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EFFECTS OF PHYTOPLANKTON ON METAL PARTITIONING IN THE LOWER RIVER RHINE

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Abstract—Since algal growth has been shown to play a key role in determining the fate of metals in lakes and marine waters, we wondered if the Rhine phytoplankton, so much stimulated by nutrient input, would affect the partitioning of metals between the dissolved and particulate phases, thereby altering the retention of metals in the Rhine delta. In a seasonal study in which variations in the partitioning of Mn, Cu, Zn, Cd and Pb (expressed as $\log K_p$ values) were correlated with phytoplankton parameters, it appeared that manganese occurred mainly in the particulate form during algal blooms, whereas dissolved manganese predominated during periods low in phytoplankton. Photosynthetic activity (up to $700 \mu\text{g C l}^{-1} \text{ h}^{-1}$) correlated slightly better with the $[\log K_p]\text{-Mn}$ than the chlorophyll *a* concentration (up to $140 \mu\text{g l}^{-1}$) and the pH (up to 8.35), suggesting that phytoplankton photosynthesis promotes Mn precipitation in the river. The variability in the partitioning of Cu, Zn, Cd and Pb in 1990 did not seem to be determined by the seasonal differences in phytoplankton and manganese partitioning, although increased values of $[\log K_p]\text{-Zn}$ had been indicated for the summer of 1983, when metal concentrations had generally been higher than in 1990. The lack of effect of riverine phytoplankton blooms on partitioning of metals other than Mn contrasts with observations in stagnant waters. However, the low levels of cellular metal observed in cultures, along with the single growth pulse that phytoplankton shows during its short residence in the river, are consistent with the observations.

Key words—river, phytoplankton, heavy metals, manganese, water/sediment partitioning

INTRODUCTION

Heavy metal concentrations in surface waters are generally assumed to be controlled by scavenging particles of abiotic or biotic origin (Wangersky, 1986). The similarity in the distribution of a group of metals (Cd, Cu, Ni, Zn) and nutrients (Martin and Windom, 1991) suggests that phytoplankton plays a key role in the oceans. For freshwaters, a biogenic flux of trace metals to the sediment has been demonstrated for deep stratified lakes (Baccini, 1984) as well as for shallow and well-mixed eutrophic lakes (Salomons and Mook, 1980; Van de Meent *et al.*, 1985). Phytoplankton could affect the behaviour of metals through different mechanisms, such as a photosynthetically induced pH rise, causing metal precipitation (Salomons and Mook, 1980), and the association of metals with biomass or (algal) detritus. Except for the microbial transformations of iron (Madson *et al.*, 1986), biological control of metal partitioning in rivers has, so far, not attracted much attention. However, nowadays, algal blooms in eutrophic rivers are widespread with any effects of riverine algal growth on metal partitioning having a

potentially large effect on the metal and nutrient fluxes from the continent to the sea.

In the River Rhine, the load of several metals has been strongly reduced in the last 15 years (Van der Weijden and Middelburg, 1989), while nutrient concentrations and phytoplankton densities have remained high (Admiraal *et al.*, 1992). Since earlier observation in the Rhine delta indicated a correlation between manganese concentration and chlorophyll *a* concentration in suspended matter (Van Eck, 1982), we also focused on this element, even more so as it was known that manganese precipitated rapidly in water from the River Tamar (Morris and Bale, 1979).

Seasonal observations on metal partitioning in Rhine water in 1990 have been combined in this study with the results of investigations on the plankton published elsewhere (De Ruyter van Steveninck *et al.*, 1992; Admiraal *et al.*, 1993). These observations were analysed along with older chemical data from the Dutch Ministry of Transport and Public Works.

MATERIALS AND METHODS

The lower 400-km reach of the R. Rhine in the German state of North Rhine-Westphalia and in The Netherlands forms a genuine lowland river. The water quality of the lower Rhine has greatly been improved since the seventies

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although it flows through one of the most densely populated and industrialized parts of Europe. There has been a noticeable return or "immigration" of many animal species in recent years.

