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# Determination of Trace Elements in the River Aare (Switzerland) by Neutron Activation Techniques†

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More than 20 trace and minor elements were determined in water samples and in the suspended load of the river Aare (Switzerland) using a simple sample preparation technique and subsequent instrumental neutron activation analysis. The water samples were irradiated without preconcentration. The interfering activity of  $^{24}\text{Na}$  was eliminated with hydrated antimony pentoxide. The trace elements were co-precipitated as sulfides and hydroxides and were analyzed on Ge(Li)gamma-ray spectrometers. Particulate matter was filtered off in the field, irradiated and assayed by  $\gamma$ -ray spectroscopy. Main results: (a) the concentrations of all the elements investigated are much lower than WHO-limits for drinking water; (b) human activities are responsible for an increase of some elements along the river; (c) concentrations of dissolved trace elements are anticorrelated to the amount of water; (d) concentrations of trace elements in particulates ( $\mu\text{g/l}$ ) are correlated to the amount of water; (e) significant correlations for elements do not exist between all four sampling stations (exception: Ca-Sr); (f) most of the elements in the suspended solids ( $\mu\text{g/g}$ ) and in the water phase ( $\mu\text{g/l}$ ) are not correlated.

**KEY WORDS:** trace elements, neutron activation, river water.

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## 1. INTRODUCTION

Due to human activities the concentrations of some trace elements like Hg and Cd have considerably increased in the environment and in the food chain and have led to chronic poisoning and to diseases.<sup>1</sup> It is, therefore, very important to establish upper limits for the concentrations of potentially toxic trace elements which may be added to an ecosystem. These limits should be based on the natural and present-day concentrations of toxic trace elements in the systems of interest.

An investigation of a river has to be as complete as possible and should include analyses of the concentrations of trace and minor elements in solution as well as in the sediments and in the suspended solid load (silt). An increasing number of values for water samples and for sediments from rivers is being published, but very little is known about the composition of the suspended material. This is probably due to the fact that the latter is more difficult to assess in amounts large enough for trace element analysis. In this work a simple technique is described which allows the simultaneous determination of more than 20 trace and minor elements in river water and in the suspended material by neutron activation (NAA).

The main advantages of NAA are: (a) High sensitivity for many elements; (b) purely instrumental or semi-instrumental techniques avoiding difficult chemical separations; (c) possibility of multi-element determinations in the same sample; (d) low risk of contamination.

## 2. EXPERIMENTAL

### 2.1 Sampling

A 10-l polyethylene bucket was filled with surface water in the middle of the river either from a boat or a bridge. Immediately after sampling the water was transferred to 2-l high-pressure polyethylene bottles (HPPE, Kautex, W-Germany). The samples were filtered in the field into 100-ml HPPE bottles containing 1 ml of concentrated nitric acid of suprapure quality. For the collection of the suspended material a further 100–1000 ml water was filtered through 0.45  $\mu\text{m}$  Millipore filters (HAWP 03700). The filters contained 1.5–35 mg of solids depending on the sampling site. The simple filtration apparatus is shown in Figure 1. The 100-ml HPPE bottles with the filtrate at  $\text{pH} < 1.5$  containing the dissolved trace elements served as irradiation vials.

### 2.2 Neutron activation

The irradiations were carried out in the swimming pool reactor SAPHIR of the Swiss Federal Institute for Reactor Research.

### 2.2.1 Water samples

A 100-ml HPPE bottle with known amounts of the elements of interest (monitor solution) and five 100-ml HPPE bottles containing the water samples were irradiated together in a tray which was rotated to minimize flux inhomogeneities. The irradiation time was 3 hours (thermal neutron flux:  $2 \times 10^{13} \text{ cm}^{-2} \text{ sec}^{-1}$ ; fast flux:  $2 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ ). This time was much longer than the one suggested by Robertson<sup>2</sup> as upper limit for irradiations under similar conditions. The selected HPPE bottles showed a remarkably high resistance to radiation damage.

