



Transport and sedimentation of Cu in a microtidal estuary, SE Norway

Aud Helland*, Torgeir Bakke

Norwegian Institute for Water Research, Brekkeveien, Oslo, Norway

Abstract

The transport and sedimentation of copper in the Glomma estuary, SE Norway during a period of 90% reduction in the industrial input of Cu, was studied from sediment trap material and compared to samples of the bottom sediments. Traps were deployed at four stations for several monthly periods during 1990, 1994 and 1995. Trapped material was analysed for suspended particulate matter (SPM), total organic carbon (TOC) and nitrogen (TN), Cu, and Al. Only about 10% of the Cu from the river is trapped in the estuary. Still there was a moderate but significant reduction in Cu concentration in the trap SPM from 1990 to 1994, reflecting the industrial reductions, but only if excluding summer samples apparently influenced by antifouling Cu from boat paint. Settling matter therefore seems appropriate and sensitive for monitoring changes in the Cu load. The results supported the view that TOC is the main carrier of Cu to the sediments. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Copper; Organic matter; Particulate matter; Sedimentation; Estuaries; South-East Norway

1. Introduction

Copper (Cu) is an essential metal for all biological life, but is toxic at high concentrations, especially in early development stages of many organisms (Spear and Pierce, 1979).

Cu is used as catalyst in many industrial processes, which has lead to large inputs of anthropogenic Cu to the marine environment. Cu is also an efficient biocide, and has been used in antifouling paint on boats for several decades. TBT (tributyltin) replaced Cu in the search for even more efficient antifouling agents in the 1970s, but turned out to give severe effects on several marine species (Matthiessen and Gibbs, 1998). Therefore TBT was banned for use on smaller boats in 1990. This has certainly lead to increased use of Cu as antifouling agent.

Generally metals are associated to particles and will therefore follow the particle transport in water. Cu is, however, known to preferentially adsorb to organic matter (Davis, 1984). Particle bound and organic complex bound Cu reduce the reactivity and hence the toxicity of Cu (Engel et al., 1981; Gardner and Ravenscroft, 1991). The reactivity will depend on both the chemical

and the physical environment to which Cu is introduced. In the mixing zone between river water and seawater the different binding forms of Cu may become unstable for shorter or longer periods. The fate of Cu is therefore closely related to any transformations in this dynamic system. Cu is found predominantly to occur in the dissolved phase in seawater, associated to organic colloids (Muller, 1996, 1998). On the other hand Cu is also found to associate with humic substances as these flocculate when river water is mixed with seawater (Scholkovitz and Copland, 1981). In the present work, we wanted to study how a recent large reduction in industrial Cu discharge to the microtidal Glomma estuary at the SE coast of Norway might affect distribution and fate of Cu in the estuary.

Another aim was to study the main factors controlling the deposition of Cu in the estuary and whether analyses of suspended particulate matter was appropriate for monitoring changes in Cu in the estuary.

2. Study area

The Glomma estuary is considered a microtidal estuary since the average tidal amplitude is only about 30 cm. The tidal influence on the hydrodynamics of the

* Corresponding author. Fax: +47-22-185-200.

E-mail address: aud.helland@niva.no (A. Helland).

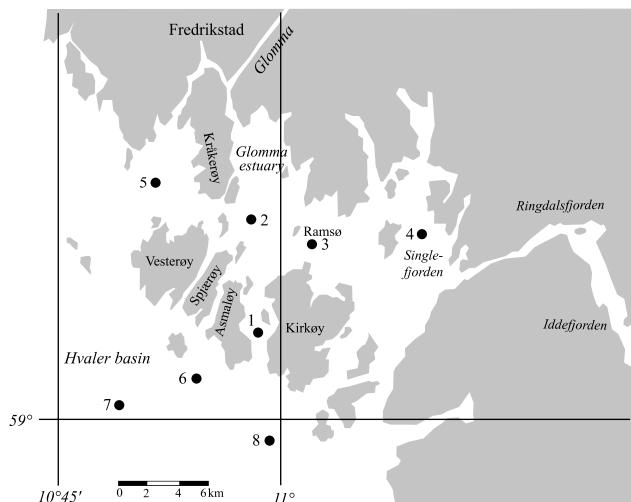


Fig. 1. Sediment trap stations in the Glomma estuary SE Norway. Stations 1–4 sampled 1990 and 1994. Stations 1–8 sampled 1995.

estuary is low compared to the effects of the river flow. The main passage of river water to the open sea is through the estuary Løperen mouthing the wide Oslofjord between Asmaløy and Kirkøy (Fig. 1). The river water sets up a salinity gradient and stratified water masses are recognised at all seasons in the surface water in the estuary, most pronounced at low river run off. A description is given in Helland (2001). Løperen is characterised by several deposition basins with maximum water depth of 64 m. The estuary is characterised by numerous islets and skerries forming a valuable recreation area in the summer season with high activity of leisure boats and fishing. The shallow estuary is recognised as dwelling site for sea mammals, fish, lobsters, and crabs and lately shellfish farming has been established.

