

## **Contents of Some Heavy Metals in Norwegian Rivers**

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Concentration data for the elements arsenic, cadmium, cobalt, molybdenum, zinc, and uranium in eleven Norwegian rivers, determined by neutron activation analysis, are presented. The mean values of the various rivers show the following range for the elements studied ( $\mu\text{g/l}$ ): As, <0.02-1.05. Cd, <0.06-0.43. Co, 0.09-0.46. Mo, <0.10-1.62. Zn, <2-53. U, 0.041-0.58. The weighted mean values in this work are similar to the estimated world averages for rivers in the case of Co and Zn. For As, Mo, and U, the present values are lower than the world averages by a factor of 3 or more. This may be due to lower abundance of sedimentary rocks and deposits in Norway compared with the drainage basins of some of the major rivers in the world.

### **Introduction**

The present investigation is devoted to the elements zinc, cadmium, arsenic, cobalt, molybdenum, and uranium in eleven Norwegian rivers especially selected for study in the International Hydrological Decade (IHD) programme. Each of these elements, which are in most cases present at very low concentrations in natural waters, is either essential to certain species or may be toxic even when present at quite low levels, and a better knowledge of their abundances is therefore desirable. Moreover all six elements are potential pollutants to the river

system from industrial or other anthropogenic progresses. The increasing environmental pollution with trace elements makes the establishment of »baseline« values for their concentrations in natural systems an important task.

## Experimental

The eleven rivers investigated and the sampling sites used are listed in Table 1. Three samples with about 2 months' interval were taken from each river during the period May-October of 1971. Samples were collected in 1-liter polyethylene bottles containing 5 ml of high-purity concentrated nitric acid (E. Merck, Suprapure) to prevent loss of trace elements due to adsorption on the container walls and the growth of algae during storage.

The analytical determinations were carried out by radiochemical neutron activation analysis according to methods described elsewhere (Steinnes 1973; Lenvik et al. 1977).

Prior to analysis the bottles were shaken and then allowed to stand for about twenty hours before aliquots of 5 ml were decanted into quartz ampoules for irradiation. By this treatment most of the suspended material is eliminated from the sample.

Possible blank contribution from the quartz ampoules and the nitric added to the samples was examined, but found to be negligible. Possible contamination of the samples from the polyethylene bottles during storage was also investigated by storing »samples« of 1 l quartz-distilled water in the presence of 5 ml concentrated

Table 1 - Rivers included in the present investigation

River	Sampling site	Drainage area km <sup>2</sup>	Mean discharge m <sup>3</sup> s <sup>-1</sup>
Glomma	Askim water works	40,013	679
Drammenselva	Vikersund	16,020	313
Aulielva	Sem station	362	7
Skienselva	Fareelva	9,975	285
Mandalselva	Buøya pump-station	1,746	87
Jostedalselva	Røneid bridge	832	58
Rauma	Romsdalshorn station	1,098	37
Gaula	Udduvoll bridge	3,055	76
Forra	Outlet in Stjørdalselva	488	21
Namsen	Grøte	3,302	154
Tana	Tana bridge	14,005	161

nitric acid for a period of time corresponding to the average storage time of the water samples between sampling and analysis. For zinc, a contribution of 2  $\mu\text{g/l}$  was found, and a corresponding correction applied to the results for the water samples. For the other elements, no contamination was evident. The practical detection limits in this work were about as follows ( $\mu\text{/l}$ ): As, 0.02; Cd, 0.06; Mo, 0.1; Zn, 2; Co, 0.02; U, 0.005. The precision of the analyses depended on the concentration levels present; for concentrations exceeding 10 times the detection limit the relative standard deviation of replicate analyses was about 10-15%.

The loss of trace elements due to adsorption to the container walls at the storage conditions employed in the present work was studied for the elements Co, Mo, and Zn using radioactive tracers. The specific activity of the added tracer was such that the concentration of each element after tracer addition was similar to that observed in the natural water samples. The results are shown in Fig. 1. In the case of Mo and Zn, the adsorption at  $\text{pH} \sim 1$  seems to be negligible. Concerning Co, in which case two different concentrations were employed, losses of about 5% and 8% were observed at 1.0  $\mu\text{g/l}$  and 0.2  $\mu\text{g/l}$ , respectively. This experience is in agreement with that of Robertson (1968) who found <5% adsorption of Co and Zn in water with  $\text{pH} = 1.5$  stored in polyethylene bottles.

