

# Heavy metal monitoring in contaminated river systems using Mayfly larvae

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Received 1 October 1996; accepted 1 November 1996

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## Abstract

Insect larvae of the orders *ephemeroptera* (mayflies), *plecoptera* (stoneflies) and *tricoptera* (caddisflies) were investigated with respect to possible use as biomonitors of heavy metal pollution in rivers affected by current or previous mining activity. Samples from two rivers in central Norway were collected 3 times during the summer of 1985 and analyzed for Cu, Zn, and Cd. Of the three orders, mayflies was the only showing promise for further work. Repeated sampling of mayflies in one of the rivers in 1993 showed the same levels of Zn and Cd as before, whereas the copper level was reduced by a factor of 3. This may be explained by measures taken by the mining company upstream the sampling sites, reducing considerably the downstream transport of particles.

Apparently Cu in this river is associated with particles to a much greater extent than Zn and Cd.

**Keywords:** monitoring; aquatic systems; insect larvae; cadmium; copper; zinc

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## 1. Introduction

Rivers draining mining areas are often strongly polluted with heavy metals characteristic of the ores being mined. The extent of contamination in such rivers is usually studied by analyses of water or sediment samples. Neither of these methods, however, is satisfactory in order to assess the heavy metal burden of the aquatic foodchain. The large temporal variation of heavy metal concentrations in water frequently observed in contaminated rivers may require a large number of samples to be analyzed in order to reflect a good average. Sediment concentrations, on the other hand, can exhibit considerable spatial variability, which may place similar requirements to the number of samples necessary.

Moreover, total concentration either in water or sediment normally does not represent particularly well the bioavailability of a given metal, and further speciation analyses may be required.

A preferable approach may be to study the metal concentration level in an animal representative of the local aquatic foodchain, i.e. using this species as a biomonitor of the heavy metal contamination of the aquatic biota. Fish are in most cases not very well suited because of their mobility. Bottom fauna should be more preferable because they are more stationary and generally less sensitive to metal intoxication. Molluscs have been frequently used as metal biomonitors in the ocean, and applications in fresh water have also been reported (Tessier et al., 1984), but the number of available species is very limited in

many fresh water systems. Another candidate group for fresh waters is larvae of insects, such as chironomids (Krantzberg and Stokes, 1988, 1989). In the present work, experience from the use of *ephemeroptera* (mayflies), *plecoptera* (stoneflies), and *trichoptera* (caddisflies) is reported. These were the insect orders generally found to be most abundant among the bottom fauna in the rivers concerned. In other studies (Arnekleiv and Størset, 1993; Røe et al., 1993), the species diversity of these orders has been used to study effects of mine drainage in other Norwegian rivers.

## 2. Study area

The river systems studied in the present work are situated in Nord-Trøndelag county, central Norway, cf. Fig. 1.

Huddingsvatnet is a lake considerably affected by metal mining activity. In 1972 a pyrite ore mine, Grong Gruber, was opened. The tailings from this operation, consisting mainly of pyrite with traces of other heavy metals, are being deposited in the lake. The tailings and waste water from the mining activity have significantly contaminated not only lake

