical parameters were determined for river sediments and river waters.

The element abundances in stream sediments clearly reflect the influence of different geological and lithological units. Stream sediments derived from source areas consisting of Carboniferous strata have distinctly higher lead, zinc, cadmium, and lithium contents than stream sediments from other geological or lithological units. The highest median values for copper, nickel, vanadium, and chromium occur in stream sediments derived from basic igneous rocks, whereas the highest median values for uranium and fluoride occur in areas of acid igneous rocks. Stream sediments from the Buntsandstein are in most cases characterized by low element abundances.

The influence of the geology or lithology on the composition of stream waters is negligible except in the case of zinc and uranium. Zinc shows a distinctly higher median value (14 ppb) over Quaternary deposits than over Permian, Alpine Triassic or metamorphic rocks (median

5 ppb). The highest median value for uranium (0.9 ppb) is that for Keuper areas, compared to 0.1 ppb in the Buntsandstein and the Devonian.

To avoid misinterpretation during evaluation of element abundances in stream sediments, as well as in waters, it is important to consider the natural abundances of the elements in the local rocks.

1.4.2. Determination of errors in the measured values

In order to check the analytical results, about 6000 sites were resampled in duplicate. Table 2 shows how many (in %) of the duplicate samples belong to the same class and how many differ by one or more classes.

The same calculation was carried out for all values above the lowest class and these results are given in brackets in the same table.

According to this calculation, 97.4 % of the duplicate analyses differ by 1 class or less; the results can be considered sufficiently accurate for interpretation. However, it is recommended that important samples be checked before being used as a basis for expensive follow-up investigations. The correctness of individual values cannot be guaranteed since only some of the results have been checked.

1.5. Presentation of the results

The data obtained during the multielement geochemical survey of the Federal Republic of Germany are represented on 1 : 2,000,000 maps using a 1.5 mm grid and, in general, six colours¹. This means that

- depending on the sampling density, there are up to 20 samples in each grid square (9 km² each) for which the arithmetic mean and the maximum value are shown;
- the results have to be grouped so that they can be represented with six colours (pH and conductivity with ten colours). Areas in which no samples were taken are left white.

For the grouping of the measured values, the two class boundaries (85 and 95 percentiles) above the 50 percentile value, i.e. median, were chosen in such a way that each roughly represents one standard deviation. Since the values above these limits are defined as anomalous, the next two class boundaries (99.0 and 99.9 percentiles) are closer together in order to achieve better resolution of the results in this critical range. However, if, as with some elements, a high percentage of the values were below the analytical detection limit, then the lowest class boundary was moved up one class. In spite of this, when rounded numbers were used (e.g. 1, 5, or 10), spurious groupings may appear even well above the detection limit due to a lack of precision; these may cause serious distortion in the histograms and cumulative frequency curves.

¹ The digital provision of the Geochemical Atlas of the Federal Republic of Germany 2022 contains further presentation variants, which are described in chapter 2.3.

Table 1. Statistical data

remarks	① number of samples								② minimum value								③ maximum value								④ geometric mean								⑤ median							
	Stream waters ppb																Stream sediments ppm																							
Geology	Cd	Co	Cu	F	Ni	Pb	U	Zn	Ba	Cd	Co	Cr	Cu	F	Li	Ni	Pb	Sr	U	V	W	Zn	Sn																	
Quaternary	①	15638	15661	15665	15606	15663	15662	15680	15642	13759	13917	13917	13759	13918	13796	11413	13917	13918	13759	13892	13759	5696	13918	801																
	②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	20	< 0.3	< 5	< 5	< 5	< 20	< 3	< 5	< 5	< 0.1	< 3	< 2	< 5	< 1																	
	③	8.7	321	1500	3000	469	410	68	11000	10000	22.2	255	1797	540	800	66	270	23000	1342	17.7	546	28	3040	450																
	④	0.3	1	1.8	90	2	2	0.2	14	308	0.5	7	35	6.8	28	6	11	18	68	0.3	19	1	36	1																
	⑤	0.3	1	1.9	84	3	2	0.2	14	305	0.6	5	38	4.9	41	6	10	21	67	0.3	26	1	39	1																
Tertiary	①	1149	1149	1149	1142	1149	1149	1149	1149	1053	1063	1064	1053	1064	1062	996	1064	1064	1053	1064	1053	1055	1064	88																
	②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	86	< 0.3	< 5	5	< 5	< 20	< 3	< 5	< 5	12	< 0.1	5	< 2	10	< 1																
	③	3.6	37	81.3	800	57	66	45.5	353	997	3	65	479	365	460	33	160	140	819	9.1	274	4	750	94																
	④	0.4	1	1.6	68	1	1	0.4	6	243	0.2	12	58	9.2	45	7	20	24	112	0.5	44	1	39	2																
	⑤	0.3	1	1.5	47	1	1	0.5	6	233	0.1	13	59	8.7	49	6	22	24	122	0.5	46	1	38	1																
Cretaceous	①	548	548	548	548	548	548	548	548	507	509	509	507	509	500	302	509	509	507	506	507	369	509	68																
	②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	43	< 0.3	< 5	15	< 5	< 20	< 3	< 5	5	< 0.1	5	< 2	5	< 1																	
	③	3.6	36	54	800	53	32	14.5	760	950	9.3	160	1147	70	800	33	330	1700	1248	3.6	202	4	2655	38																
	④	0.3	1	1.1	78	2	2	0.1	10	262	0.4	16	65	12.6	33	12	28	32	115	0.3	52	1	73	2																
	⑤	0.3	1	1.1	47	2	1	0.1	8	260	0.3	16	65	10	45	11	28	31	133	0.3	56	1	67	1																
Jurassic	①	2398	2398	2395	2397	2398	2396	2399	2398	1994	2028	2029	1994	2029	2004	1729	2029	2029	1994	2021	1994	1848	2029	400																
	②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	34	< 0.3	< 5	6	< 5	< 20	< 3	< 5	< 5	< 0.1	< 3	< 2	5	< 1																	
	③	5.7	19	55.8	700	240	30	13	940	10000	16.8	100	1463	205	460	48	1230	540	8100	4.4	196	10	990	30																
	④	0.4	1	1.1	94	2	2	0.3	7	256	0.5	15	65	10.7	29	9	25	29	67	0.3	43	1	56	1																
	⑤	0.3	1	1	85	2	2	0.3	8	256	0.5	15	66	9.4	41	8	25	31	71	0.3	49	1	57	1																
Triassic	①	8551	8554	8552	8562	8553	8554	8558	8550	7723	7770	7777	7723	7777	7772	4723	7777	7777	7723	7745	7723	7537	7778	1574																
	②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	5	< 0.3	< 5	5	< 5	< 20	< 3	< 5	9	< 0.1	5	< 2	5	< 1																	
	③	20.7	42	212	800	62	6211	56.7	4500	10000	21.6	285	2504	1000	700	96	510	5550	2569	17	710	30	985	100																
	④	0.3	1	1.1	83	2	1	0.4	7	549	0.5	9	38	8.7	25	12	16	25	101	0.5	29	1	45	1																
	⑤	0.3	1	1	82	2	1	0.4	8	620	0.6	9	42	8.6	24	11	16	24	104	0.5	36	1	45	1																
Germanic Triassic	Keuper	①	4277	4279	4275	4284	4278	4279	4283	4279	3649	3693	3700	3649	3700	3686	3101	3700	3700	3649	3675	3649	3520	3700	667															
		②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	5	< 0.3	< 5	< 5	< 5	< 20	< 3	< 5	9	< 0.1	< 5	< 2	5	< 1																
		③	7.8	17	69.9	600	48	398	56.7	4500	10000	9	115	676	260	500	96	105	800	2569	8	710	30	900	100															
		④	0.4	1	1.3	96	2	2	0.8	8	685	0.4	10	40	9.4	29	13	17	25	119	0.7	30	1	49	1															
		⑤	0.3	1	1.2	87	2	2	0.9	8	769	0.3	9	43	8.8	42	12	20	24	121	0.7	39	1	47	1															
	Muschelkalk	①	986	986	987	989	986	987	988	986	861	866	866	861	866	856	429	866	866	861	866	861	842	867	128															
		②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	19	< 0.3	< 5	8	< 5	< 20	< 3	< 5	5	24	< 0.1	< 5	< 2	10	< 1															
		③	20.7	33	212	600	62	6211	12	990	3158	21.6	35	842	290	260	90	510	5550	1262	17	163	4	560	31															
		④	0.3	1	1.2	89	1	1	0.4	7	394	0.5	14	56	16	43	16	25	45	111	0.4	44	1	69	1															
		⑤	0.3	1	1.1	85	1	1	0.5	7	382	0.5	14	59	15	49	15	25	44	111	0.4	50	1	68	1															
	Buntsandstein	①	2834	2835	2836	2835	2835	2834	2833	2831	2757	2743	2743	2757	2743	2764	768	2743	2743	2757	2736	2757	2708	2743	769															
		②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	135	< 0.3	< 5	< 5	< 5	< 20	< 3	< 5	9	< 0.1	< 5	< 2	< 5	< 1																
		③	6.9	42	180	800	36	292	15	1100	10000	9.6	285	373	1000	700	45	165	620	889	6.5	185	10	985	50															
		④	0.3	1	1	68	2	1	0.1	8	664	0.7	6	32	6.2	15	8	11	17	74	0.3	24	1	36	1															
		⑤	0.3	1	0.9	48	2	1	0.1	8	637	0.8	5	35	4.7	9	6	10	16	76	0.4	28	1	40	1															
Alpine Triassic	①	377	377	377	377	377	377	377	377	394	406	406	394	406	404	406	406	394	406	394	406	406	406																	
	②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	5	< 0.3	10	5	5	20	< 3	10	20	62	0.2	5	< 2	15																	
	③	0.6	3	5.7	400	5	5	2.3	37	428	2.1	40	2504	60	160	27	110	200	2535	5.6	199	1	255																	
	④	0.2	1	0.5	66	1	1	0.4	5	60	0.2	27	37	10.2	58	6	38	64	179	1.6	42	1	37																	
	⑤	0.2	1	0.5	47	1	1	0.5	5	64	0.2	26	39	9.2	56	6	41	66	166	1.8	50	1	36																	
Permian	①	644	647	647	646	647	647	644	647	585	601	601	585	601	598	174	601	601	585	601	585	597	601	108																
	②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	201	< 0.3	< 5	10	< 5	< 20	3	< 5	< 5	28	< 0.1	5	< 2	10	< 1																
	③	4.5	11	13.5	1000	28	15	21	345	10000	3.3	75	527	240	760	42	100	400	1194	53	289	8	610	91																
	④	0.2	1	1.1	67	2	1	0.3	5	602	0.8	11	62	9.4	15	13	22	26	107	0.6	48	1	62	2																
	⑤	0.2	1	1	48	1	1	0.3	5	594	0.8	13	60	8.9	9	13	23	24	111	0.6	54	1	64	1																
Carboniferous	①	983	983	983	980	981	983	982	983	864	872	872	864	872	869	156	872	872	864	872	864	849	872	151																
	②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	159	< 0.3	< 5	16	< 5	< 20	6	< 5	10	17	0.1	16	< 2	20	< 1																
	③	7.8	200	98.4	600	350	2400	6.4	2300	10000	21.9	155	1106	1150	240	60	395	9540	738	21.5	210	8	3090	100																
	④	0.3	1	1.3	67	2	2	0.1	12	634	1.3	19	78	31.6	13	26	39	117	71	0.6	79	1	183	2																
	⑤	0.3	1	1.1	47	2	2	0.1	10	561	1.2	21	78	27.3	9	27	39	70	65	0.5	81	1	173	2																
Devonian	①	3125	3137	3137	3140	3138	3138	3134	3124	2575	2699	2700	2575	2700	2694	2375	2700	2700	2575	2697	2575	2546	2698	147																
	②	< 0.3	< 1	< 0.3	< 100	< 1	< 1	< 0.1	< 1	124	< 0.3	< 5	19	< 5	< 20	3	< 5	< 5	8	< 0.1	5	< 2	10	< 1																
	③	7.5	80	167	1000	288	424	6.5	7100	10000	26.1	185	760	1295	560	69	390	9585	1241	4.4	265	40	13800	295																
	④	0.4	1	1.3	63	3	2	0.1	12	471	1.1	17	125	16.7	15	19	43	53	103	0.4	64	1	119	2																
	⑤	0.3	1	1.2	47	3	2	0.1	11	468	1	16	124	14.7	10	19	44	45	109	0.4	67	1	112	1																
Basic igneous rocks	①	63	63	63	63	63	63	63	63	54	54																													