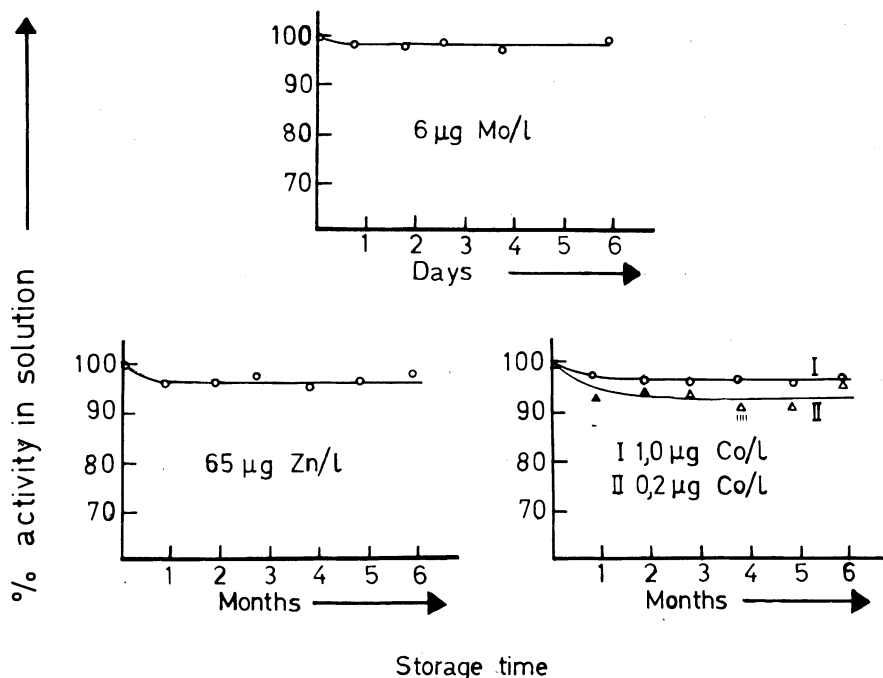


Fig. 1. Diagram showing the loss of Mo, Zn, and Co from water of  $\text{pH} \sim 1$ , stored in 1-l polyethylene bottles, as a function of time.

## Results

Parallel to this work a broader study has been carried out where purely instrumental activation analysis (Salbu et al. 1975) was used for the determination of a great number of elements in the same samples as investigated in the present work. A statistical analysis of that material, including the data from this work, will be presented elsewhere. In this paper, the discussion will be concentrated on each individual element determined in the present work.

The analytical data obtained in this work are listed in Table 2. Mean values of the three observations at different seasons are also given for each element in each individual river. Geometrical mean is used, assuming that the data are more adequately described by a lognormal distribution than by a Gaussian. The lognormal distribution has previously been shown to represent a good description of geochemical trace-element data (Ahrens 1954). Also for data from the present

Table 2 – Concentrations of As, Cd, Co, Mo, Zn, and U in Norwegian rivers ( $\mu\text{g/l}$ .\*

River	Date of sampling	As	Cd	Co	Mo	Zn	U
	1971						
Glomma	6/15	0.43	0.12	0.07	0.11	57	0.066
	8/16	0.33	0.10	0.08	0.07	51	0.066
	10/21	0.41	0.23	0.12	0.12	53	0.071
	Mean	0.39	0.14	0.09	0.10	53	0.068
Drammenselva	6/15	0.13	<0.06	0.07	0.21	<2.0	0.090
	8/16	0.13	0.10	0.13	0.14	2.2	0.122
	10/18	0.20	0.16	0.12	0.16	7.0	0.112
	Mean	0.15	$\leq 0.10$	0.10	0.17	$\leq 3.1$	0.107
Aulielva	6/15	1.27	0.11	0.40	1.91	3.8	0.62
	8/16	0.72	0.10	0.43	1.41	4.8	0.31
	10/18	1.25	0.65	0.35	1.57	21	1.02
	Mean	1.05	0.19	0.39	1.62	7.3	0.58
Skieselva	6/16	0.22	0.51	0.13	0.21	5.6	0.084
	8/15	0.15	0.28	0.08	0.24	6.4	0.142
	10/15	0.31	0.42	0.09	<0.10	21	0.110
	Mean	0.22	0.39	0.10	$\leq 0.17$	9.1	0.110