The estuary receives large amounts of erosion material from the river Glomma, which drains a 41,800 km² large area, or about 13% of the total land area of Norway. The river itself has been monitored under the Oslo Paris Commission since 1990. An extensive industrial activity has been executed in the lower reaches of the river since the beginning of the 1800 (details in Helland, 2001). Production of lignin, vanillin and spirits, with use of Cu as a catalyst, resulted in large inputs of Cu to the estuary, with maximum in 1990. In that year, the industrial discharge of Cu was 81 t, and when including natural and other sources from the Glomma itself, the total Cu input to the estuary reached 150 t (Holtan et al., 1991; Holtan, 1996). During the 1990s, process adjustments resulted in a 90% reduction of the discharges, giving an annual industrial input of about 10 t Cu. In 1994 the total load including Glomma, constituted 45 t Cu. Over the months of sampling in 1990, the load of Cu went from 12 t in June to 3 t in October. During the corresponding sampling months

in 1994, Cu was steadily decreasing from 700 to 100 kg per month, giving a daily input of Cu between 10 and 20 kg.

During the 1980s and 1990s, the main focus was on Cu from the industry and little attention was paid to antifouling paint on boats as a Cu source in the estuary. Because of the ban on TBT since 1990 and a concurrent reintroduction of Cu-based coatings on leisure boats, the estuary water was probably more exposed to Cu from antifouling paint in 1994 than in 1990. In 1990, about 30,000 leisure boats with a mean hull size of 15 feet were registered in the area bordering the Glomma estuary. The annual increase in number of boats is in the order of 2000. We can assume that all these boats are on the water during the most popular summer vacation month of July. Boats from other parts of the fjord are also frequent visitors in the estuary during this time. An average hull size of 15 feet gives approximately 9 m² of wetted surface covered with antifouling paint. At a suggested average leaching rate of 10 µg Cu cm⁻² d⁻¹ (De la Court, 1987; Alzieu et al., 1989; Matthiessen et al., 1999), this gives 27 kg Cu d⁻¹ to the estuary water in the summer month. This input is in the same order of magnitude as the Cu from the river.

3. Material and methods

3.1. Sampling and sample preparation

Field surveys focused on sampling of suspended particulate matter (SPM) by use of traps. A total of eight trap sampling sites were established in the estuary and the open fjord (Fig. 1). The main sites, stations 1–4, were sampled in 1990, 1994 and 1995. In 1995 four additional stations (stations 5–8) were included, three of them in the Oslofjord outside the estuary. Field sampling covered five monthly sampling periods from May to October in 1990 and 1994, and one two-month sampling period from June to July in 1995.

Each sediment trap consisted of two Perspex cylinders (10 cm width and 100 cm length) pivoted to ensure vertical position. The appliance was moored to the bottom with the traps positioned in 20 m water depth. The cylinders were equipped with exchangeable boxes at the lower end. These were replaced and sampled after each sampling interval. Sodium azide was added to the boxes at deployment to prevent decay of organic matter. Microscopy revealed no visual difference in sample appearance from the various stations. The sampled material consisted of a homogeneous unspecific mass of aggregates, with no conspicuous amount of fibres or identifiable biological structures. The trap samples were kept cool at 4 °C not more than 48 h prior to further treatment in the laboratory. The samples were washed with distilled water and centrifuged three times to