Table 2. Error analysis (in %)

Stream waters	No. of compared values	Values				Stream sediments	No. of compared values	Values			
		in same class	differ by					in same class	differ by		
			1 class	2 classes	3 classes				1 class	2 classes	3 classes
Cd	12563 (4052)	94.2 (82.0)	4.3 (13.2)	1.2 (3.7)	0.2 (0.8)	Cd	10830 (4964)	94.8 (88.7)	4.1 (9.0)	0.9 (2.0)	0.1 (0.3)
Co	12631 (3139)	92.0 (67.6)	3.9 (15.8)	2.4 (9.6)	0.8 (3.3)	Co	10913 (87207)	89.0 (83.4)	8.9 (13.5)	1.4 (2.2)	0.5 (0.7)
Cu	10208 (4285)	92.7 (82.5)	4.5 (10.8)	1.6 (3.9)	0.9 (2.0)	Cu	10897 (7351)	89.0 (83.6)	7.9 (11.7)	1.9 (2.8)	0.7 (1.0)
F	12106 (5192)	89.8 (76.2)	3.4 (7.9)	5.3 (12.3)	0.6 (1.3)	F	10564 (3453)	95.0 (84.6)	4.2 (12.8)	0.7 (2.1)	0.2 (0.5)
Ni	12621 (10744)	89.2 (87.3)	8.7 (10.2)	1.5 (1.8)	0.4 (0.5)	Li	8766 (4538)	97.9 (95.9)	2.0 (3.9)	0.1 (0.2)	0.0 (0.0)
Pb	12628 (5178)	90.3 (76.3)	5.6 (13.7)	2.4 (5.9)	0.9 (2.2)	Ni	10915 (7749)	94.5 (92.2)	4.7 (6.6)	0.7 (1.0)	0.2 (0.2)
U	12458 (2641)	97.9 (89.9)	1.7 (8.1)	0.3 (1.6)	0.1 (0.4)	Pb	10837 (8356)	91.8 (89.4)	6.0 (7.8)	1.5 (1.9)	0.5 (0.7)
Zn	12582 (11147)	87.8 (86.2)	9.0 (10.2)	1.8 (2.0)	0.8 (0.9)	Sn	1017 (600)	73.6 (55.3)	15.2 (25.8)	8.7 (14.7)	2.0 (3.3)
						U	10885 (6235)	94.7 (90.8)	4.7 (8.2)	0.5 (0.9)	0.1 (0.1)
						W	8438 (361)	97.8 (48.5)	0.8 (19.7)	0.7 (16.6)	0.3 (7.8)
						Zn	10880 (8448)	91.6 (89.2)	6.2 (8.0)	1.9 (2.4)	0.2 (0.3)

For the representation of the maximum values, colours are combined with columns drawn in 3 dimensions, the lengths of which are proportional to the size of the corresponding maximum value. The longest column on each map corresponds to the maximum value given in the legend for that map. The 3-dimensional representation causes a certain amount of distortion of the map; the scale is therefore not altogether true¹.