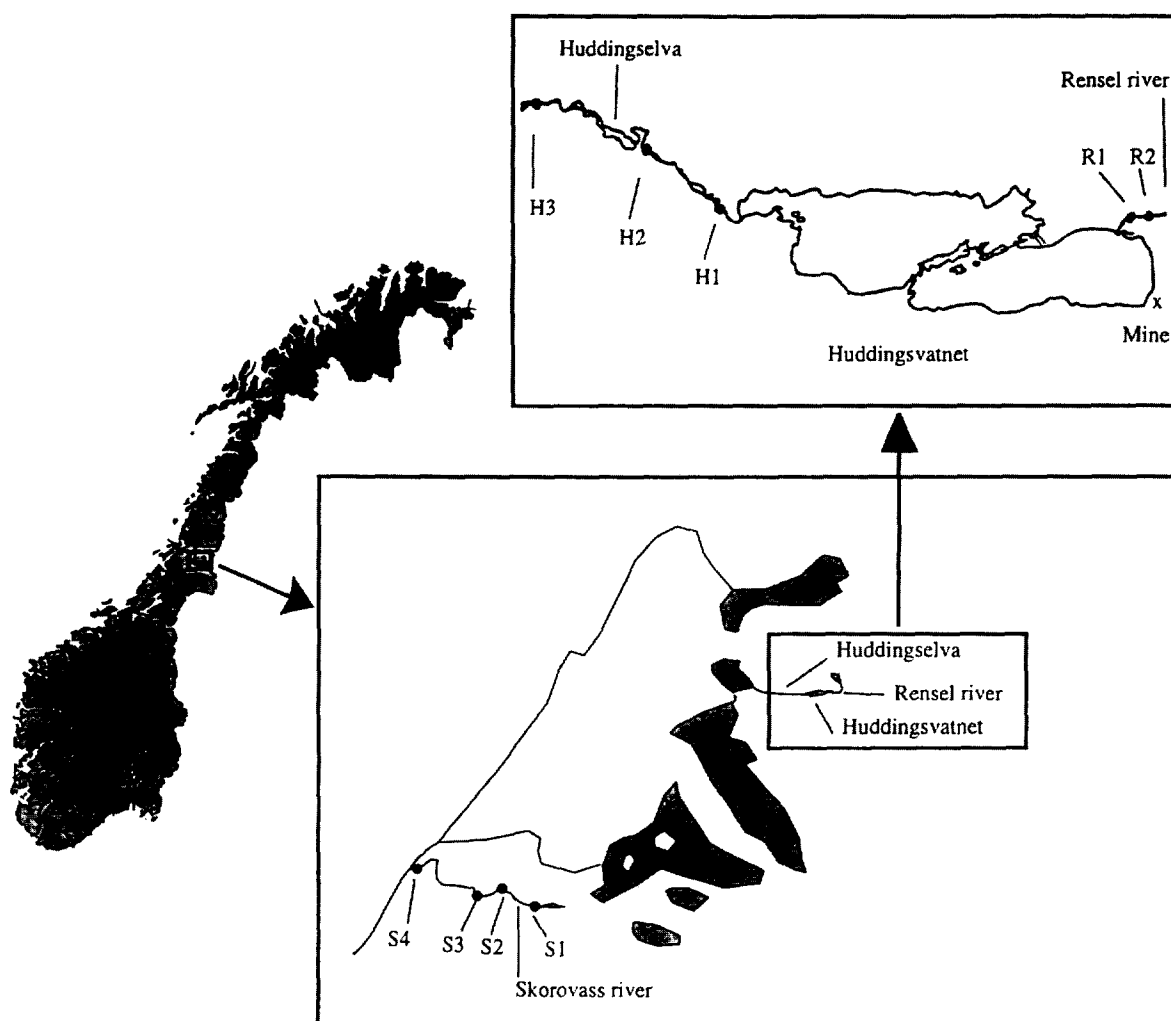


Fig. 1. Map showing the rivers system with sample locations.

Huddingsvatnet, but also Huddingselva, the downstream river, with metals such as Cu, Zn, and Cd. Typical water concentration levels in Huddingselva 1985 were as follows: Zn, 30  $\mu\text{g/L}$ ; Cu, 15  $\mu\text{g/L}$ ; Cd, 0.2  $\mu\text{g/L}$  (Grande and Iversen, 1985). A dam was built across Huddingsvatnet in 1989 in order to reduce the flow of particles further down the river.

Skorovas river receives drainage water from mines and tailings associated with ore extraction activities at Skorovas Gruber during the period 1952–1984. In 1985, typical levels of metals in the river were in the range 5–30  $\mu\text{g/L}$  for Cu and 30–250  $\mu\text{g/L}$  for Zn within the section of the river sampled for this work (Grande et al., 1985).

Sampling stations were established at regular intervals along the two rivers as indicated on the map in Fig. 1. The sites were placed where the water speed was relatively high, and where the bottom substrate was similar. Two control sites to represent normal background conditions in the area were established in Rensel river, a tributary to Huddingselva not affected by any mining activities.