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Table 2 continued

River	Date of sampling		As	Cd	Co	Mo	Zn	U
	1971							
Mandalselva	6/15		0.72	0.16	0.10	0.28	16	0.086
	8/16		0.44	0.22	0.10	0.20	22	0.088
	10/15		0.40	0.27	0.10	0.17	23	0.067
	Mean		0.50	0.21	0.10	0.21	20	0.080
Jostedalselva	5/16		0.03	0.18	0.25	<0.10	4.2	0.161
	8/17		0.03	0.86	0.30	0.18	7.7	0.188
	10/18		0.07	0.53	0.68	0.30	26	0.45
	Mean		0.04	0.43	0.37	≤0.17	9.5	0.240
Rauma	May		<0.02	0.13	0.18	<0.10	<2.0	-
	June		<0.02	<0.06	0.08	<0.10	<2.0	-
	September		<0.02	<0.06	0.05	<0.10	<2.0	-
	Mean		<0.02	≤0.08	0.09	<0.10	<2.0	-
Gaula	6/18		0.16	0.14	0.94	<0.10	8.6	0.066
	8/24		0.07	0.12	0.42	<0.10	9.8	0.093
	10/18		0.21	0.09	0.25	0.12	30	0.088
	Mean		0.13	0.11	0.46	≤11	14	0.082
Forra	6/16		0.11	<0.06	0.32	<0.10	<2.0	0.083
	8/16		0.35	<0.06	0.30	<0.10	<2.0	0.026
	10/18		0.10	<0.06	0.32	0.35	<2.0	0.033
	Mean		0.16	<0.06	0.31	≤0.15	<2.0	0.041
Namsen	6/18		0.08	0.08	0.47	0.15	4.6	0.143
	8/16		0.14	0.08	0.36	<0.10	3.8	0.206
	10/15		0.36	0.08	0.68	<0.10	7.3	0.074
	Mean		0.16	0.08	0.48	≤0.12	5.0	0.130
Tana	6/16		0.03	<0.06	0.21	0.30	6.0	0.063
	8/22		<0.02	<0.06	0.27	0.17	10	0.041
	10/19		<0.02	<0.06	0.20	0.33	7.0	0.056
	Mean		≤0.02	<0.06	0.22	0.26	7.5	0.052

\* Geometric mean values

material (Salbu et al. 1977), observed frequency distributions show that the lognormal distribution gives a better fit to the experimental data than the Gaussian.

On the basis of the mean discharge data given in Table 1, weighted mean values have been calculated. The eleven rivers dealt with here include more than 50% of the total runoff in Norway and form a quite representative selection of Norwegian rivers. Determination of Ca, Cl, Fe, K, Mn and Na in the same samples and comparison with mean values of monthly samples collected at the same locations during 1966-70 indicate that the present samples may be quite representative at least for those components (Salbu et al. 1978). Therefore assuming that the individual mean values in Table 1 are representative on an annual basis these values may be considered as fairly good averages for the whole country. The weighted means are presented in Table 3 and compared with data from rivers in Northern Sweden (Landström and Wenner 1965) and with the estimate of world averages by Turekian (1969).

## **Discussion**

*Arsenic* – The weighted mean value  $0.25 \mu\text{g}/\text{l}$  is substantially lower than the estimated world average for rivers of  $2 \mu\text{g}/\text{l}$  (Turekian 1969). It should be noted, however, that the latter value is based on two literature reports only, neither of which was concerned with any of the large rivers of the world. Another fact that must be borne in mind, is that the arsenic content of sedimentary rocks and marine clays is of the order of a factor of 5 higher than that of common igneous rock types (Onishi and Sandell 1955; Turekian and Wedepohl 1961). Corresponding differences in the arsenic concentrations of river water may be expected depending on the geology of the drainage areas. In the present work the arsenic concentrations in Aulielva ( $1.1 \mu\text{g}/\text{l}$ ) and to some extent also in Mandalselva ( $0.50 \mu\text{g}/\text{l}$ , where recent marine deposits are represented in the drainage basins, are high compared with those of the other rivers. The lowest values ( $<0.02 \mu\text{g}/\text{l}$ ) are found in rivers with drainage areas dominated by precambrian rocks.