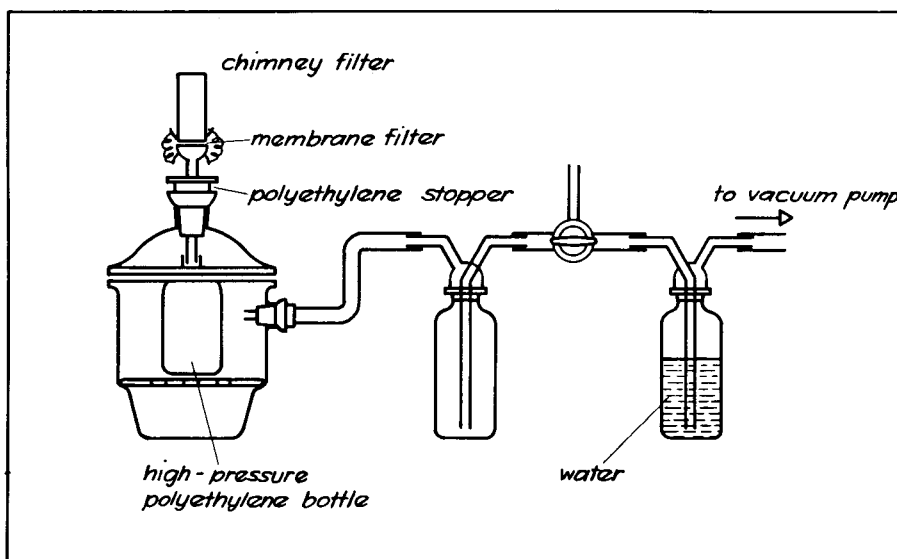


FIGURE 1 Apparatus for the field-filtration of water samples.

### 2.2.2 Solid samples

The dried membrane filters were sealed in polyethylene foils and stacked together with a filter (monitor) containing known amounts of the elements to be analyzed. The filter stack was wrapped in aluminium foil and sealed in a cylindrical polyethylene container which was rotated during the two hours' irradiation (thermal neutron flux:  $6.5 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ ; fast flux:  $8 \times 10^{11} \text{ cm}^{-2} \text{ sec}^{-1}$ ).

## 2.3 Post-irradiation treatment

### 2.3.1 Water samples

0.1–5 mg of inactive carriers for all the elements to be analyzed (see Table I) were added to the 100-ml samples. The solutions were evaporated to about 5 ml. The interfering  $^{24}\text{Na}$  was eliminated on hydrated antimony pentoxide columns (HAP-RS, Carlo Erba Milano, Italy) using 6 N HCl solutions. The columns had a length of 5 cm, an internal diameter of 5 mm, and contained 1 g of dry HAP. The samples were adsorbed from solutions of 7–8 ml and were washed with 10 ml 6 N HCl at rates of 1–2 ml min<sup>-1</sup>.

TABLE I  
Removal of elements with hydrated antimony pentoxide (HAP) and coprecipitations with sulfides + hydroxides

Element	Added carrier ( $\mu\text{g}$ ) %	Removal with HAP		Coprecipitation % <sup>b</sup>
		This work	Literature [11] % <sup>a</sup>	
As	1000	34 ± 3	4	97
Ba	120	1.3	14	—
Br	100		8	100
Ca	5000	3.5	8	98
Cd	100	2.0	4	97
Co	100	0.3	4	100
Cr	100	<0.8	2	100
Cu	100	<1.1	3	95
Eu	10	<1.1	3	100
Fe	200	<0.3	2	100
Hg	1100	<1	1	97
K	200	29	10	—
La	100	<1.2	3	100
Mn	100	<0.2	1	—
Mo	100	0.6	3	95
Na		100	100	—
Sb		1.4	3	100
Sc	100	2.1	2	100
Se	100	3.8	5	100
Sr	150	11	8	—
Np		0.4	2	92
W	1200	17–52	5	—
Zn	100	<1.3	1	96

<sup>a</sup>Elution with 15 ml 6N HCl.

<sup>b</sup>Results from tracer experiments.

10 ml aliquots of the eluate were counted for  $^{139}\text{Ba}$ ,  $^{42}\text{K}$ ,  $^{56}\text{Mn}$  and  $^{87\text{m}}\text{Sr}$ . The dissolved compounds in the whole 100 ml samples were subsequently scavenged from acid solutions with antimony sulfide, and from alkaline solutions with iron hydroxide and iron sulfide. The radioactivity of the precipitates was measured.

### 2.3.2 Solid samples

The  $\gamma$ -activity of the filters containing the activated solids were counted directly without chemical separations.

## 2.4 Counting and computations

Each sample was counted for about 10, 100, 300 and 600 min starting  $\sim 3$  hours and ending  $\sim 1$  month after the irradiation, Ge(Li) $\gamma$ -ray spectrometers and a Ge X-ray planar detector (for  $^{197}\text{Hg}$ ) with multichannel analyzers and magnetic tape output were used. The  $\gamma$ - and X-ray energies, and the half-lives of the analyzed nuclides are compiled in Table II. Also shown are the characteristics used for an unequivocal identification of the

TABLE II  
Characterization of the analyzed radionuclides

Element	Nuclide	Most intensive		Mode of identification
		$\gamma$ -rays (keV)	Half-life (h)	
As	As-76	559.1	26.3	B
Ba	Ba-131	496.3	276	A C
		373.2		
Br	Ba-139	165.8	1.38	B C
	Br-82	554.3	35.4	A B
		619.1		
Ca	Ca-47	698.4	109.0	A B
		1296.8		
Cd	Cd-115	807.8	53.5	A
		527.9		
Co	Co-60	1332.5	46130	B
		1173.2		
Cr	Cr-51	320.1	667.2	A
Cu	Cu-64	511	12.8	A B
		1345.8		
Eu	Eu-152	344.3	111300	A C
		778.9		
		964.0		
		963.5		
	Eu-152m	841.6	9.3	A B C