### 3. Sampling and analysis

The main sampling in the two contaminated rivers and the reference river occurred at 3 times in the summer of 1985, viz. 12–14 June, 20–22 July, and

23–25 August. Bottom fauna was collected by kick sampling (Frost et al., 1971) using a net with 250  $\mu\text{m}$  mesh size. Insect larvae were sorted in the field according to order, and samples of *ephemeroptera*, *plecoptera* and *tricoptera* were collected for analysis. The samples were enclosed in small polyethylene bags, frozen with dry ice and transported to the laboratory. The sample size varied over the range 10–300 mg.

Repeated sampling of *ephemeroptera* was carried out in 1993 in Renseelva and the reference river at the same sites as in 1985 (Almli et al., 1995), using the same procedure as before.

Samples of 5–100 mg were weighed into erlenmeyer flasks and decomposed with 5 ml of supra-pure concentrated nitric acid on a hot plate at gentle heat. After evaporation to dryness the residue was dissolved in 10 ml of 0.1 M nitric acid and analysed by atomic absorption spectrometry using flame (Cu, Zn) or graphite furnace (Cd). Accuracy was checked by analysing the standard reference material NBS 1577a Bovine Liver. Good agreement with certified values was observed.

### 4. Results and discussion

Mean values for the 1985 samples over the summer season are given in Table 1. It is obvious that

Table 1

Mean concentrations of copper, zinc, and cadmium ( $\mu\text{g g}^{-1}$  wet weight) in larvae of *ephemeroptera* (E), *plecoptera* (P), and *tricoptera* (T) from the rivers studied in this work

			R1	R2	H1	H2	H3	S1	S2	S3	S4
Cu	E	1985	6.8	7.3	62.1	48.1	42.8	NP	57.0	21.7	16.4
	E	1993	7.3	7.2	21.7	16.0	11.0	—	—	—	—
	P	1985	6.8	7.8	59.1	46.2	66.7	75.6	45.0	16.2	14.1
	T	1985	4.5	4.1	16.1	10.8	9.0	17.3	8.3	8.9	7.1
Zn	E	1985	125	96	753	348	279	NP	437	298	209
	E	1993	129	110	516	442	222	—	—	—	—
	P	1985	65	73	106	78	98	82	112	83	101
	T	1985	68	48	53	63	45	164	44	67	58
Cd	E	1985	2.1	1.3	11.5	6.2	7.8	NP	1.9	2.6	2.0
	E	1993	1.8	1.8	15.0	6.0	4.2	—	—	—	—
	P	1985	0.18	0.43	0.84	0.45	0.27	0.36	0.38	0.33	0.34
	T	1985	0.08	0.30	1.18	0.31	0.95	0.68	0.08	0.29	0.42

NP: Not present at this location.

Table 2

Metal "contrast" values (mean concentration in contaminated river divided by corresponding value for reference river) for larvae of *ephemeroptera* (E), *plecoptera* (P), and *tricoptera* (T), based on 1985 data

		H1	H2	H3	S1	S2	S3	S4
Cu	E	9.0	6.9	6.2	—	8.4	1.7	2.3
	P	5.7	6.1	8.7	9.9	5.9	2.4	2.2
	T	4.3	2.6	2.2	4.0	2.0	1.6	1.5
Zn	E	6.8	3.2	2.5	—	4.6	1.9	2.1
	P	1.5	1.3	1.7	1.4	1.9	1.4	1.6
	T	1.0	1.0	0.8	2.9	0.7	1.3	0.7
Cd	E	11.2	6.0	7.8	—	1.5	2.0	2.0
	P	4.2	2.4	1.5	1.9	2.0	1.8	1.6
	T	5.9	2.0	6.1	3.9	0.5	1.6	3.5

the heavy metal accumulation pattern is quite different in larvae of the three orders. For Cu, *ephemeroptera* and *plecoptera* show similar values at the contaminated sites, whereas levels in *tricoptera* are about 5 times lower. At the reference sites *tricoptera* is still lower but only by about 50%. In the case of Zn, *ephemeroptera* is of the order of 5 times higher than the others at contaminated sites and twice as high in the reference river. For Cd the difference is even greater, *ephemeroptera* being about tenfold higher at all sites. Altogether this points to the mayflies being the most promising candidate.