Table 1

Sediment trap analyses from 1990, 1994 and 1995 in the Glomma estuary SE Norway

Date	Days	St.	Flux mg m ⁻² d ⁻¹	Cu (mg kg ⁻¹)	PF-Cu (µg m ⁻² d ⁻¹)	TOC (mg g ⁻¹)	PF-Cu (µg m ⁻² d ⁻¹)	TN (mg g ⁻¹)	PF-N (mg m ⁻² d ⁻¹)	TOC:TN	Al (mg g ⁻¹)
7.6.90	42	1	6324	118	746	37.4	237	5.6	35	6.7	80.4
7.6.90	42	2	18,650	117	2182	35.6	664	4.7	88	7.6	83
7.6.90	42	3	6445	107	690	51.9	335	7.9	51	6.6	79.9
7.6.90	42	4	1862	120	223	176	328	33.2	62	5.3	56.1
2.7.90	25	1	8107	119	965	101	819	17.3	140	5.8	62.2
2.7.90	25	2	18,558	123	2283	37.9	703	5.8	108	6.5	76.2
2.7.90	25	3	7083	153	1084	82.3	583	14.2	101	5.8	66.8
2.7.90	25	4	2680	324	868	174	466	27.8	75	6.3	44.1
1.8.90	30	1	4735	636	3011	49.7	235	7.5	36	6.6	75.6
1.8.90	30	2	16,607	179	2973	27.8	462	3.6	60	7.7	79.7
1.8.90	30	3	4582	120	550	44.4	203	7.2	33	6.2	78.9
1.8.90	30	4	1520	520	790	110	167	18.9	29	5.8	61.7
10.9.90	40	1	3334	165	550	67.6	225	10.8	36	6.3	64.6
10.9.90	40	2	14,229	110	1565	45.9	653	6.3	90	7.3	72.9
10.9.90	40	3	3210	137	440	101	324	15.9	51	6.4	62.4
10.9.90	40	4	1685	196	330	256	431	43.1	73	5.9	25.3
8.10.90	28	1	6210	195	1211	53.8	334	8.3	52	6.5	70.4
8.10.90	28	2	12,402	166	2059	37.5	465	5.3	66	7.1	82.2
8.10.90	28	3	4577	119	545	66.5	304	9.3	43	7.2	72.7
8.10.90	28	4	3076	279	858	110	338	17.3	53	6.4	36.6
9.6.94	38	1	7530	83.5	629	37.2	280	5.8	44	7.5	83.6
9.6.94	38	2	20,474	430	8804	29.3	600	4.1	84	8.3	81.2
9.6.94	38	3	6850	93.5	641	33.7	231	4.5	31	8.7	83.6
9.6.94	38	4	1481	458	678	70.4	104	10.6	16	7.7	70.7
6.7.94	27	1	3328	82.5	275	58.9	196	9.9	33	6.9	68
6.7.94	27	2	10,203	185	1887	33.1	338	4.6	47	8.4	74.8
6.7.94	27	3	3628	453	1644	45.4	165	6.7	24	7.9	77.6
6.7.94	27	4	1330	75	100	83.6	111	13.6	18	7.2	61.3
4.8.94	29	1	2893	533	1542	55.4	160	8.6	25	7.5	69.8
4.8.94	29	2	11,970	96.5	1155	31.8	381	4.3	51	8.6	76.6
4.8.94	29	3	2779	137	381	45.7	127	6.9	19	7.7	73.3
4.8.94	29	4	929	159	148	104	97	18.2	17	6.7	56.6
5.9.94	32	1	918	196	180	67.2	62	11	10	7.1	63.7
5.9.94	32	2	7602	91.5	696	29.6	225	4.1	31	8.4	75.5
5.9.94	32	3	2332	113	264	51	119	8	19	7.4	73.4
5.9.94	32	4	931	92.5	86	121	113	20.3	19	7	51.6
11.10.94	36	1	7068	161	1138	38.7	274	6.4	45	7.1	75.2
11.10.94	36	2	11,998	89	1068	25.5	306	3.3	40	9	77.2
11.10.94	36	3	7193	93.5	673	33.4	240	4.7	34	8.3	78.7
11.10.94	36	4	1676	82.5	138	60.6	102	9.7	16	7.3	66.8
7.8.95	59	1	25,762	36.8	948	18.8	484	2.4	62	7.8	75
7.8.95	59	2	88,620	32	2836	13.9	1232	1.5	133	9.3	68.1
7.8.95	59	3	33,001	32.8	1082	16.4	541	2	66	8.2	71
7.8.95	59	4	5559	42.4	236	33	183	4.8	27	6.9	76.1
7.8.95	59	5	8836	34	300	27	239	4.3	38	6.3	73.3
7.8.95	59	6	6011	48	289	33.9	204	5.3	32	6.4	70.5
7.8.95	59	7	2161	180	389	66.7	144	11.2	24	6	59.4
7.8.95	59	8	4314	48	207	42.7	184	6.7	29	6.4	67.4

Date = sampling date, Days = number of days before sampling, St. = station number, Flux = flux of SPM (suspended particulate matter) to the sediment traps. The notation PF means particulate flux of Cu, TOC (total organic carbon), and TN (total nitrogen), respectively. TOC:TN given as mole ratio.

remove salt, freeze-dried, and powdered by use of an agate mortar before analysis.