TABLE II (continued)

Element	Nuclide	Most intensive		Mode of identification
		$\gamma$ -rays (keV)	Half-life (h)	
Fe	Fe-59	1099.3	1070	A B
		1291.6		
Hg	Hg-197	68.8	64.1	A B
		77.4		
		77.9		
		1524.7		
K	K-42	12.36	12.36	A B
		312.9		
La	La-140	1596.2	40.3	A B
		328.8		
		815.8		
Mn	Mn-56	846.6	2.58	A B
		1811.2		
Mo	Tc-99m	140.5		A
	Mo-99		66.2	
Na	Na-24	1368.5	15.0	A B
		346.6		
		1732.1		
Sb	Sb-122	564.1	64.8	A B C
		692.8		
	Sb-124	602.7	1445	A C
Sc	Sc-46	1691.0	2014	A
		1120.5		
		889.3		
Se	Se-75	264.5	2880	A
		135.9		
Sr	Sr-87m	388.4	2.81	B
U	Np-239	228.2	56.4	A B
		106.1		
		209.8		
W	W-187	685.7	24.0	B
Zn	Zn-65	1115.5	5851	C
	Zn-69m	438.9	13.8	B C

A: Use of several  $\gamma$ -lines.  
 B: Verification of the decay.  
 C: Two isotopes used.

nuclides. The areas of the photopeaks were computed with a modified program of Barnes<sup>3</sup> which is based on the iterated best Gaussian and a linear background reduction. The data of the monitor and sample spectra were converted into concentrations and were corrected for the blank

values. Concentration limits were calculated in analogy to De Soete<sup>4</sup> if the critical level of detection  $L_c$

$$L_c = 1.645 \times (2\sigma_b^2)^{1/2}$$

where:  $\sigma_b$ , standard deviation of the blank was not reached due to a high blank correction or if a  $\gamma$ -ray peak was not found in the spectrum. The following criteria for the lowest determinable peak area  $P_m$  was used<sup>4</sup>:

$$P_m = \frac{1 + 2 \cdot \left(\frac{Y}{100}\right) \cdot (2U_z \cdot T_m)^{1/2}}{2 \cdot \left(\frac{Y}{100}\right)^2}$$

where:  $Y$ , allowed statistical error in %,

$T_m$ , counting time,

$U_z$ , background activity at the position of the expected  $\gamma$ -ray photopeak.

### 3. DISCUSSION AND TEST OF THE METHOD

#### 3.1 Loss of trace elements

Losses of trace elements due to adsorption on container surfaces are well known. In order to minimize losses, the samples were field-filtered within 1 hour after collection into HPPE bottles containing acid. Adsorption losses at  $\text{pH} \leq 1.5$  are greatly reduced in HPPE containers.<sup>5</sup>

#### 3.2 Contamination and blanks

In NAA contamination of the samples is only critical before the irradiation. The number of operations performed in this work with the unirradiated samples was kept minimal. In particular no preconcentration was made and the HPPE bottles were carefully selected among plastic products. The chosen bottles showed, in agreement with results of Refs. 6 and 7, the lowest trace element contents. Struempfer<sup>8</sup> has found that also some makes of polypropylene are unsuitable for water sampling due to interfering contents of Zn and Cd. We have demonstrated that polystyrene and polyacrylnitril products contain significant amounts of Br, Co, Sb and Zn and of Ba, Ga, Sb and Sr, respectively.



TABLE III  
Mean blank values for dissolved and suspended trace elements

Element	Dissolved elements (ppb)		Suspended elements ( $\mu\text{g}/\text{filter}$ )	
	This work	Literature [9]	This work	Literature [10]
As	0.009		0.001	
Ba	<1		<0.1	0.007
Br	0.2		0.031	
Ca	<20	1		
Cd	0.012	<0.1		
Co	0.0043	<0.1	0.0026	0.0009
Cr	0.042	<0.1	0.26 <sup>a</sup>	0.11
Cu	0.2	0.2	<0.3	0.14
Eu	0.00008		0.00005	
Fe	<1	0.2	2 <sup>a</sup>	0.21
Hg	0.007	<0.1	0.012	
K	1.1		0.6	0.70
La	0.0006		0.0009	
Mn	0.034	0.05	0.012	0.018
Mo	0.027	<0.1	0.0043	0.003
Na	30	1	1.5	2.8
Sb	0.005	<0.5	0.0024	
Sc	0.0005		0.00026	
Se	0.014		0.003	
Sr	0.2		0.1	0.016
U	0.005		0.0021	
W			0.0025	
Zn	0.28	<0.1	0.071	0.12

<sup>a</sup>Possible contamination due to the punching of the filters.