The practical use of the Atlas is subject to certain limitations resulting from the two different forms of representation, since the first is based on the mean values of a variable number of samples and in the second, the location of the maximum values on the map is relatively inaccurate. However, for each element, the same grid was used in both forms of representation so that a given arithmetic mean and the corresponding maximum value fall on the same grid square. Two transparent overlays are provided in the Appendix with a key to the 1 : 25,000 topographic sheets and showing towns and villages of significance for this work².

The colour models for the printing plates were prepared on an Applicon colour plotter using the UNIRAS program package on a Siemens 7.741 computer³.

1.6. Use of the file⁴

All data collected within the scope of this research project are stored in the GEOMULDAT datafile (GEOchemical MULtielement DATAfile) and are available on request on an actual cost basis. Any portion of the Geochemical Map of the Federal Republic of Germany can be obtained at any scale. It is possible to present the frequency class of the individual values at scales of 1 : 200,000 and less; all of the analytical values for any one element can be given on a map at a scale of 1 : 50,000 or less. Examples are given on page 76 - 79. When printouts are requested, the area should be chosen, indicating the scale in such a way that they coincide with one or more sheets of the 1 : 25,000 topographic maps (TK 25) of the FRG. For this purpose, a

¹ The calculation of the maximum values of the grid cells as well as their three-dimensional columnar representation has been omitted in the digital edition. They were replaced by point maps of the individual values, from which the maximum values are also recognisable. In addition, the digital edition contains colour shaded contour maps with 72 classes, from which both the levelling of the geochemical background and the distribution of elevated and anomalous contents are recognisable in more detail than from the maps of the 1985 print edition.

² These overlays are not included in the digital edition. However, the downloadable maps in PDF and PNG format are backed with much higher resolution topography.

³ The maps included in the digital version of the atlas were produced using Golden Software® Surfer® to calculate the grids and ESRI ArcGIS® to generate the downloadable shapes and maps.

⁴ The content of this chapter is obsolete. The GEOMULDAT file is a relational Microsoft ACCESS database with an integrated query program. However, this query program is no longer executable under current operating systems. Moreover, Microsoft ACCESS is only available under Microsoft Windows. Therefore, the data were converted into a tabular structure and into current data formats (*.xlsx, *.csv). The converted data can be downloaded free of charge from the BGR Product Center (<https://produktcenter.bgr.de>).

It is no longer possible to request data lists and detailed maps. Instead, in addition to the complete data set, ESRI shapefiles of all maps contained in the digital edition are made available for download via the BGR Product Center (<https://produktcenter.bgr.de>). Furthermore, the maps can be integrated into own GIS projects via WMS (Web Map Services) provided by the BGR or visualised with the BGR Geoviewer (<https://geoviewer.bgr.de>) in most current browsers. Finally, all maps on a scale of 1 : 2,000,000 including a background topography can be downloaded from the BGR Product Centre (<https://produktcenter.bgr.de>) in PDF and PNG formats with a resolution of either 300 or 600 dpi.

transparent overlay of the TK 25 index grid is provided for the 1 : 2,000,000 maps. In exceptional cases, the coordinates of the corners of the required portion of the map may be quoted as a reference. Using the same method, lists of analytical results and coordinates of the sampling locations can be requested. In addition, the results of the optical emission spectrography analysis for 14 further elements which are not included in the atlas are stored in the file (see Section 1.3). Among these elements, molybdenum should have special mention; 8300 samples were analysed for Mo by atomic absorption. It is intended that this additional information and the data in the geochemical atlas be made widely available to those interested in environmental research or prospecting.

1.7. General information concerning the data

It is not intended to include a detailed discussion of the results in this geochemical atlas since

- it would involve detailed treatment of the extensive data requiring a considerable amount of time,
- the additional field and laboratory work necessary in following up the newly discovered anomalies has not yet been started,
- the 1 : 2,000,000 geochemical map with no cartographic information is not an entirely suitable basis for a detailed evaluation as it only provides a general overview.

Brief explanations are included with the maps on which the stream sediments and water analyses are plotted. These are only intended to draw attention to some characteristic features and relationships, as well as to mention mining districts and important geological aspects.

Nevertheless, without reference to the individual maps, some examples of the complexity of any geochemical interpretation should be given.

Firstly, the strong influence of the geology on the analytical results has to be taken into account. It can be seen in Table 1 that variations in different statistical parameters commonly correspond to variations in the geology. The elements Co, Cr, Ni, and V tend to be considerably enriched in gabbroic and basaltic rocks; Ba, Li, Pb, and U in granitic rocks; and Cu, Pb, U, V, and Zn in black shales. In these areas, the natural concentrations of individual elements in water, stream sediments and soils may far exceed recommended limits without being detrimental to the environment or an offence against environmental protection laws having been committed.

Such occurrences are more serious in zones in which ore minerals are concentrated in joints, veins or beds. These kinds of deposits are and have been prospecting targets for centuries. Ore deposits containing Pb, Zn, U, Cu, Fe, Sn, F, and Ba occur in many old mining areas in the Federal Republic of Germany, e. g. in the Harz Mountains, Sauerland, Eifel, Black Forest, Bavarian Forest, and Fichtelgebirge. Centuries of mining and smelting activity in these areas have brought heavy metals to the surface in the neighbourhood of the countless lodes, shafts, open workings, mine dumps, as well as around stamping and smelting works. The heavy metals find their way into streams and rivers and are spread over the fields as suspended matter in floodwaters.

The results presented here broadly document the natural and the historical anthropogenic heavy-metal contamination in the FRG. But the pollution of most recent origin, due to dust, smoke and contaminated precipitation, has probably not been documented by this survey, since this kind of pollution is initially usually resorbed by the soil, and either buffered or accumulated there before it can be detected as an anomaly in stream waters or sediments.

An example is the area around the Nordenham lead-smelting works on the Weser estuary. Here, no distinct indications of lead appeared in stream sediments or waters, although the soils of the area showed high lead contents and cases of lead poisoning in animals are known. In this case, lead-bearing dust brought down by the rain had settled on the grass and, finding its way into the cows' stomachs, had accumulated as a toxic substance in the tissues of the muscles and gut, as well as in the milk.

Two further examples should be given in connection with geochemical prospecting:

A number of high values for lead in stream waters and sediments in northern Sauerland were correlated with extremely high natural concentrations of lead (up to 35,000 ppm) in the soil. Since this area has been prospected for lead for centuries, this is a remarkable result.

Areas in the Black Forest and Bavarian Forest regions were also found in which the relatively rare element tungsten occurs in elevated concentrations in stream sediments, soils, and rocks. This is a confirmation of our assumption that the data in this atlas on previously little prospected elements will provide indications of economically useable enrichments.

581 water and sediment samples were collected from rivers and streams specifically for environmental studies¹. They were analysed for Cd, Co, Cu, F, Ni, Pb, U, and Zn. The frequency classes for Cd, Cu, Pb, and Zn are plotted on maps (page 68 - 75). The actual concentrations of all of the analysed elements can be made available in analogous plots or in lists. It can be seen in the maps and in Table 1 that in terms of heavy metal concentrations there is no significant difference between the small streams and the rivers.

In some of the rivers, however, the effects of man's activities are serious, especially in old mining areas. Locally (the Innerste and Oker in the Harz foreland) higher concentrations occur than in the feeding streams; even the flood plains of the next larger rivers (in this case, the Leine and Aller) are still contaminated.

Except for these and a few other cases, the river waters were not contaminated with heavy metals to the extent that they could be considered hazardous. Of the 581 river water samples, a higher concentration than the limit allowed by the German drinking water regulations was

¹ The data of the 581 water and sediment samples taken separately for environmental studies in rivers and streams are not included in the currently available version of GEOMULDAT and their whereabouts are unknown. Therefore, neither the analysis data nor the maps mentioned here are included in the digital version of the atlas.

found in only one sample for each of the following elements: lead (0.04 ppm) and zinc (2.0 ppm).