3.2. Chemical analysis

Total Cu content was obtained by atomic absorption spectrometry after total digestion with hydrofluoric acid

and aqua regia according to Loring and Rantala (1991). The certified reference material MESS-1 (National Research Council of Canada) was used as external standard for Cu. The laboratory obtained an average value of 26.3 ± 2.4 (SD) mg Cu kg⁻¹ ($n = 14$) on the certified value of 25.1 ± 3.8 mg Cu kg⁻¹. The content of total organic carbon (TOC) and nitrogen (TN) was measured

by total catalytic combustion with oxygen saturated helium gas (1800°C) after pre-treatment with 1.2 M HCl to expel inorganic carbon. The method is mainly based on the Instruction Manual for Model 1106, Carlo Erba Strumentazione and partly by the method of Pella and Colombo (1978). All results are given in dry weight (d.w.). The total amount of trapped SPM was used to calculate vertical flux of particles given as mg or $\text{g m}^{-2} \text{ d}^{-1}$.

4. Statistical analyses

One way analysis of variance (ANOVA) was used to test if Cu concentration varied with sampling year. Residual plots were used to check that the data did not violate the assumption of normal distribution in the

analysis. If necessary, data were log transformed or the non-parametric Kruskal–Wallis one-way ANOVA was used. *T*-tests were performed to test differences in mean concentrations between years. Simple regression analyses were used to test correlations between variables. Test confidence levels were set at 95.0%.

5. Results

The flux of SPM to the traps varied between 918 and $88,620 \text{ mg m}^{-2} \text{ d}^{-1}$ (Table 1). The largest flux was registered at station 2 near the river mouth (Fig. 2(a)) during a very large spring flood in 1995, when the river flow reached a maximum of $3600 \text{ m}^3 \text{ s}^{-1}$ (Holtan et al., 1996). Normal spring early summer flow rate is about $1200 \text{ m}^3 \text{ s}^{-1}$, as opposed to about $700 \text{ m}^3 \text{ s}^{-1}$ at other times of the year. There was a significant positive correlation between river flow and flux of SPM at station 2, across all three years ($p = 0.0000$, $r^2 = 88\%$ cor. coef. = 0.94). The extreme 1995 record has a strong influence on the correlation, but also when excluding this observation the correlation was retained for station 2 ($p = 0.0047$, $r^2 = 65\%$, cor. coef. = 0.81). There was, however, no significant correlation between flux of SPM and river flow across all stations.

The concentration of Cu in the SPM varied between 32 and 636 mg kg^{-1} (Table 1). Most samples had concentrations $<200 \text{ mg Cu kg}^{-1}$. Unusually high concentrations were found in six samples from the summer months from June to August both in 1990 and 1994 ($>400 \text{ mg Cu kg}^{-1}$) (Fig. 2(b)). These appeared as outliers in the regression analysis between Cu and TOC (cf. Fig. 3). All samples collected during the large flood in 1995 had significantly lower concentrations of Cu (Fig. 2(b)) and TOC (Fig. 2(c)) than the samples from 1990 and 1994. The fluxes of Cu and TOC averaged over 1990 and 1994 were $607 \text{ mg Cu m}^2 \text{ y}^{-1}$ and $120 \text{ g TOC m}^2 \text{ y}^{-1}$ in the inner part of the estuary (station 2). Corresponding fluxes in the outer part of the estuary (station 1) were $206 \text{ mg Cu m}^2 \text{ y}^{-1}$ and $67 \text{ g TOC m}^2 \text{ y}^{-1}$. The fluxes were calculated on basis of the six months of trapping of SPM (Table 1) and adjusted against annual river flow (given in Holtan et al., 1991, 1995). Such an adjustment is justified since there was a significant positive correlation between the flux of SPM and river flow at station 2.