Blank tests were performed in order to assess possible contributions by contamination. Blanks for the liquid samples were obtained by filtering at each sampling site quartz-doubly distilled water with subsequent irradiation and analysis according to the described procedure. Blank values for the solid samples were deduced from irradiated empty membrane filters. Mean values for the liquid and solid blanks are shown in Table III and are compared with literature values.<sup>9,10</sup> The high value for Fe in the solid sample might reflect a contamination of the filters due to punching.

### 3.3 Analytical procedures

#### 3.3.1 Losses during the evaporation of the irradiated samples

Trace element losses during volume reduction were tested with radio-tracers and were significant only for Hg (20%  $\pm$  10%). Since similar losses

can be assumed for the samples as well as for the monitors, they were only considered in the error estimation.

### 3.3.2 Hydrated antimony pentoxide (HAP)

A decontamination factor for Na of  $10^3$ – $10^4$  was reached. The elution for the elements of interest was tested and compared with values of Girardi and Sabbioni<sup>11</sup> (Table I). Significant differences to Ref. 11 were found in the sorption of As and W. While the As retention was constant and reproducible, W varied considerably and led to the exclusion of a determination of this element in the water samples. The As retention in our investigation may be due to a partial reduction to  $As^{3+}$  which was completely adsorbed on HAP from concentrated HCl.<sup>12</sup> The other differences in Table I are less significant and could probably have been eliminated with a more extensive column wash.<sup>11</sup>

### 3.3.3 Co-precipitation

The yields of all elements in the combined precipitates were  $>90\%$ . Results from tracer experiments are shown in Table I. Since the solutions of the monitors and samples were treated in the same way equal losses for both were assumed in the separations on HAP as well as in the precipitations.

### 3.3.4 Errors

The errors include counting statistics ( $1\sigma$ ) and uncertainties due to incomplete chemical separation and due to the blanks.

## 3.4 Test of the method

The accuracy and precision of the determination of each element in solution was tested in an interlaboratory comparison of the International Atomic Energy Agency (IAEA, Vienna).<sup>13</sup> The trace element determinations in the solids were checked with samples of the U.S.-Geological Survey. The results for the liquid and solid tests are shown in Table IV together with “true” values, means and standard deviations of all accepted individual laboratory means for the dissolved samples, and values from Flanagan<sup>14</sup> for the solids. The tests demonstrate the suitability and quality of our method.

## 4. ANALYZED RIVER SYSTEM

Figure 2 shows a map of Switzerland with the Aare river. During a period of one year, 6–8 samples were collected at each of four different locations

TABLE IV  
Precision and accuracy of the method

Element	Dissolved trace elements in IAEA-W3 <sup>a</sup> (ppm)			Solid trace elements in standard rock <sup>c</sup> (ppm)	
	This work	"True" value	Mean + $\sigma^b$	This work	Literature [14]
As	14.6 ± 2.1	16	15.6 ± 6.8	0.35 ± 0.27	0.70
Ba	39.0 ± 2.3	32	47.6 ± 27.5	840 ± 80	675
Cd	4.36 ± 0.08	4	5.2 ± 2.7		
Co	11.4 ± 1.4	12.1	11.9 ± 4.2	38.7 ± 3.5	38
Cr	11.0 ± 1.0	12	11.0 ± 5.0	14.9 ± 1.7	17.6
Cu	12.2 ± 0.4	12	12.5 ± 3.5		
Eu				2.1 ± 0.2	1.94
Fe	37.2 ± 1.4	32	49.6 ± 37.2	142500 ± 7500	134000
Hg	1.03 ± 0.13	1	1.6 ± 0.6		
K				17600 ± 2600	17000
La				27.6 ± 1.2	26
Mn	7.77 ± 0.08	12	10.8 ± 3.2	1330 ± 160	1406
Mo	10.4 ± 0.3	8	7.5 ± 3.5		
Sb				0.54 ± 0.11	0.69
Sc				32.6 ± 1.4	33
Se	10.3 ± 1.0	8	7.8 ± 2.9		
Sr				250 ± 100	330
U	3.43 ± 0.11	3.2	3.5 ± 1.9	1.95 ± 0.33	1.96 <sup>d</sup>
W				2.7 ± 1.6	0.4
Zn	12.7 ± 0.3	12	13.6 ± 6.8		

<sup>a</sup>Interlaboratory comparison of the International Atomic Energy Agency 1975.<sup>13</sup>

<sup>b</sup>Mean values and standard deviation of all accepted individual laboratory means.<sup>13</sup>

<sup>c</sup>USGS-BCR-1 (Basalt Columbia River).