This statement cannot, however, be generalized to include organic and other contamination of the rivers.

1.8. Concluding comments

The results of about 80,000 water analyses and about 70,000 sediment analyses for 15 elements in samples from streams and rivers are shown in 62 maps.

The following can be said on the basis of the preliminary evaluation of the data contained in these maps:

- In most of the streams and rivers we have investigated, the transport of elements in the natural cycle predominate so much that anthropogenic changes in the natural system could not be determined within the scope of our study.
- Local environments of heavy metals were determined, however, and these should be examined in order to specify and limit possible environmental hazards.
- The anthropogenic input of cadmium, copper, lead, and zinc in the rivers (ca. 600 samples taken in 1983) is low.
- Prospecting possibilities in the Federal Republic of Germany for the more rare metals were opened. This is shown by the positive preliminary results of follow-up work on tungsten begun on the basis of the results in this Atlas.

It is not possible to print here a comprehensive compilation of literature references. Several summary publications are cited so that those with widely differing interests are provided with a wide range of references to the present literature.

1.9. References

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2. Maps 1 : 2,000,000

2.1. Sample sites¹

2.2. Geological map²

2.3. Geochemical maps³

2.3.1. Stream waters

2.3.1.1. pH and Conductivity

Comparison of the maps of pH and conductivity with the geological map shows up numerous significant similarities indicating that these factors are closely interrelated.

The peat bogs of North Germany, the granites and gneisses in the Harz Mountains, the Black Forest and eastern Bavaria, the Bunter Sandstone areas of Hesse and the Rhineland-Palatinate, for example, all have relatively acidic surface waters (pH of 4 - 6) and low conductivity values. On the other hand, limestone areas are characterized by alkaline waters (pH of 7 - 9) and higher conductivity values. The main variations in pH and conductivity are caused by the different solubilities and reactivities of the different outcropping rocks and soils in water.

In certain region, this natural equilibrium is being disturbed by man's activities. The burning of fossil fuels (coal, oil and gas) releases large quantities of sulphur and nitrogen oxides into the atmosphere lowering the pH of rain. In areas of calcareous rock, rain with pH values between

1 In contrast to the 1985 paper edition of the Geochemical Atlas of the Federal Republic of Germany, the sample point maps are provided separately for stream sediment and stream water samples. In addition to the sample points, the sampled areas are shown on the map in the form of a (smoothed) 2 km buffer around the sample points. The maps can be downloaded from the BGR Product Centre (<https://produktcenter.bgr.de>) at a scale of 1 : 2,000,000 including a background topography in PDF and PNG formats with a resolution of either 300 or 600 dpi. Simultaneously, they are also available for download as ESRI shapefiles. Furthermore, the maps can be integrated into own GIS projects via WMS (Web Map Services) provided by the BGR or visualised with the BGR Geoviewer (<https://geoviewer.bgr.de>) in most common browsers.

2 The geological map shown in the 1985 paper edition of the Geochemical Atlas of the Federal Republic of Germany is not included in the digital version of the atlas. The most recent version of the geological map of Germany can be obtained at a scale of 1 : 1,000,000 or in individual sheets at a scale of 1 : 200,000 from the BGR Product Centre (<https://produktcenter.bgr.de>).

3 The distribution of the element contents is presented in the digital version of the Geochemical Atlas of the Federal Republic of Germany in each case in a map produced according to the calculation method described in Chapter 1.5. In addition, colour shaded contour maps are provided that were generated using newer interpolation methods (Kriging). These are available firstly in the class boundaries of the map from the 1985 paper edition of the atlas and secondly in a map with a variable colour gradient scale of 72 classes, in the latter of which the shades of green approximate the geochemical background. In addition, two point maps are offered, which show the element contents at the sample point in the class boundaries of the original map from the paper edition of 1985 and in the class boundaries of the 72 class map with variable colour gradient scale. All maps can be downloaded from the BGR product centre (<https://produktcenter.bgr.de>) at a scale of 1 : 2,000,000 including a background topography in PDF and PNG formats with a resolution of either 300 or 600 dpi. Simultaneously, they are also available for download as ESRI shape files. Furthermore, all maps can be integrated into own GIS projects via WMS (Web Map Services) provided by the BGR or visualised with the BGR Geoviewer (<https://geoviewer.bgr.de>) in most common browsers.

3 and 5 is more or less fully neutralized and the effects minimized. But in areas of granite and sandstone, no natural buffer is present and the pH of the naturally soft, acidic (from atmospheric CO₂) waters in such areas is reduced even further by "acid rain".

As a consequence of the above, the environmental conditions in these areas become modified to such a degree that, coupled with other detrimental effects due to exhaust fumes, heavy metals etc., serious damage to the vegetation may take place. Among the anthropogenic influences, a desired effect on pH and conductivity values may be caused by intensive use of mineral fertilizers in agriculture. Although these measures are intended to increase the pH and conductivity, they may simultaneously introduce pollutants (nitrate and cadmium) into the groundwater.

2.3.1.2. Cadmium in stream waters

The cadmium concentrations range between 0.3 ppb (detection limit) and 48 ppb. The median (50 percentile) is 0.3 ppb.

In nature, cadmium is associated with zinc.

Elevated values occur in the surface waters of old mining districts

- in the Harz Mountains (up to 21 ppb),
- in the Rhenish Schiefergebirge on the right bank of the Rhine (up to 48 ppb),
- to the east of Aachen near Stolberg (up to 13 ppb),
- in the Spessart,
- in the Freihung area (Upper Palatinate Trias basin) (up to 41 ppb),
- in the Bavarian Forest near Bodenmais (up to 47 ppb).

Further elevated cadmium concentrations occur at various other places, as well as over considerable areas, such as near Augsburg and to the east of Braunschweig, for which the source of the cadmium is as yet unknown.

Cadmium is a heavy metal and as such is toxic for humans and animals. The statutory limit according to the drinking water regulations (Bundesgesetzblatt, 1975) is 6 ppb Cd.

In 0.08 % of all the surface waters monitored in the Federal Republic of Germany was this limit of 6 ppb Cd exceeded.

2.3.1.3. Cobalt in stream waters

The cobalt concentrations range from 1 ppb (detection limit) to 540 ppb. The median (50 percentile) is also 1 ppb.

In nature, cobalt is commonly associated with nickel, iron and arsenic sulphides.

The source of the few known occurrences of elevated cobalt values in surface waters is not yet known. The solubility of cobalt increases with decreasing pH. For this reason, a slight increase in cobalt concentration is found in several areas in which the waters are acidic (see map of pH

values), although no corresponding accumulations of cobalt were detected in the soils, rocks or stream sediments in these places (e.g. in the peatlands of Lower Saxony).

In geochemical prospecting, cobalt values in surface waters are difficult to interpret because geogene cobalt accumulations and ore deposits are very rarely the source of elevated cobalt values in waters. In principle, therefore, cobalt values in stream sediments should be considered as more significant than those of surface waters.

No statutory limits exist as yet for cobalt in drinking water. Normally, the concentration in drinking water is between 0.1 and 10 ppb (MERIAN, 1984: 429). In 0.6 % of all the waters of the Federal Republic of Germany analysed there is over 10 ppb Co.

2.3.1.4. Copper in stream waters

The copper concentrations range from 0.3 ppb (detection limit) to 1500 ppb. The median (50 percentile) is 1.5 ppb.

In surface waters, elevated copper values are scattered throughout the Federal Republic of Germany, while in stream sediments discrete areas of elevated copper values occur. The distribution of copper in surface waters is primarily influenced by man. This can be best demonstrated in the grape-growing areas of Rhine-Hesse and Rhine-Palatinate, as well as in the hop-growing district in the Hallertau. In these areas, copper salts were used as pesticides.

Owing to this extensive anthropogenic influence, direct correlations between copper values in surface waters and ore deposits or specific lithological units are seldom recognizable. Although the old mining districts, e.g. near Bodenmais and Erbdorf in eastern Bavaria, are indicated by elevated copper concentrations, the Kupferschiefer outcrop areas, for example, do not stand out significantly.