The ANOVA showed that the samples from 1995 had significantly lower Cu concentrations than those from 1990 and 1994. There was, however, indications of non-normality in the data. When comparing the medians by use of Kruskal–Wallis test, all three years differed from one another. To confirm the assertion of difference between years a paired sample comparison on the 1990 and 1994 data was performed. The *t*-test did not, however, reject the null hypothesis that the means were

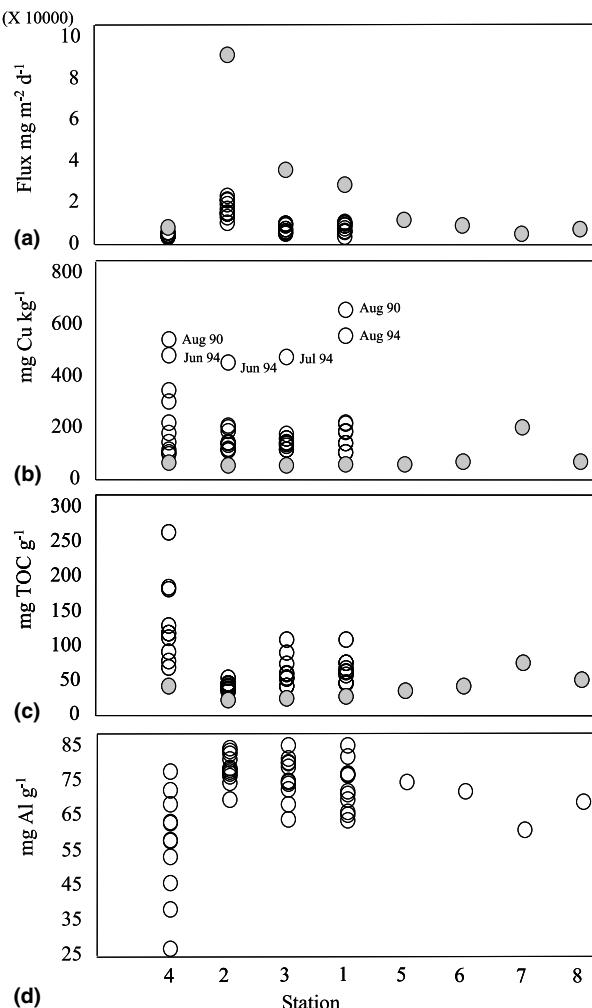


Fig. 2. Flux of SPM in sediment traps (a); concentration of Cu (b); TOC (c), and Al (d) in the SPM from the traps, in the Glomma estuary and the estuary mouth to the Oslofjord in 1990, 1994 and 1995. The 1995 samples are shaded.

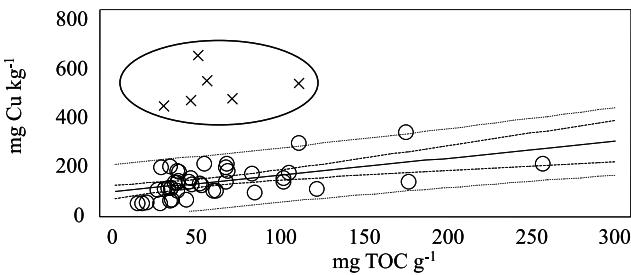


Fig. 3. Cu as a function of TOC in SPM from sediment traps in the Glomma estuary and the estuary mouth to the Oslo fjord in 1990, 1994 and 1995. Very high Cu concentrations in the summer months (encircled) are excluded from the correlation.

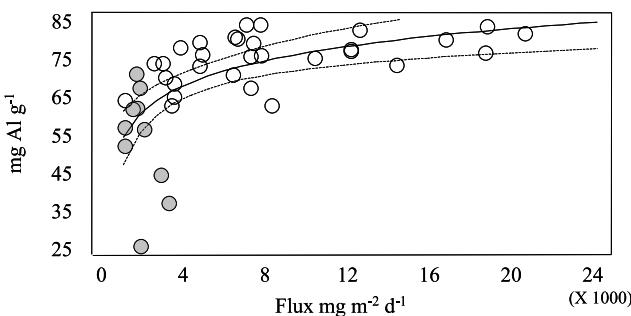


Fig. 4. Correlation plot of Al concentration and flux of SPM in all trap samples from 1990 and 1994. Samples from station 4 are shaded.

equal. When excluding the six summer outlier samples with very high Cu concentrations relative to TOC (cf. Fig. 3) from the comparison the null hypothesis was rejected.

The two main components in river discharge are minerals and organic matter. Organic carbon is said to be the main carrier of Cu to the watershed (Bergkvist et al., 1989), and a significant correlation between TOC and Cu could therefore be expected. There was, however, no significant correlation between the two variables when all estuary samples were included. When excluding the six summer outlier samples mentioned above a moderately strong positive correlation was found between Cu and TOC (Fig. 3) ($p = 0.0003$, cor. coef. = 0.53, $r^2 = 28\%$).