<sup>d</sup>USGS-GSP-1 (Granite Standard).

between the source region and the lake of Bienne: (1) Meiringen, (2) Thun, (3) Bern, (4) Hagneck. The four sampling places are very dissimilar due to intermediate sedimentation basins, tributaries from different geological formations, differences in inclination, waterload and influence of civilization. Schematically the four locations can be classified as follows:

- (1) Meiringen: Sparsely inhabited, drainage area mostly crystalline rocks, steep slope of the river, large suspended load.
- (2) Thun: Sampling after two sedimentation basins (lakes), characterized through the Kander river, lake inflow from a limestone drainage area.

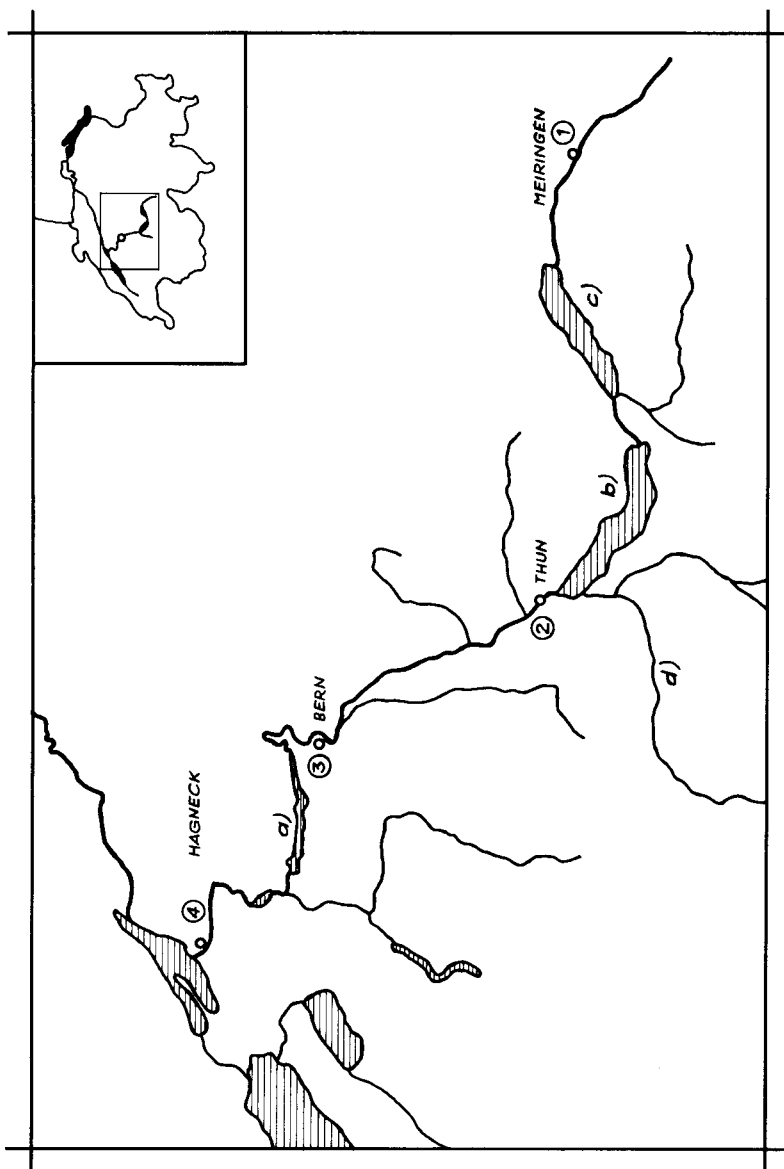


FIGURE 2 Map with the sampling stations (1), (2), (3), (4) along the river Aare. (a) Wohlensee, (b) Thunersee, (c) Brienersee, (d) Kander. The insert (upper right corner) shows the situation of the investigated region within Switzerland.

- (3), (4) Bern, Hagneck: Weather dependent influence from tributaries with variable amounts of weathered products.
- (2), (3), (4) Drainage area more inhabited, increasing influence of the dissolved components.

## 5. RESULTS AND DISCUSSION

### 5.1 Dissolved trace elements

Mean values for the measured elements at the four sampling locations are listed in Table V. Also shown are values for other river systems and WHO-limits for drinking water. All elements except the alkaline earths, Mn, Mo and U are lower than the mean values given by Garrels<sup>16</sup> for "natural" river systems. The high concentrations for Ba, Ca and Sr at several sampling stations reflect drainage from limestone areas. Meiringen with water mainly from a crystalline area exhibits low alkaline earths concentrations. Within the overall low concentrations of most trace elements, Br, Cr, Cu, Na, Sb and Zn increase significantly with increasing inhabitation, although most waste waters are processed before entering the river. Compared with the amounts of trace elements in the Arve river (Geneva, Switzerland) or the Rhine (Germany) the Aare river still represents a quite clean, barely polluted river system.