In the period January to December 1990 water samples were taken fortnightly at Lobith station (Rhine km 863), near the German/Dutch border. Samples of 60 l were obtained from the stream with a plastic bucket from a suspended measuring platform located *ca* 20 m from the bank. Samples were transported in pre-rinsed polypropylene jerry cans to the laboratory and processed within 4 h. Subsamples of 100 ml for determinations of total metal concentration were transferred to acid-washed polyethylene bottles and 1 ml HNO₃ (65%, Merck, suprapur) was added for determinations of Cu, Pb and Cd. For the analysis of the other metals, a subsample of 100 ml was completed with the same amount of HNO₃ and 1 ml hydroxylammonium-chloride (10%). Each sample (50 ml) was also filtered through a membrane (Acrodisc, pore size 0.45 µm) and processed in the same way to determine the "dissolved" metal concentration. The metal concentrations (Ca, Fe, Mg, Mn, Na, Zn, Cd, Pb, Cu) were determined by atomic absorption spectrometry at the Laboratory of Inorganic Chemistry of the National Institute of Public Health and Environmental Protection. The filtration did not contribute substantially to the blanks of distilled water, processed as for the samples.

Concentrations of particulate metals were obtained by subtracting dissolved concentrations from the total concentrations. The partitioning of the metal over the two phases was expressed as the log K_p value (unit l kg⁻¹), calculated as:

$$\log K_p = \log \left[\frac{C_p}{C_w \cdot DW} \right],$$

where C_w is the concentration in the water (M), C_p the concentration in suspension (M) and DW the dry weight of the suspended matter (kg l⁻¹). The dry weight of suspended material was determined gravimetrically using pre-weighed cellulose acetate filters (Satorius SM 12303, pore size 1.2 µm). Chlorophyll *a* in glassfibre-filtered material (pore size >0.3 µm, Schleicher & Schuell, No. 6) was extracted in 80% ethanol at 75°C. Extinction was measured at 665 nm and 750 nm before and after adding HCl to a final concentration of 4 mM. The concentration of chlorophyll *a* was calculated according to the Netherlands Standards Method (NEN No. 6520).

The photosynthetic rate of the phytoplankton was determined at *in situ* temperature with the ¹⁴C method as described in De Ruyter van Steveninck *et al.* (1992).

Data on river discharge were obtained from the Institute for Inland Water Management and Waste Water Treatment of the Ministry of Public Works (RIZA). Data on dissolved and total metal concentration and supporting parameters, collected in 1983, were also provided by this institute (Anonymous, 1983).

RESULTS

Dense blooms of phytoplankton developed in the Rhine in May and July/August, as indicated by the chlorophyll *a* concentration (Fig. 1), which led to slightly increased pH values in the (well buffered) water. Observations on Na and Ca in filtered and unfiltered samples showed that these metals are in the dissolved state, almost completely, as expected. Further, the observations show that the analytical procedures were reproducible.

Iron and lead were primarily found in the particulate phase, whereas manganese, copper, cadmium and zinc were distributed more equally over the

dissolved and particulate phases (Fig. 2). Partition coefficients (log K_p) were calculated and correlated with the presence or absence of algal blooms. Figure 3 shows that for manganese the log K_p co-varied with the photosynthetic rate ($n = 20$; $R = 0.83$), the chlorophyll *a* concentration ($n = 20$; $R = 0.79$), the temperature ($n = 18$; $R = 0.74$), and the pH ($n = 16$; $R = 0.72$), but not with water discharge. There was no obvious correlation between the partitioning of the other metals and the presence of phytoplankton, or with the log K_p of manganese. Table 1 shows that for Zn, Cd and Cu, metal fractions in the particulate phase were found in samples with high chlorophyll *a* concentrations were more-or-less similar to those with low chlorophyll *a* values. However, the variability in the partitioning between the sampling dates is high, so that minor effects of the blooms may have been obscured.

Fig. 1. Seasonal variation in biological, physical and chemical parameter in the River Rhine at Lobith station (German/Dutch border) during 1990. DW: dry weight.