Mineral particles are the other main carrier of Cu. Al appears to be a good tracer of clay minerals, but there was no correlation between Cu and Al concentrations in the trap samples. There was a significant negative correlation between Al and TOC concentrations across all stations ($p = 0.0000$, cor. coef. = -0.9, $r^2 = 77\%$), which might be expected, but no correlation between Al concentration and flux of SPM. Apparently the 1995 spring flood samples influenced greatly on the SPM flux, and when excluding the flood impacted samples, a positive correlation was found ($p = 0.0000$, cor. coef. = 0.6, $r^2 = 39\%$, Fig. 4).

The variability in Al (Fig. 2(d)), and to some extent in TOC concentrations (Fig. 2(c)) was particularly high at station 4. This station is located to the east of the main estuary, and so far away that one may expect that the trap samples here are influenced by other particle sources than the river Glomma. The correlation between Al concentration and SPM flux in the traps was, however, not improved by excluding this station ($p = 0.006$, cor. coef. = 0.5, $r^2 = 24\%$).

6. Discussion

As a result of the large reductions in the total Cu discharge with the river Glomma from 1990 to 1994, a significant reduction of Cu in settling matter in the estuary was expected. The results showed, however, no such reduction. This corresponds to analysis of the upper layers of the bottom sediments in the estuary, which showed a significant reduction in Cu concentrations between 1980 and 1994, but not between 1990 and 1994 (Helland, 2001).

Sediments can be exposed to continuous disturbances such as bioturbation and resuspension, which can mask changes over few years. By collecting fresh settling matter by use of sediment traps such disturbance is avoided. Particles collected by the traps may, however, include resuspended sediments from older deposits. We believe that older deposits have not to any extent contaminated the trap material in this study. During each annual spring flood fine material deposited in the Glomma river mouth area are resuspended and flushed out into the estuary (Helland, 2001; Helland et al., submitted). Hence, each spring flood removes material that has been deposited at the river mouth only since the last spring flood. At other times of the year the estuary receives mostly new material from the river, i.e. not resuspended. The trap samples, especially in the inner part of the estuary, should therefore be representative of what would settle out from recent outputs from the river. Lack of reduction in Cu concentrations of the trap material when the Cu input was lowered by as much as 70% from 1990 to 1994 could be due to two factors: either that the Cu does not associate with the settling material or that the variability in the data was too high for reduced Cu to be detected.

The variability in the data was high due to the six outlier samples (cf. Fig. 3). Apparently the Cu in these samples was not associated to TOC. As discussed later the likely cause is a different origin of the Cu, i.e. from antifouling paint on boats. When excluding these six samples the variability decreased and a significant reduction in Cu concentration in the trap material between 1990 and 1994 was detected. We therefore conclude that SPM collected by the sediment traps represents recent outputs from the river Glomma and is

more sensitive in revealing changes over a short time span than surface sediments. The flux of Cu to the traps appeared to be in the same range as the flux to the sediments (Table 2). Both the traps and sediments showed that the downward flux of Cu in the inner part of the estuary is about twice as high as in the outer part. This suggests that the SPM collected by traps is representative for the SPM input to the bottom sediments at the same station.

Only a small amount of Cu associates with particulate matter and settles out. Earlier studies in the estuary have suggested that only 10% of the Cu from the river Glomma is trapped in the sediments of the estuary (Helland, 2001). The low entrapment of Cu in the estuary suggests that the bulk of the metal stays complexed, probably with humic substances, and is transported out of the estuary. As stated earlier Cu has a strong binding strength to humic substances. According to the Irving–William series only Hg exceeds Cu in affinity (Chester, 1990). When the humic complexes from the river are mixed with seawater one might expect a competition for the humic ligands from Ca and Mg, but several studies have shown that Cu remains complexed with humic substances and hence in solution when mixed with seawater (Van Den Berg et al., 1987; Muller, 1996, 1998). Most of the organic carbon in river Glomma (98% Holtan et al., 1992) occurs as DOC, and with a C:N mole ratio of about 30 indicating dominance of humic substances. Humic substances do to some extent flocculate in the mixing zone between river water and seawater and Cu is entrained in this process (Scholkovitz and Copland, 1981). In the present study, there was a correlation between TOC and Cu in the trap material (Fig. 3), but with a C:N mole ratio as low as 5–8 the contribution of humic substances in this TOC must have been low compared to the contribution from algal production. The C:N ratio in the sediments was in the range of 8–14, hence more influenced by humic substances. This may explain why there was a weak negative correlation between Cu and C:N ratio in the traps, in contrast to the estuary sediments where there was a positive correlation (Helland, 2001).