*Cadmium* – Cadmium values of unpolluted river water do not seem to be available in the literature, and no estimate for rivers was given by Turekian (1969). The present work indicates that the normal concentration of cadmium in rivers is very low. The weighted mean value of  $0.17 \mu\text{g}/\text{l}$  is close to the  $0.11 \mu\text{g}/\text{l}$  reported for ocean water (Turekian 1969). In relation to the geochemically associated element zinc the cadmium values of this work however still seem surpris-

singly high, considering the Zn/Cd ratios of 400-600 reported for common types of igneous and sedimentary rocks (Turekian and Wedepohl 1961). A ratio of that order is observed in the present material only in the case of Glomma. In the other cases where the results allow this ratio to be calculated, values in the range of 20-130 are obtained for the Zn/Cd ratio. This substantial difference might indicate that processes other than the weathering of rocks contribute to the supply of these elements to the rivers. Possible cadmium contamination in the analysis would lead to low Zn/Cd ratios, but this is not a probable explanation to the observed trend, considering our experience from blank analyses.

Since the drainage basins of the rivers showing low Zn/Cd ratios are in general closer to the coast and exposed to higher precipitation than that of Glomma, it may be assumed that the chemical composition of the precipitation could contribute to the trend observed. Analyses of moss samples have indicated that the airborne supply of cadmium in Norway is much higher in the southernmost areas of the country than in places further north, and also depends to a certain extent on the amount of precipitation (Rühling and Tyler 1973; Steinnes 1977). The regional differences for zinc were considerably less than those for cadmium. Presumably high-temperature anthropogenic processes, that seem to be mainly responsible of the observed fall-out of cadmium in southern Scandinavia, lead to an enrichment of cadmium relative to zinc in the aerosol derived from the process. The considerable supply of cadmium through the precipitation might then even affect the Zn/Cd ratio of natural waters in Norway.

*Cobalt* – The weighted mean of 0.16  $\mu\text{g}/\text{l}$  for cobalt is in correspondence with the 0.2  $\mu\text{g}/\text{l}$  world average estimated by Turekian (1969), and also shows fairly good agreement with the level found for the rivers in Northern Sweden (Landström and Wenner 1965). It may be noted that the cobalt data for rivers in Trøndelag (Gaula, Forra, Namsen), mainly draining areas of Cambro-Silurian sedimentary rocks, are distinctly higher (0.3-0.5  $\mu\text{g}/\text{l}$ ) than those for the major watercourses in Eastern Norway (Glomma, Drammenselva, Skienselva) showing concentrations of about 0.1  $\mu\text{g}/\text{l}$ .

*Molybdenum* – The present values are in the same range as those from Sweden (Landström and Wenner 1965) but the weighted mean is almost a factor of ten lower than the estimated world average. In this case, as for arsenic, the considerably higher concentrations in certain sedimentary rocks relative to the most common igneous rocks (Turekian and Wedepohl 1961) may explain the difference between the Norwegian and the world averages. In the present material, Aulielva by far showed the highest molybdenum concentration, which may be explained by the fact that molybdenum is high in marine deposits.

*Zinc* - The weighted mean in Table 3 is in agreement with the estimated world average. In most rivers, the October sample shows the highest concentration among the single samples. From the rivers studied, Glomma shows by far the highest zinc concentration, which may partly be explained by the presence of sulfide ore deposits in the Northern part of the drainage basin, some of which are being mined.