For this reason, analyses of surface waters are by no means always useful for copper prospecting in the Federal Republic of Germany. There is, as yet, no statutory limit for copper in drinking water in the FRG. In Switzerland, drinking water is allowed to contain a maximum of 1500 ppb Cu (MERIAN, 1984: 461). The World Health Organization (WHO) recommends a limit of 50 ppb (MERIAN, 1984: 461). Even the highest copper concentrations measured in the surface waters in the FRG do not exceed the Swiss limit of 1500 ppb Cu. In 0.1 % of all the water samples analysed there is a copper concentration higher than that recommended by the WHO (50 ppb Cu).

2.3.1.5. Fluoride in stream waters

The fluoride concentrations range from 100 ppb (detection limit) to 4700 ppb. About 85 % of all water samples were beneath 200 ppb, and these are spread relatively evenly throughout the Federal Republic of Germany.

The highest fluoride concentrations recorded in surface waters occur in the vicinity of the fluorite deposits in the Bavarian and Upper Palatinate Forests and in the Black Forest.

In the coastal areas bordering the German part of the North Sea, fluoride values were found to range up to 800 ppb; this is due to the influence of seawater, through the tides and spray. Seawater contains an average of 1300 ppb F⁻. The slightly elevated fluoride concentrations east of Hannover have been shown to be caused by phosphate fertilizers.

Fluoride values from north of Koblenz and in the Laach volcanic area reflect the presence of tuffs in those areas.

In geochemical prospecting for fluorite, analysis of stream sediments for fluoride is more effective than analysis of water.

In 0.01 % of all fluoride analyses the statutory limit of 1500 ppb F⁻ laid down in the regulations governing drinking water is exceeded (Bundesgesetzblatt, 1975). Fluoride concentrations up to 1000 ppb are considered to be beneficial for the prevention of caries in teeth.

2.3.1.6. Nickel in stream waters

The nickel concentrations range from 1 ppb (detection limit) to 900 ppb. The median (50 percentile) is 2 ppb.

The frequency of slightly elevated Co and Ni values in the North German lowlands is probably due to the low pH of surface waters in the peatlands. Metals are considerably more soluble under these conditions.

Elevated nickel values in surface waters are predominantly anthropogenic in origin. Nickel compounds can be released into the environment by industrial processes, particularly smelting, by burning coal and oil, as well as by car exhaust.

Nickel from natural sources enters the groundwater and surface waters in relatively insignificant quantities. It could not be determined whether the generally elevated Ni values in the areas of silica-poor igneous rocks in the Vogelsberg, Westerwald and Rhön regions were of anthropogenic or natural origin. So far, no criteria that could be used for nickel prospecting have been found.

There are as yet no statutory limits governing the concentration of nickel in drinking water.

2.3.1.7. Lead in stream waters

The lead concentrations range between 1 ppb (detection limit) and 6200 ppb. The median (50 percentile) is also 1 ppb.

For stream sediments, elevated values are concentrated in a few areas; in comparison, elevated values in water samples are scattered over the whole area of the Federal Republic of Germany.

Particularly high lead concentrations were found in surface waters in the Harz Mountains (up to 2400 ppb Pb), in several areas of the Rhenish Schiefergebirge (up to 430 ppb Pb), and south

of Heidelberg (up to 100 ppb Pb). The highest values of 6200 ppb Pb were determined on samples from the Freihung area. These areas have a centuries-old history of lead mining and smelting. Today, lead mining is carried out only at Rammelsberg, Bad Grund, and Meggen.

Significantly elevated lead values (about 500 ppb Pb) of natural origin occur near Brilon in the Sauerland and west of Weiden (Upper Palatinate Triassic basin).

Lead anomalies in other areas may be due to anthropogenic contamination. Considerable amounts of lead are released by some industrial processes, coal furnaces, and motor vehicles.

The annual precipitation rate of lead is given by the Federal Environmental Agency as 15 – 620 mg Pb per square meter. The emission of lead is substantially higher in the vicinity of large sources of industrial pollution; however, the lead is retained in the soil so that the effect on the hydrologic system is relatively small.

Altogether, 220 water samples (0.3 % of the total number) were found to have over 40 ppb Pb. This is the statutory limit laid down in the drinking-water regulations (Bundesgesetzblatt, 1975).

2.3.1.8. Uranium in stream waters

The uranium concentrations lie between 0.1 ppb (detection limit) and 200 ppb with a median (50 percentile) of 0.2 ppb.

The uranium in the surface waters has for the most part an oxidation state of +6. Uranium in an oxidation state of +4, as in pitchblende and other major uranium ores, is considerably less soluble than in the +6 state. For this reason, the highest uranium concentrations in the water samples are an indication of uranium enrichments in the +6 form. Secondary enrichments produced by weathering are often due to remobilization and concentration of uranium in porous rocks and organic matter.

In the area of the Keuper sandstone - from Coburg in northern Bavaria, southwest through the Steigerwald, to Stuttgart and further - there is a wide zone of uranium concentrations up to 40 ppb in the surface waters.

South of the Danube, the highest concentrations (up to 60 ppb) occur in the Hegau area and in the peatlands north of Munich.

In eastern Schleswig-Holstein, elevated uranium concentrations in the surface waters coincide with the limit of the last Weichsel ice age. The moraines contain till consisting of granite from Scandinavia, from which uranium is released by weathering.

The elevated uranium concentrations in the surface waters east of Hannover correlate with the use of phosphate fertilizers. The cause of the high uranium concentrations in Rhine Hesse have not been explained yet.

The uranium concentration in the surface waters around the Menzenschwand deposit in the southern Black Forest is low because the uranium in the deposit is present mainly in the +4 oxidation state.

Limits for uranium in drinking water have not been established.

2.3.1.9. Zinc in stream waters

The zinc concentrations range between 1 ppb (detection limit) and 11,700 ppb. The median (50 percentile) is 9 ppb.

Elevated zinc values occur in the surface waters of old mining districts in the Federal Republic of Germany, e.g. in the Harz Mountains (up to 1300 ppb Zn), in the Rhenish Schiefergebirge (up to 11,700 ppb), near Maubach and Mechernich at the north edge of the Eifel, and near Bodenmais in the Bavarian Forest (up to 10,000 ppb Zn).

The other zinc anomalies probably represent anthropogenic contamination, e.g. near Duisburg where zinc concentrations up to 6200 ppb were found. Very high zinc values also occur north of Lüneburg (up to 10000 ppb), north of Heidelberg (up to 10,000 ppb), and south-east of Fulda (up to 5000 ppb).

In geochemical prospecting, the zinc concentration of surface waters is a good indication for the presence of mineralization due to the high mobility of zinc. However, any interpretation is hampered by the predominantly anthropogenic origin of the zinc.

In 0.03 % of all the samples, there is more than the statutory limit of 2000 ppb Zn as laid down in the drinking water regulations (Bundesgesetzblatt, 1975). Drinking water is sometimes contaminated by zinc pipes; normally this does not exceed 5000 ppb Zn. According to LEWIN (quoted by HÖLL, 1979: 264), drinking water containing zinc concentrations of over 8000 ppb Zn is harmful only if consumed over long periods.

2.3.2. Stream sediments

2.3.2.1. Barium in stream sediments

The barium concentrations range between 5 ppm (detection limit) and more than 10,000 ppm. The median (50 percentile) is 412 ppm.

The most important barium minerals are barite (BaSO_4) and witherite (BaCO_3). Barium substitutes for potassium in many rock-forming minerals, especially in feldspar and mica.

The high barium concentrations in the stream sediments can in most cases be traced back to known barite mines.