The trap material had in general much higher Cu and TOC concentrations than the sediments, but the Cu:TOC ratio was within the same range in the two compartments (Table 2). This supports the assumption that TOC is the main carrier of Cu to the sediments. Since the fluxes of Cu and TOC were about the same to traps and sediments the lower concentrations of the two in the sediments suggests that there must be an additional input of mineral particles poor in Cu and TOC to the sediments, which dilutes the concentrations.

The investigation has shown that both flux and concentrations of Cu in the trap material were relatively constant through the year and from one year to another. There are, however, some samples in the data set each year that showed unusually high concentrations of Cu (Fig. 2(b)). The common feature of these samples is that they were trapped in the summer. The separation of these samples in the correlation plot between Cu and TOC (Fig. 3) indicates a different origin of this Cu, and apparently the carrier SPM is not organic in character. During the years of large industrial discharges of Cu little consideration was devoted to other sources of Cu such as antifouling paint on boats. The boating activity is especially high during the summer months coinciding with the high Cu concentrations in the trap samples. The estimated leaching of Cu to the estuary water from antifouling paint in the summer months is about equal to the Cu input from the river. Hence antifouling Cu can readily explain the very high concentrations of Cu in the summer months. In 1994, high concentrations of Cu was registered in all the summer months, June, July and August, while in 1990 the highest concentrations were found in August. This is probably because Cu biocides were more extensively used in 1994 than in 1990. Another supporting feature is that the high concentrations were most often registered at the stations positioned in the most highly visited leisure boat areas (stations 1 and 4).

In conclusion most of the SPM collected by the traps are characterised by Cu from the river Glomma settling in association with organic matter. During the summer season particles probably originating from antifouling

Table 2

Selected characteristics of sediment trap material and bottom sediments in the inner and outer part of the estuary

	Cu	Flux Cu	TOC	Flux TOC	Cu:TOC	Flux SPM
Traps inner estuary	183	607	33	120	0.4	3522
Traps outer estuary	193	206	53	67	0.4	1234
Sediment inner estuary	76 ^b	469 ^a	23 ^b	142 ^a	0.4	6170 ^a
Sediment outer estuary	79 ^b	290 ^a	22 ^b	81 ^a	0.4	3666 ^a

Cu: mg kg⁻¹, TOC: mg g⁻¹, flux Cu: mg m⁻² y⁻¹, flux TOC and flux SPM: g m⁻² y⁻¹. The trap values are average between 1990 and 1994.

^a Recalculated from Helland, 2001.

^b From Helland, 2001.

paint are trapped as well, causing very high concentrations of Cu.

7. Conclusions

Analysis of settling matter reflected the reduction in discharge of industrial Cu to the estuary. Settling matter therefore appears appropriate for monitoring changes in Cu load and is more sensitive than bottom sediments in that it reflects changes earlier. The fluxes of settling matter to sediment traps were within the same range as fluxes to the sediments.

The main carrier of Cu is organic matter, but since Cu favours organic complexes or true solution only minor amounts follow the particulate phase and settle out. Only about 10% of Cu from the river Glomma is trapped in the estuary and about twice as much is trapped per m² in the inner part than in the outer part of the estuary.

The use of antifouling coating on leisure boats during the summer season appears to be a source of Cu to the estuary comparable in magnitude to the Cu input from the river.

Acknowledgements

This work was founded by a grant to AH from the Norwegian Research Council (grant no. 111237/730). We are most obliged to F. Kjellberg and A. Juliussen for field assistance and the NIVA analytical laboratory for performing the chemical analyses.