Lobith 1990

Fig. 2. Variation in the total metal concentrations (upper graphs) and dissolved metal concentrations (lower graphs) in the River Rhine at Lobith station in the period April to December 1990. Few measurements in February and March were restricted to copper and manganese.

To verify the observations in 1990, similar data on metal concentrations and phytoplankton (indicated by chlorophyll *a* only) were analysed using data collected in 1983 (Fig. 4). The $\log K_p$ for Mn showed a strong seasonal variation that correlated well with the chlorophyll *a* concentration ($\text{Chl } a$ in $\mu\text{g l}^{-1}$): $[\log K_p] \text{ Mn} \approx 0.015 \text{ Chl } a + 4.516$ ($R = 0.74$, $n = 23$). The average Mn concentration and the correlation with chlorophyll *a* are very similar to the observations in 1990. Also, the Zn concentrations, being somewhat higher in 1983 than in 1990, showed seasonal variability in the partitioning over the two phases (Fig. 4), but a positive correlation of the $[\log K_p] \text{ Zn}$ with the chlorophyll *a* concentration could not be assessed. This also applied to $[\log K_p] \text{ Cu}$ and $[\log K_p] \text{ Cd}$ (results not shown).

DISCUSSION

Manganese oxidation in rivers

Redox transitions of manganese and concurrent phase changes in rivers are not well characterized. Dissolved Mn (II) dominates the manganese budget in dystrophic acid waters drained from the precambrian shield, Canada (Lazerte and Burling, 1990), while Laxen *et al.* (1984) reported particulate manganese hydroxides (Mn IV) amounting to 80% of the

total Mn at a pH of 7–8. Using radiotracer techniques Maggi *et al.* (1987) found percentages of 20–39 particulate Mn in the River Po (Italy). The data provided for the River Rhine (1975–1984) by Van der Weijden and Middelburg (1989) indicated that 45% of the total Mn was dissolved, with percentages much higher in winter and much lower in summer, consistent with the present observations. The two fractions (Mn II and Mn IV) are thought to result from decoupled terrestrial inputs (Laxen *et al.*, 1984), but there is also evidence of biotic or abiotic oxidation and precipitation in rivers (Morris and Bale, 1979). Chemical oxidation of Mn (II) seems to proceed slowly at the prevailing pH values (Laxen *et al.*, 1984) and may even be counteracted by photochemical reduction of any Mn (IV) formed (Waite *et al.*, 1988). Therefore, it seems likely that biological oxidation is involved. A great variety of organisms, including heterotrophic bacteria, fungi, algae and protozoa, have been shown to deposit Mn oxides (Ghiorse, 1984).

The present study also indicates that phytoplankton may be effective in Mn deposition. This seems to realistically explain the observations since (marine) phytoplankton have also been shown to bind Mn (Stauber and Florence, 1985; Davidson and Marchant, 1987; Lubbers *et al.*, 1990). There is no direct evidence that the Mn precipitation occurs on

the phytoplankton cells, but the high correlations with photosynthetic rate suggest that (extracellular) precipitation in the oxidative micro-environment of photosynthetic active cells with a high pH, may initiate the process (Chiswell and Mokhtar, 1986; Richardson *et al.*, 1988).

Extracellular precipitation by phytoplankton does, however, not exclude acceleration by autocatalytic oxydation of Mn (II) (Strumm and Morgan, 1981). The intracellular Mn concentrations of 1 mM in *Chlamydomonas* (Sunda and Huntsman, 1985) is far too low to explain the observed concentration in particulate matter, including phytoplankton cells, in the Rhine.