Thick barite veins are mined in the Harz Mountains near Bad Lauterberg; barite occurs in the Rammelsberg base metal deposit near Goslar. The barite veins near Sontra and Witzenhausen,

as well as in the Rhenish Schiefergebirge (near Dreislar, Meggen, Ürsfeld, etc.) are distinctly indicated by high barium concentrations in the stream sediments.

Extensive barium anomalies are observed in the area of the barite occurrences in the Spessart, Black Forest, and Odenwald regions.

Elevated barium concentrations, whose source is not yet definitely known, were measured in stream sediments in the Keuper area between Stuttgart and Coburg and at the edge of the Frankenwald and Fichtelgebirge areas.

Analysis of barium in stream sediments is well suited for barite prospecting and is little disturbed by anthropogenic influences.

2.3.2.2. Cadmium in stream sediments

The cadmium concentrations range from 0.3 ppm (detection limit) to 110 ppm. About 75 % of all samples contain less than 1.0 ppm.

Cadmium is concentrated in sphalerite (ZnS), which normally contains between 0.1 and 0.5 % Cd. The map of cadmium distribution in stream sediments thus shows a conspicuous similarity with that of zinc.

High cadmium values occur in the Harz Mountains where they are caused by the presence of base-metal mineralization.

Similar elevated cadmium values are encountered over considerable areas of the Rhenish Schiefergebirge, the highest being in the Sauerland, on the southern margin of the Siegerland and Hunsrück, as well as in the Aachen-Stolberg area. These are all associated with base-metal mineralization and the associated mining activities.

High cadmium values are found in the Black Forest in the area around the Schauinsland and Münstertal ore deposits, as well as in the Freihung (Upper Palatinate Triassic basin) and Frankenwald areas.

Most of the remaining cadmium anomalies, such as those near Kaiserslautern (75 ppm Cd), Braunschweig and Hamburg, are probably anthropogenic in origin. Same anthropogenic cadmium concentrations in the soil are due to the application of sewage sludge, harbour dredgings or fertilizer on the land. There is commonly a considerable delay before the corresponding anomalies are detected in stream waters or sediments.

According to the regulations on sewage sludge (Bundesgesetzblatt, 1982), the statutory limit is 20 ppm Cd. In 25 stream sediments (about 0.04 % of the total analysed), concentrations higher than 20 ppm Cd were determined.

2.3.2.3. Cobalt in stream sediments

The cobalt concentrations range between 5 ppm (detection limit) and 1400 ppm. The median (50 percentile) is 9 ppm.

High cobalt (and Ni) concentrations occur in silica-poor igneous rocks, whereas granite, gneiss and sandstone show conspicuously low values. The distribution of cobalt in stream sediments, as with that of nickel, reflects the distribution of silica-poor igneous rocks.

High cobalt values were encountered in stream sediments in the area of the basalts in the Vogelsberg, Westerwald and the Rhön. Some of the high cobalt values in the Frankenwald and the Fichtelgebirge areas may also be due to silica-poor igneous rocks.

In the Schiefergebirge¹, particularly in large parts of the Sauerland, Hunsrück, and Taunus areas, elevated cobalt concentrations occur in stream sediments and in many cases are connected with the diabases and mineralized rocks in these regions.

The former cobalt mining district near Bieber, Spessart, is characterized by high cobalt values. The regional cobalt concentrations on the northern margins of the Swabian Alb and the Alps largely coincide with those of nickel.

Cobalt is one of the essential trace elements for maintaining the health of higher animals and man. There are large areas in which cobalt deficiency of the soil causes widespread disease in animals. More attention should be paid to the problem of cobalt deficits in the soil due to natural transport processes than to the dangers of cobalt contamination.

2.3.2.4. Chromium in stream sediments

The chromium concentrations range between 5 ppm (detection limit) and 5700 ppm. The median (50 percentile) is 54 ppm.

Chromium occurs in the oxide and silicate minerals of early magmatic differentiates; thus it is considerably more concentrated in silica-poor rocks (e.g. gabbro and basalt) than in silica-rich rocks (e.g. granite and gneiss). This enrichment of chromium in certain rock types is reflected fairly accurately by its distribution pattern in this atlas.

High concentrations are associated with the basalts of the Vogelsberg, Westerwald, and Rhön areas.

Elevated chromium concentrations are also observed in other areas in which silica-poor igneous rocks crop out rather extensively, e.g. in the Frankenwald, Fichtelgebirge, Hoher Bogen, and Eifel areas, around the Swabian volcanoes, in the Habichtswald and Knüll areas, in the Harz mountains, and in the Dill depression.

¹ Rhenish Schiefergebirge

The cause of elevated chromium concentrations that occur in the stream sediments over wide areas of the Rhenish Schiefergebirge is probably geological. The widely distributed shales in this region contain naturally elevated chromium concentrations.

The source of high chromium concentrations that occur locally just north of the Calcareous Alps is not known with certainty.

In many of the cases of isolated anomalous chromium concentrations, anthropogenic contamination is probable.

Chromium is an essential trace element for the metabolism of sugar and fats. A chromium deficit can lead to diabetes and arteriosclerosis. Chromium concentrations (especially in the +6 oxidation state) that are too high are poisonous and can also cause allergies.

A concentration of 1200 ppm Cr has been suggested as the upper limit for sewage sludge in the FRG (Bundesgesetzblatt, 1982). Of the stream sediment samples, 52 (0.08 %) had higher values than this, most of which are of natural origin.

2.3.2.5. Copper in stream sediments

The copper concentrations range between 5 ppm (detection limit) and 2560 ppm with a median (50 percentile) of 9 ppm.

Extensive areas show concentrations of less than 10 ppm. There are also areas of anomalously high Cu values. These anomalies coincide with old mining districts in which the high Cu values are of geological origin, and with zones in which copper has been introduced by man's activities.

The Harz Mountains, where the maximum Cu concentration in the stream sediments is 1500 ppm, stand out conspicuously from their surroundings. The source of the copper is the Rammelsberg deposit near Goslar and other smaller deposits and old smelters.

High copper values also occur in the Rhenish Schiefergebirge, where numerous ore lodes (particularly in Siegerland, in the Dill depression, and near Bensberg) have yielded copper as a by-product.

Other known copper mineralizations also show up in the data, for example, near Marsberg, Sontra, Bieber, Kupferberg (Frankenwald), Fischbach, Bodenmais, and Donnersberg.

The high copper values for the stream sediments in the German grape- and hop-growing areas are due to the use of pesticides. Especially prominent are areas in Rhine Hesse, Rhine Palatinate, and Hallertau.

The other copper anomalies are probably also due to anthropogenic contamination, e.g. near Hamburg, Teublitz-Maxhütte, and Hanau.

Copper is one of the essential trace elements for living organisms. There are many metabolic control mechanisms for preventing damage caused by concentrations that are too high or too low. For this reason, cases of copper poisoning or deficiency seldom occur.

In 0.01 % of the analysed stream sediments samples, there were copper concentrations above the limit of 1200 ppm given in the sewage sludge regulations (Bundesgesetzblatt, 1982).

2.3.2.6. Fluoride in stream sediments

The fluoride concentrations range between 20 ppm (detection limit) and 5400 ppm. The median (50 percentile) is 25 ppm.

Fluoride is concentrated in silica-rich rocks during magmatic differentiation. Thus, the distribution of fluoride in stream sediments reflects that of silica-rich and intermediate igneous rocks.

High fluoride values occur in the crystalline basement areas of the Black Forest, Fichtelgebirge, Upper Palatinate Forest, Bavarian Forest, and the Odenwald.

The elevated fluoride concentrations in the stream sediments of the volcanic districts of Laacher Lake, the Neuwied basin, and the Hegau area are all of natural origin.

In some areas, high fluoride concentrations in stream sediments are associated with fluorspar deposits, a few of which are still being worked. Among these are the fluorspar district near Nabburg-Wölsendorf, the fluorspar veins near Donaustauf and Nittenau in the Bavarian Forest, and the occurrences in the Black Forest such as those near Pforzheim, Wolfach, Wittichen, Oberkirch and associated with the mineralization at Schauinsland and Münstertal.