### 5.2 Suspended trace elements

Mean values for the suspended solids are listed in Table VI together with values of Bockris<sup>17</sup> for sediments. Sb and Zn show significantly higher concentrations than in Ref. 17. This could be due to human influences. Br and Sb exhibit low values at Meiringen. This area is only slightly populated. Ba, the rare earths and some minor elements (Fe, K and Na) display the same concentration pattern at all sampling stations indicating possibly the same rock origin.

### 5.3 Relation between dissolved and suspended trace elements

The circle-segments of Figure 3 illustrate for all sampling stations the distribution of the analyzed elements between solution and suspension. Br is prevalently found in solution. Co, Cr, Fe, Sc and the rare earth elements are mainly transported as solids. The contribution of the amount of dissolved elements is in general steadily increasing from Meiringen to Hagneck. The major reason for this is a decreasing overall amount of

TABLE V  
Mean concentrations ( $\mu\text{g/l}$ ) of the dissolved trace elements at the sampling stations Meiringen, Thun, Bern and Hagneck.  
Comparison with literature values

Element	Mean values				Arve, Geneva <sup>a</sup>	Rhine, W-Germany <sup>b</sup>	Estimated mean for rivers [16]	WHO-limits for drinking water <sup>c</sup>
	Meiringen	Thun	Bern	Hagneck				
As	0.60	0.48	0.42	0.69	2.8		2	
Ba	10	15	26	30	23		20	
Br	0.68	1.5	2.7	4.7	4.7		20	
Ca	7890	42800	43900	57500			15000	
Cd	0.07	<0.55	<0.42	0.13	0.88	5	0.2	5
Co	0.090	0.013	0.043	0.063	0.125	10	0.1	50
Cr	0.061	0.052	0.254	0.191	1.44	10	1	50
Cu	0.53	0.67	1.42	2.35	14.8	30	7	50
Eu	0.00051	0.00008	0.0003	0.0011	0.018		0.007	
Fe	12.4	1	6.4	5.4	57		670	
Hg	0.047	0.012	0.020	0.009	0.017	0.5	0.07	0.5
K	971	903	979	1450	1980		2300	
La	0.011	0.0055	0.0078	0.0078	0.093		0.2	
Mn	8.90	0.97	2.26	5.23	7.9		7	
Mo	1.12	0.77	0.77	0.74	4.08		0.6	
Na	1120	1370	2130	3030			6300	
Sb	0.068	0.066	0.124	0.138	0.32		2	
Sc	0.0023	0.0006	0.0009	0.002	0.031		0.004	
Se	0.10	0.12	0.11	0.10	1.2		0.2	
Sr	34	380	368	441	390		70	
U	0.37	0.46	0.47	0.49	1.36		0.3	
Zn	1.94	1.86	5.13	4.13	630	250	20	5000

<sup>a</sup>Determined in our laboratory (filtered at the Département de Chimie Minérale et Analytique de l'Université de Genève).

<sup>b</sup>Rhine kilometer 420-852.<sup>15</sup>

<sup>c</sup>Values from Foerstner.<sup>15</sup>

suspended material further down the river, and at several places an increasing concentration of dissolved elements probably due to human activities.

Schindler<sup>19</sup> has proposed a simple adsorption-desorption model for trace elements on artificial silicagel surfaces. Experimental distribution coefficients  $D_e$  can be determined for each element according to

$$D_e = \frac{\text{Trace element concentration in suspension } (\mu\text{g/g})}{\text{Trace element concentration in solution } (\mu\text{g/l})}$$

The  $D_c$ -values calculated with the model description are always lower than the experimental data (exception Zn). This result may reflect the presence

TABLE VI  
Mean concentrations of the suspended trace and minor elements for all sampling locations

Element	Mean values								Average in sediments [17] (ppm)
	Meiringen		Thun		Bern		Hagneck		
	(ppm)	( $\mu\text{g/l}$ )	(ppm)	( $\mu\text{g/l}$ )	(ppm)	( $\mu\text{g/l}$ )	(ppm)	( $\mu\text{g/l}$ )	
As	16	1.9	7.6	0.015	8.2	0.16	11	0.088	6.6
Ba	960	120	220	0.44	300	6.0	370	3.0	690
Br	3.2	0.38	29	0.058	24	0.48	20	0.16	
Co	21	2.5	8.4	0.017	7.4	0.15	12	0.096	22
Cr	84	10	130	0.26	130	2.6	130	1.0	130
Eu	1.3	0.16	0.22	0.00044	0.63	0.013	0.86	0.0069	
Fe	58000	7000	11000	22	23000	460	33000	260	
K	38000	4600	11000	22	14000	280	18000	140	
La	41	4.9	11	0.022	27	0.54	34	0.27	
Mn	720	86	390	0.78	590	12	1200	9.6	760
Na	27000	3200	2100	4.2	5000	100	5900	47	
Sb	0.70	0.084	7.4	0.015	26	0.52	4.7	0.038	1.25
Sc	17	2.0	3.6	0.0072	7.3	0.15	9.6	0.077	
U	14	1.7	19	0.038	2.5	0.050	4.3	0.034	3.2
W	8.4	1.0	2.6	0.0052	5.2	0.10	4.1	0.033	2
Zn			320	0.64	400	8.0	390	3.1	80