Table 3 Comparison of weighted mean values from the present work with literature ( $\mu\text{g/l}$ )

Element	Present work, weighted mean	Rivers, estimated world average (Turekian, 1969)	Ocean water (Turekian, 1969)	Rivers in Northern Sweden (Landström and Wenner, 1965)
As	0.25	2	2.6	0.2 - 0.4
Cd	0.17	-	0.11	-
Co	0.16	0.2	0.39	n.d. - 0.1
Mo	0.15	1	10	n.d. - 0.3
Zn	24	20	5	7 - 19
U	0.093	0.04*	3.3	0.04 - 0.09

\* According to Turekian and Chan (1971) more recent analyses suggest a world average of about 0.3  $\mu\text{g/l}$ .

*Uranium* - For this element the individual mean values of the Norwegian rivers are also in the same range as those reported for rivers in Northern Sweden. The present weighted mean is a factor of 3 lower than the most recently estimated world average (Turekian and Chan 1971). The reason for this may be the same as indicated above for As and Mo.

The concentrations of the six elements investigated in this work show large variation among different Norwegian rivers, the ratio of the highest and lowest geometric mean value being least for cobalt (5.3) and highest for arsenic (>50). In some cases the contents were below the detection limits of the analytical method employed, especially in the cases of Rauma, Forra, and Tana. Except perhaps for zinc, there is no clear tendency that samples collected at one part of the year show trace elements concentrations systematically deviating from those collected at other seasons. None of the observed concentrations seem to be alarmingly high from a toxicological point of view. With a possible exception for cadmium in some of the rivers, all the observed elemental concentrations may be explained from natural sources and processes.



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## **References**

- Ahrens, L.H. (1954) The lognormal distribution of the elements. *Geochim. Cosmochim. Acta*, Vol. 5, pp. 49-73.
- Kharkar, D.P., Turekian, K.K., and Bertine, K.K. (1968) Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium and cesium to the oceans. *Geochim. Cosmochim. Acta*, Vol. 32, pp. 285-298.
- Landström, O., and Wenner, C.G. (1965) Neutron-activation analysis of natural water applied to hydrogeology. Report AE-204. Aktiebolaget Atomenergi, Stockholm, Sweden.
- Lenvik, K., Steinnes, E., and Pappas, A.C. (1977) Simultaneous determination of As, Cd, Co, Hg, Mo, and Zn in fresh water by neutron activation analysis. *Anal. Chim. Acta*, in press.
- Onishi, H., and Sandell, E.B. (1955) Geochemistry of arsenic. *Geochim. Cosmochim. Acta*, Vol. 7, pp. 1-33.
- Robertson D.E. (1968) Adsorption of trace elements in sea water on various container surfaces. *Anal. Chim. Acta*, Vol. 42, pp. 533-536.
- Rühling, Å., and Tyler, G. (1973) Heavy metal deposition in Scandinavia. *Water, Air, and Soil Pollution*, Vol. 2, pp. 445-455.
- Salbu, B., Steinnes, E., and Pappas, A.C. (1975) Multielement neutron activation analysis of fresh water using Ge(Li) gamma spectrometry. *Anal. Chem.*, Vol. 47, pp. 1011-1016.
- Salbu, B., Steinnes, E., and Pappas, A.C. (1978) Elemental composition of Norwegian rivers. To be published.
- Steinnes, E. (1973) A rapid and sensitive neutron activation method for uranium in water. *Radiochem. Radionucl. Letters*, Vol. 16, pp. 25-29.
- Steinnes, E. (1977) Atmospheric deposition of trace elements in Norway studied by means of moss analysis. Report KR-154. Institutt for atomenergi, Kjeller, Norway.
- Turekian, K.K. (1969) The oceans, streams, and atmosphere. *Handbook of Geochemistry* (K.H. Wedepohl, ed.), Vol. I, pp. 297-323. Springer Verlag.
- Turekian, K.K., and Wedepohl, K.H. (1961) Distribution of the elements in some major units of the Earth's crust. *Bull. Geol. Soc. America*, Vol. 72, pp. 175-192.
- Turekian, K.K., and Chan, L.H. (1971) The marine geochemistry of the uranium isotopes, <sup>230</sup>Th and <sup>231</sup>Pa. *Activation Analysis in Geochemistry and Cosmochemistry* (A.O. Brunfelt and E. Steinnes, eds.) pp. 297-323. Universitetsforlaget, Oslo.

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