The cause of the high fluoride concentrations in the stream sediments in the other areas, such as between Karlsruhe and Wiesloch and in the Frankenhöhe and Steigerwald areas, is not known.

2.3.2.7. Nickel in stream sediments

The nickel concentrations range between 5 ppm (detection limit) and 1400 ppm. The median (50 percentile) is 21 ppm.

Nickel is highly concentrated in silica-poor rocks (e.g. gabbro and basalt) by magmatic differentiation. Silica-rich rocks (granite, gneiss, sandstone) contain markedly little nickel.

In igneous rocks, nickel may replace Mg^{2+} ion in silicates or be enriched in sulphides.

The distribution of nickel in stream sediments in the Federal Republic of Germany reflects the occurrence of silica-poor igneous rocks. Elevated nickel values in stream sediments occur in the vicinity of the basalts of the Vogelsberg, Westerwald, Rhön, the Eifel, and the Frankenwald areas.

Outside the areas where silica-poor igneous rocks crop out, elevated nickel concentrations were found in stream sediments over large areas particularly in the Schiefergebirge¹. In some cases, these can be explained as nickel accumulations associated with the iron mineralization in these districts.

Elevated nickel values accompany elevated cobalt values northeast of Saarbrücken within the outcrop area of Carboniferous rocks. In the Harz Mountains, elevated nickel values are associated partly with silica-poor igneous rocks and partly with mineral deposits.

The stream sediments of the Nördlinger Ries are conspicuously high in nickel.

The nickel concentrations in stream sediments along the northern margins of the Swabian Alb and the Alps, between Lake Constance and Salzburg are natural in origin.

About 0.1 % of all analysed stream sediment samples have nickel values over 200 ppm Ni, which is the statutory limit given by the regulations on sewage sludge (Bundesgesetzblatt, 1982).

2.3.2.8. Lead in stream sediments

The lead concentrations range between 5 ppm (detection limit) and 57,000 ppm with a median (50 percentile) of 24 ppm.

High lead values occur in the Harz Mountains and the Rhenish Schiefergebirge. The source of these concentrations is the Pb-Zn mineralizations and the associated mines, which are centuries old, in these districts, e.g. in Bad Grund, at Rammelsberg near Goslar, near Meggen, near Bensberg and Bad Ems, in the Hunsrück area, near Aachen, Mechernich, and Bleialf. Only the Bad Grund, Rammelsberg, and Meggen mines are still in operation.

The high lead concentrations around Schauinsland and Münstertal in the Black Forest are also due to the ore deposits in these areas.

High lead concentrations occur in stream sediments in the northern Calcareous Alps. Only in some places (Garmisch and Berchtesgaden) can this be related to lead mineralizations.

The high lead concentrations in the area of Freihung are related to the cerussite and galena sandstone ores in the Triassic rocks of the Weidener basin.

Natural lead concentrations were encountered around Brilon and near Endorf.

Lead-bearing material has been washed into the streams from weathering ore deposits and lead-bearing rocks (natural contamination). In addition, the ground around mines, smelters, and waste dumps is contaminated with considerable amounts of lead and over the years this anthropogenic lead has also been washed into the streams.

In those cases where lead sulfide is involved, which is relatively insoluble, there is little hazard for the environment.

¹ Rhenish Schiefergebirge

But the exhaust from motor vehicles and the smoke from smelters are more dangerous. The lead from these sources is more reactive and is spread in finer particles on plants and in this way enters the food cycle.

About 0.4 % of the stream sediment samples had lead concentrations above the limit of 1200 ppm Pb given for sewage sludge (Bundesgesetzblatt, 1982).

2.3.2.9. Strontium in stream sediments

The strontium concentrations range between 5 ppm (detection limit) and 8100 ppm with a median (50 percentile) of 89 ppm.

The strontium ion is bound to oxygen in most of the 25 strontium minerals. The ionic radius of Sr^{2+} lies between those of calcium Ca^{2+} and barium Ba^{2+} and is less than that of Pb^{2+} . Therefore, strontium often replaces these elements or they replace it. Strontium occurs in feldspars (up to 5100 ppm), micas (up to 450 ppm), amphiboles (up to 1060 ppm), clinopyroxenes (up to 850 ppm), and carbonate minerals (up to 6600 ppm). The strontium contents of rocks vary depending on the origin and relative amounts of the constituent minerals.

Strontium is very mobile during weathering and is released especially during the breakdown of carbonate minerals and feldspars. About 80 % of the strontium transported to the ocean by streams is derived from carbonates and sulfates and only 20 % from silicates.

High strontium values were found in the area of Upper Cretaceous limestone between the Ems and Ruhr Rivers. Strontianite veins were formerly mined in the southeast part of the Münsterland area.

The stream sediments in the area of the volcanic rocks of the following regions also have high strontium concentrations: Vogelsberg, Rhön, Westerwald, Siebengebirge, Neuwied basin, Regau, the Saar-Nahe depression and the northern Calcareous Alps.

High strontium concentrations contents are found in the Münchberg gneiss massif, in the Tertiary of the Mainz basin, and in large areas of the Keuper and Muschelkalk northeast of Stuttgart (Frankenhöhe, Steigerwald, and Hassberge). Also of interest is a N-S trending zone of elevated strontium values in the Hunsrück region.

Individual anomalies occur at Eschershausen, west of Steinhuder Lake, between Marl and Dorsten, near Duisburg, and in the central and southern parts of the Black Forest (see map of maximum values).

2.3.2.10. Uranium in stream sediments

The uranium concentrations range between 0.1 ppm (detection limit) and 280 ppm. The median (50 percentile) is 0.4 ppm.

High uranium values occur in stream sediments over the crystalline rocks of the Black Forest, the Fichtelgebirge, the Bavarian Forest, and the Upper Palatinate Forest. The hydrothermal vein mineralizations of these districts are locally uranium bearing. Known occurrences are near Menzenschwand and Wittichen in the Black Forest and near Nabburg and Mähring in the Upper Palatinate.

A deposit near Menzenschwand in the Krunkelbach valley was discovered in 1960. Uranium ore is mined there only within the scope of exploration work for assessing the potential of the deposit. The deposit is unmistakably indicated by the high uranium concentrations in the stream sediments in the area.

In Nabburg, uranium occurs in accessory minerals in fluorspar veins, and in Mähring it forms the main ore.

Uranium concentrations are also found near Weissenstadt in the tin granite of the Fichtelgebirge, as well as in the Falkenberger granite near Tirschenreuth. Leaching and remobilization caused the small amounts of uranium in the granite to be concentrated in joints, where values of 200 to 2500 ppm U are found. Both of these areas are characterized by high uranium concentrations in stream sediments.

Elevated uranium concentrations occur in the outcrop area of Keuper rocks from northeast of Stuttgart as far as Coburg. Numerous small, mostly lenticular uranium mineralizations are present.

Elevated uranium values were found in stream sediments in the area of the Saar-Nahe depression; these are caused by uranium mineralizations in the Rotliegendes sediments, as well as in the volcanic and subvolcanic rocks. Uranium was mined for a short period of time from a very small deposit near Ellweiler.

Elevated uranium values also occur in stream sediments in the area of the Müllenbach uranium deposit near Baden-Baden, which is hosted by Upper Carboniferous sandstones.

2.3.2.11. Vanadium in stream sediments

The vanadium concentrations range between 3 ppm (detection limit) and 710 ppm with a median (50 percentile) of 40 ppm.

During magmatic differentiation, vanadium is enriched more in silica-poor magmas than in ultrabasic or silica-rich magmas. The average crustal abundance of vanadium in basalts is 200 ppm.

Vanadium minerals are very rare. The V^{3+} ion, which is stable under reducing conditions (little or no oxygen), has an ionic radius similar to that of Fe^{3+} and can thus occupy the same lattice positions. Magnetite contains up to 2000 ppm V.