of non-distributable species or a too slow exchange between dissolved material and solids of possibly crystalline origine. Positive correlations for the distribution between the solid and the dissolved elemental freight were only obtained for Co, Fe, La and Sc. These correlations are shown in Fig. 4. They suggest for these elements the existence of an adsorption-desorption mechanism between solution and solids.

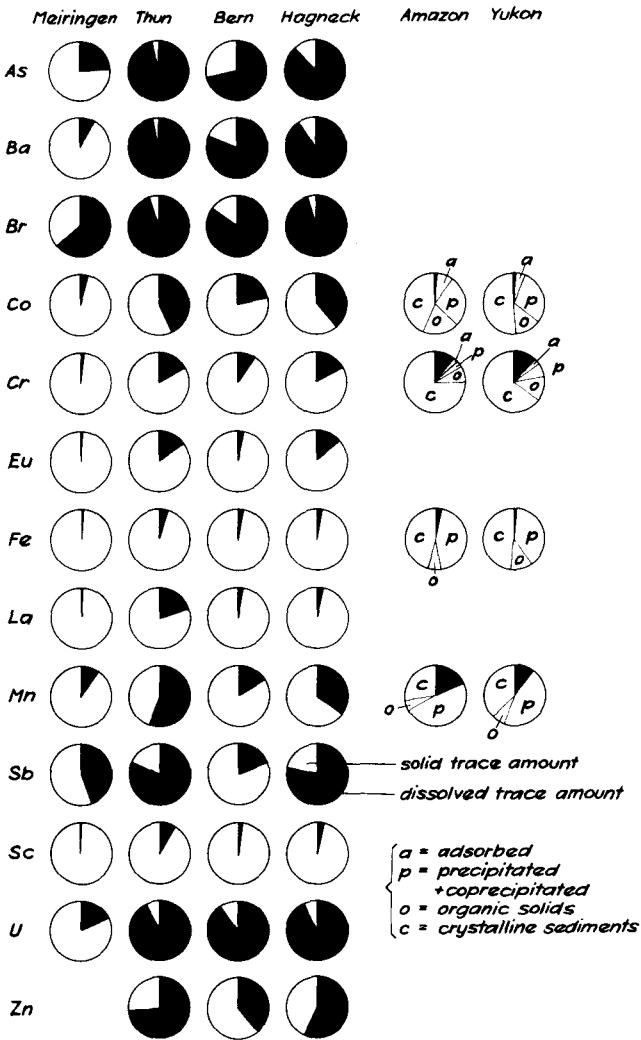


FIGURE 3 Distribution of trace elements between solids and solution at the sampling stations Meiringen, Thun, Bern, Hagneck. The values for Co, Cr, Fe, Mn for the Amazon and Yukon-river are from Ref. 18.