References

- Alzieu, C., Heral, M., Dremo, J.P., 1989. Les peintures marines antiallisseuses et leur impact sur l'ostreiculture. *Equinoxe* 24, 22–31.
- Bergkvist, B., Folkesson, L., Berggren, D., 1989. Fluxes of Cu, Zn, Pb, Cd, Cr, and Ni in temperate forest ecosystems. A literature review. *Water Air and Soil Pollution* 47, 217–286.
- Chester, R., 1990. *Marine Geochemistry*. Unwin Hyman, London (698 p.).
- Davis, J.A., 1984. Complexation of trace metals by adsorbed natural organic matter. *Geochimica et Cosmochimica Acta* 48, 679–691.
- De la Court, F., 1987. The minimum leaching rate of some toxins from antifouling paints required to prevent settlement of fouling organisms. *Biodeterioration* 7, 305–308.
- Engel, D.W., Sunda, W.G., Fowler, B.A., 1981. Factors affecting trace metal uptake and toxicity to estuarine organisms. I Environmental parameters. In: Vernberg, F.J., Calabrese, A., Thurnberg, F.P., Vernberg, W.B. (Eds.), *Biological Monitoring of Marine Pollutants*. Academic Press, New York, pp. 127–144.
- Gardner, M.J., Ravenscroft, J.E., 1991. The range of copper complexing ligands in the Tweed estuary. *Chemical Speciation and Bioavailability* 3, 22–29.
- Helland, A., 2001. The importance of selective transport and sedimentation in trend monitoring of metals in sediments. An example from the Glomma estuary, east Norway. *Water Air and Soil Pollution* 126, 339–361.
- Helland, A., Åberg, G., Andresen, B., Skei, J., Source dependent behaviour of lead and organic matter in the Glomma estuary, SE Norway: evidence from isotope ratios. *Marine Chemistry*, submitted.
- Holtan, G., 1996. Monitoring of the Hvaler–Singlefjord and the Iddefjord mouth area 1989–1994. Pollution supply 1970–1993. The Norwegian State Pollution Control Authority (SFT), TA1329/1996, p. 81 (in Norwegian).
- Holtan, G., Berge, D., Holtan, H., Hopen, T., 1991. Report 452B/91 Paris Convention. Annual report on direct riverine inputs to Norwegian coastal waters during the year 1990. The Norwegian State Pollution Control Authority (SFT), TA755B/1991, p. 103.
- Holtan, G., Berge, D., Holtan, H., Hopen, T., 1992. Report 488B/92 Paris Convention. Annual report on direct and riverine inputs to Norwegian coastal waters during the year 1991. B. Data Report. The Norwegian State Pollution Control Authority (SFT), TA841B/1992, 104 p.
- Holtan, G., Berge, D., Holtan, H., Hopen, T., 1995. Report 623B/95 Paris Convention. Annual report on direct riverine inputs to Norwegian coastal waters during the year 1994. The Norwegian State Pollution Control Authority (SFT), TA1262/1995, 136 p.
- Holtan, G., Berge, D., Holtan, H., Hopen, T., 1996. Report 674B/96 Paris Convention. Annual report on direct riverine inputs to Norwegian coastal waters during the year 1995. The Norwegian State Pollution Control Authority (SFT), TA1382/1996, p. 137.
- Loring, D.H., Rantala, R.T.T., 1991. Manual for the geochemical analyses of marine sediments and suspended particulate matter. *Earth and Science Review* 32, 235–283.
- Matthiessen, P., Gibbs, P.E., 1998. Critical appraisal of the evidence for tributyltin mediated endocrine disruption in molluscs. *Environmental Toxicology and Chemistry* 17, 37–43.
- Matthiessen, P., Reed, J., Johnson, M., 1999. Sources and potential effects of copper and zinc concentrations in the estuarine waters of Essex and Suffolk, United Kingdom. *Marine Pollution Bulletin* 38 (10), 908–920.
- Muller, F.L.L., 1996. Interactions of copper, lead and cadmium with dissolved, colloidal and particulate components of estuarine and coastal waters. *Marine Chemistry* 52, 245–268.
- Muller, F.L.L., 1998. Colloid/solution partitioning of metal-selective organic ligands, and its relevance to Cu, Pb and Cd cycling in the Firth of Clyde. *Estuarine Coastal and Shelf Science* 46, 419–437.
- Pella, E., Colombo, B., 1978. Simultaneous C–H–N and S micro-determination by combustion and gas chromatography. *Mikrochimica Acta* 1, 271–286.
- Scholkovitz, E.R., Copland, D., 1981. The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. *Geochimica et Cosmochimica Acta* 45, 181–189.
- Spear, P.A., Pierce, R.C., 1979. Copper in the aquatic environment. Chemistry, distribution and toxicology. National Research Council of Canada, Publ. No. NRCC 16454.
- Van Den Berg, C.M.G., Merks, A.G.A., Duursma, E.K., 1987. Organic complexation and its control of the dissolved concentrations of copper and zinc in the Scheldt estuary. *Estuarine Coastal and Shelf Science* 24, 785–797.