Especially high vanadium concentrations also occur in bituminous shales, which in the Permian Kupferschiefer average 1650 ppm V. Lias shales in northwest and southwest Germany contain an average of 260 ppm V.

The distribution of vanadium in stream sediments reflects mainly the occurrence of silica-poor igneous rocks and bituminous shales. Values over 160 ppm V occur, in particular, in the stream sediments in the area of the basalts of the Westerwald, Vogelsberg, and Rhön. Elevated vanadium values were also obtained for the areas of silica-poor igneous rocks of the Saar-Nahe depression and the volcanic rocks of the Laacher Lake area. High vanadium concentrations occur in the Frankenwald area, in the area of the Harzburg gabbro, the amphibolites near Furth i. W. (Bavarian Forest), and northeast of Weiden (Upper Palatinate).

The high vanadium concentrations in the stream sediments in the northeast part of the Sauerland area are probably due to metabasites and black shales.

The extent to which the remaining vanadium anomalies are due to anthropogenic contamination is not yet clear. Such sources are primarily emissions from the burning of coal and oil.

2.3.2.12. Zinc in stream sediments

The zinc values range between 5 ppm (detection limit) and 13,800 ppm with a median (50 percentile) of 52 ppm.

To a greater extent than in stream waters, the highest Zn values in stream sediments are concentrated in a few areas and in individual anomalies.

Similar to lead, zinc concentrations are high in the Harz Mountains, resulting from the ore deposits in that area. Only the mines at Bad Grund and Rammelsberg near Goslar are still in operation.

High zinc values occur in the stream sediments of the Rhenish Schiefergebirge. The source of these enrichments is the lead-zinc deposits and the associated mines, e.g. near Ramsbeck, Meggen, Bensberg, Bad Ems, Tellig, and in the Aachen-Stolberg area.

In the Black Forest, high zinc values were observed in the areas of the Schauinsland and Münsstertal.

High zinc concentrations (up to 5000 ppm) in Berchtesgaden Land are probably due to lead-zinc mineralizations.

Elevated zinc concentrations observed in the stream sediments in the areas of Frankenwald and the Münchberger gneiss massif probably have lithological sources (e.g. black shale, basite, metabasite) since in these areas there are only minor mineralizations.

Most of the remaining zinc values are probably of anthropogenic origin.

The zinc concentrations in 0.05 % of the stream sediment samples were above the limit of 3000 ppm given for sewage sludge (Bundesgesetzblatt, 1982).

2.3.2.13. Lithium in stream sediments

Between 1977 and 1979, lithium analyses were carried out using an optical emission spectrometer (see Section 1.3). It became apparent that this method was subject to such serious matrix effects that, from 1979 onwards, it was replaced by AA analysis, which is more accurate. All the lithium values plotted on the maps were determined using this method. It is planned to reanalyse the samples from the first years in order to complete the lithium map.

This is of importance because lithium can be used as an indicator for the presence of pegmatites. These pegmatites are associated genetically with the granites and gneisses of the Upper Palatinate and the Black Forest. So far there are no reliable lithium analyses covering these regions. At times, the pegmatites in the Upper Palatinate have been mined for lithium, which occurs as lithium phosphate.

The distribution of lithium in stream sediments is largely controlled by the occurrence of shales, which in comparison with other types of rock, have a high lithium content (on average 60 ppm).

The median concentration in all the stream sediments analysed so far is 9 ppm Li; the highest value is 96 ppm Li.

2.3.2.14. Tungsten in stream sediments

Altogether, 95 % of the samples contain less than 2 ppm W (detection limit) and 0.1 % of them (about 50 samples) are above 16 ppm W. The North German lowlands were only randomly sampled.

Tungsten is invariably bound to oxygen and occurs in magmatic, metamorphic, and sedimentary mineral deposits. Magmatic tungsten deposits are formed by latestage silica- and water-rich differentiates from quartz- and feldsparrich intrusive rocks (granite, granodiorite, monzonite).

There are about twenty known tungsten minerals. Scheelite, CaWO_4 , and wolframite, $(\text{Fe},\text{Mn})\text{WO}_4$, are the most important tungsten ores.

Scheelite and wolframite are relatively insoluble under the pH conditions of most natural waters. They have a high specific gravity and are readily concentrated as heavy minerals in stream sediments.

Elevated tungsten values were encountered primarily in the crystalline basement areas of the Odenwald, Black Forest, Fichtelgebirge, Upper Palatinate Forest and the Bavarian Forest. Only small areas of tungsten mineralization are known, for example those near Mackenheim in the

Odenwald, near Nordrach, Untermünstertal, Eisenbach in the Black Forest, and near Pleystein in the Upper Palatinate Forest. None of these deposits has been mined.

Apart from the above areas, there are a few anomalies with over 16 ppm W, namely between Wuppertal and Remscheid, on the River Lahn west of Wetzlar, north of Darmstadt, southeast of Rothenburg and in the foothills of the Harz.

The tungsten analyses carried out within the framework of the geochemical survey proved to be a most successful means of prospecting. Follow-up work carried out in some areas where elevated tungsten concentrations were found in stream sediments demonstrated zones prospective for tungsten.

2.3.2.15. Tin in stream sediments

Tin analysis is not only very involved but also expensive. For this reason, a systematic determination of tin in stream sediments was carried out only for certain areas.

The tin concentrations range between 1 ppm (detection limit) and 1900 ppm; 85 % of all the samples contain less than 4 ppm Sn.

Tin mineralization is associated with the late differentiates of silica-rich igneous rocks (granite, rhyolite) and tin deposits are formed particularly in the pneumatolytic (300 - 500°C) and hydrothermal (250 - 350°C) stages.

The most important tin mineral is cassiterite (SnO_2), although other tin-bearing oxides and sulphides exist. A few other minerals can contain considerable amounts of tin: zinnwaldite and muscovite up to 3500 ppm, biotite up to 1300 ppm, and amphibole and sphene up to 1100 ppm Sn.

Cassiterite is chemically stable and very resistant to weathering and thus occurs as a heavy mineral in stream sediments.

High concentrations of tin in stream sediments are found predominantly in the areas of crystalline rocks in the Black Forest and the Fichtelgebirge and less commonly in the Upper Palatinate and Bavarian Forests. They can locally be shown to be associated with known tin occurrences.

Tin was once mined near Weissenstadt in the Fichtelgebirge, concentrated mainly on placer tin, although primary (postmagmatic) tin ores were also worked. In the Black Forest, cassiterite has been found in the Triberg and Eisenbach granites.

The remaining four anomalies (over 200 ppm Sn), which are probably of anthropogenic origin, are located south of the Ruhr near Iserlohn (1900 ppm Sn), north of Koblenz, in the Hunsrück and west of Bad Tölz.

2.3.3. River waters¹

2.3.4. River sediments²

3. Maps 1 : 200,000 and 1 : 50,000, Pb - Lead³

¹ The data of the 581 water and sediment samples taken separately for environmental studies in rivers and streams are not included in the currently available version of GEOMULDAT and their whereabouts are unknown. Therefore, neither the analysis data nor the maps mentioned here are included in the digital version of the atlas.

² The data of the 581 water and sediment samples taken separately for environmental studies in rivers and streams are not included in the currently available version of GEOMULDAT and their whereabouts are unknown. Therefore, neither the analysis data nor the maps mentioned here are included in the digital version of the atlas.

³ As it is no longer possible to request detailed maps (see chapter 1.6). The digital edition of the atlas therefore omits the sample maps included in the paper edition. Instead, in addition to the complete data set, ESRI shapefiles of all maps contained in the digital edition are made available for download via the BGR Product Center (<https://produktcenter.bgr.de>). Furthermore, the maps can be integrated into own GIS projects via WMS (Web Map Services) provided by the BGR or visualised with the BGR Geoviewer (<https://geoviewer.bgr.de>) in most current browsers.