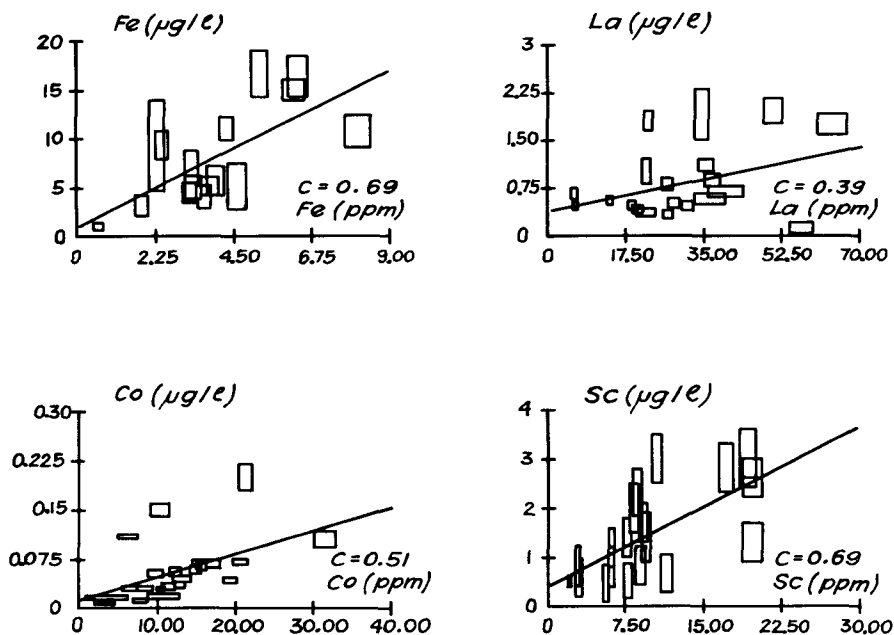


FIGURE 4 Correlations for the concentrations of Co, Fe, La, Sc between solids (ppm) and solution ( $\mu\text{g/l}$ ). The values of all sampling sites are shown.  $C$ =correlation coefficient.

## 5.4 Correlations among trace elements, water load and overall suspended load

In order to recognize systematic tendencies in the behaviour of trace elements and of major components, correlation matrices and linear regressions were compiled for the dissolved and suspended material and the sampling locations. The main results are listed below.

### 5.4.1 Dissolved trace elements and amount of water

The concentrations of most of the dissolved trace elements are anti-correlated to the amount of water. This can be interpreted as a dilution effect. The constant anthropogenic contribution becomes also less important with an increasing flow rate. Since the overall suspended load rises generally with an increasing amount of water, the result indicates again an unequilibrated system of dissolved and solid material. Figure 5 shows an example for each sampling place. Cr and Cu are significantly anti-correlated, whereas much smaller correlation coefficients are obtained for Sb and Ba (confidence level  $>90\%$ ).

### 5.4.2 Suspended trace elements and overall suspended load

A significant positive correlation was generally found between the concentrations of suspended trace elements (in  $\mu\text{g l}^{-1}$ ) and the amount of suspended material (in  $\text{mg l}^{-1}$ ). The amount of suspended material rises mostly with an increasing amount of water. Therefore, positive correlation coefficients are also observed between the suspended trace element concentrations and the water flow rate. The trace element concentrations expressed in ppm, however, show a more complex relation to the overall amount of suspended material.

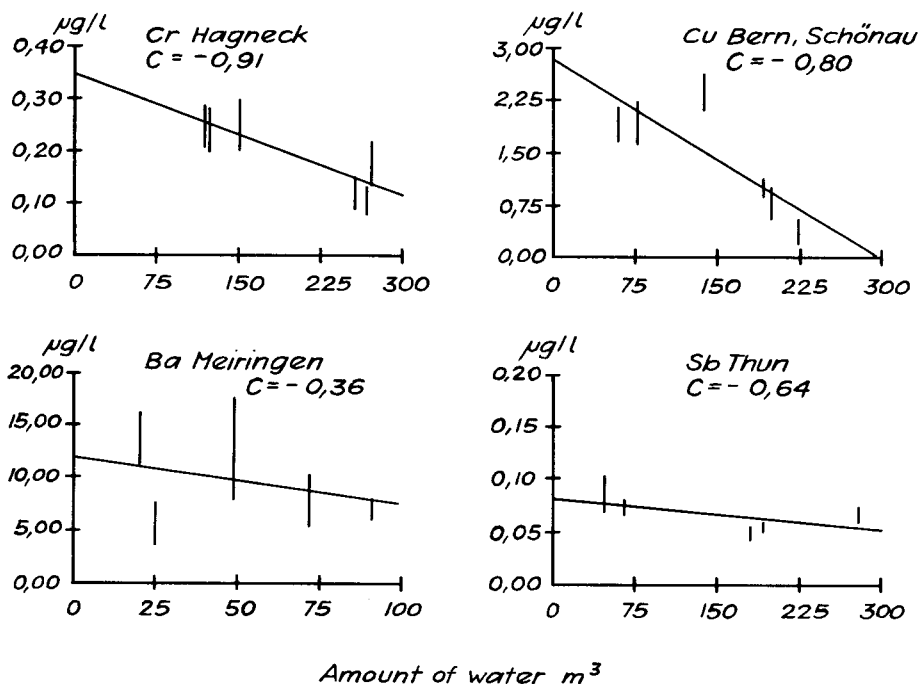


FIGURE 5 Examples for the dependency of the concentrations of dissolved trace elements (Ba, Cr, Cu, Sb) on the flow rate of the river.  $C$  = correlation coefficient at a confidence level  $>90\%$ .

### 5.4.3 Correlations between trace elements

Significant correlations among trace elements were found at each location in the dissolved as well as in the suspended fractions. The reasons for these concentration patterns are not understood. Since only a small number of samples was analyzed, some of these correlations may be

accidental. Correlations for single element pairs are only found for Ca and Sr throughout all sampling location.

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