The feasibility of a given group to serve as a biomonitor may be further illustrated by calculating "contrast" values, i.e. mean concentration at a contaminated site divided by the corresponding value for the reference site. Such values are presented for each insect order and heavy metal in Table 2. Also in this respect *ephemeroptera* exhibit higher values than the other candidates in most cases. In the case of Zn it is obviously the only usable monitor, and also for Cd

Table 3

Pearson correlation coefficients between the three metals in the 1985 material

	Cu–Zn	Cu–Cd	Zn–Cd
<i>Ephemeroptera</i>	0.75 ***	0.64 ***	0.79 ***
<i>Plecoptera</i>	0.26 NS	0.42 NS	0.60 **
<i>Tricoptera</i>	0.49 *	0.60 **	0.27 NS

NS:  $p > 0.1$ ; \*:  $0.1 > p > 0.01$ ; \*\*:  $0.01 > p > 0.001$ ; \*\*\*:  $p < 0.001$ .

and Cu it appears to show greater promise. Table 3, listing inter-element correlations for the three orders, further supports the conclusion that *ephemeroptera* is the only among the three insect orders concerned that deserves further study as a biomonitor candidate for heavy metals in contaminated fresh waters. A possible weakness of *ephemeroptera* apparent from the present work is the sensitivity to high levels of metals indicated by the fact that these larvae were absent at the most contaminated site S1. This indicates that the use of this biomonitor may be restricted to waters with moderate to low levels of the metals concerned.

Results from the repeated sampling of *ephemeroptera* in 1993 are also shown in Table 1. Comparisons of the 1993 values with those from the same sites in 1985 are shown in Fig. 2 for the three metals. While the Cu exposure is obviously strongly

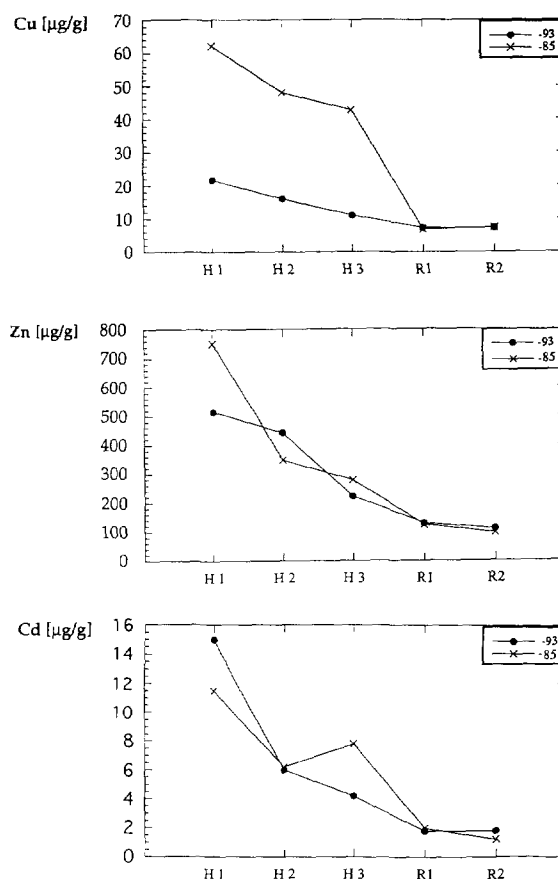


Fig. 2. Comparison of results for heavy metals in *ephemeroptera* in river Huddingselva and the reference river in 1985 and 1993.

reduced, the efforts made to reduce the particle transport downstream lake Huddingsvatn have apparently had little effect on the situation for Zn and Cd, at least until 1993. A possible reason for this difference in behaviour is that Zn and Cd in 1985 were transported mainly as soluble species in Huddingselva while Cu to a great extent was associated with the particulate fraction. If so, there should be no strong reason to expect any appreciable decrease for these two metals. This is in accordance with the results from a study of the same metals in another Norwegian river contaminated by mine drainage (Røe et al., 1993). By using dialysis in situ and comparing metal concentrations in the dialysate with those in unfiltered water, they showed that 70–100% of Zn and Cd was present in a dialysable, i.e. low-molecular form, whereas only 20–30% of Cu was contained in this fraction.

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