Table 1. Comparison of the partitioning coefficients of Zn, Cd and Cu during phytoplankton blooms ($>30 \mu\text{g}$ chlorophyll $a \text{ l}^{-1}$) and non-bloom periods ($<30 \mu\text{g}$ chlorophyll $a \text{ l}^{-1}$) in 1990 and also compared according to high (>0.85) and low (<0.85) fractions of Mn in the particulate phase

	$>30 \mu\text{g Chl } a \text{ l}^{-1}$	$<30 \mu\text{g Chl } a \text{ l}^{-1}$
$\text{Log } K_p \text{ Zn}$	4.90 ± 0.14 ($n = 10$)	4.59 ± 0.30 ($n = 8$)
$\text{Log } K_p \text{ Cd}$	4.92 ± 0.53 ($n = 10$)	5.10 ± 0.25 ($n = 5$)
$\text{Log } K_p \text{ Cu}$	4.27 ± 0.24 ($n = 9$)	4.15 ± 0.27 ($n = 11$)
	Fraction Mn part. >0.85	Fraction Mn part. <0.85
$\text{Log } K_p \text{ Zn}$	4.73 ± 0.31 ($n = 11$)	4.81 ± 0.19 ($n = 7$)
$\text{Log } K_p \text{ Cd}$	5.01 ± 0.49 ($n = 10$)	4.93 ± 0.40 ($n = 5$)
$\text{Log } K_p \text{ Cu}$	4.23 ± 0.32 ($n = 11$)	4.15 ± 0.18 ($n = 8$)

$\pm$ Standard deviations data from Figs 1 and 2.

Fig. 3. Correlations between the partitioning coefficient for Mn and: (1) photosynthetic carbon uptake at near saturation irradiance levels, (2) chlorophyll a concentration, (3) water temperature, (4) pH and (5) water discharge. Panels are arranged in decreasing order of the R -value to the regression equation. Data from Figs 1 and 2.

Fig. 4. Seasonal variation in chlorophyll a concentration and the partitioning of Mn and Zn in the River Rhine in 1983. Data from Anonymous (1983).

Precipitation of heavy metals?

Algae and manganese hydroxide are widely recognized accumulators of heavy metal ions (Wangersky, 1986), yet metal precipitation on these substrates did not seem to be a factor of overriding importance for the River Rhine. Earlier studies on habitats where the residence time of the water was longer did provide evidence for metal precipitation by algal blooms. Salomons and Mook (1980) indicated that algae accounted for 4–14% of the removal of cadmium, chromium, zinc and copper in Lake IJssel apart from the effects of a pH rise caused by the algae's photosynthesis. Also valenta *et al.* (1986) found increased particulate cadmium levels during phytoplankton blooms in the eastern Scheldt estuary in accordance with observations by Knauer and Martin (1973) in Monterey Bay. The effect of phytoplankton on metal partitioning in lakes and the sea may involve a repeated cycle of particle production and adsorption onto new surfaces (Baccini, 1984). Essentially insidious is the unimodal growth of phytoplankton in the River Rhine (cf. De Ruyter van Steveninck *et al.*, 1992). Together with the low affinity for cadmium determined by Koelmans and Lijklema (1992) in short-term sorption experiments with algae from the Rhine delta (and from cultures), short-lived riverine algal blooms do not seem to have a major impact on metal partitioning. Also, the highest cellular zinc concentration, observed in zinc-poisoned cultures of *Thalassiosira weissflogii* (a marine species; Sunda and Huntsman, 1992), were not high enough when extrapolated to Rhine phytoplankton to modify the zinc partitioning substantially.

The role of manganese precipitates in metal partitioning in Rhine water has, so far, remained obscure. The low concentrations of manganese of up to ca 1.5 μM as compared to ca 18 μM of particulate iron, may render this substrate of low relevance to metal partitioning in river water, despite its high affinity (at least for Cd) (Koelmans and Lijklema, 1992). However, this does not exclude manganese precipitation (if it actually occurs on the surface of riverine algal cells) being part of a protective mechanism against elevated metal concentrations, as demonstrated in algal cultures (Stauber and Florence, 1985; Bennett, 1990).

In summary, it appeared that Mn (II) oxidation in eutrophic river water may be much accelerated by intense phytoplankton growth. However, the strong increase in particulate, oxidized manganese seems to have little influence on the partitioning of other metals, limiting the consequences for metal retention in the lower part of the rivers.

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