Biogeochemistry **44:** 1–27, 1999.

The role of phytoplankton in pollutant transfer processes in rivers. Example of River Marne (France)

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Accepted 24 March 1998

Key words: phytoplankton, nutrients, heavy metals, colloids, ultrafiltration, river

Abstract. The impact of the spring phytoplanktonic blooms on the partition of nutrients and metals between the dissolved and particulate phases was studied over two years in the river Marne, upstream of its confluence with the river Seine. Particular attention was devoted to copper and manganese, determined in the dissolved phase ($< 0.22\ \mu$m), subdivided into the colloidal phase and the 'truly dissolved' phase (< 10 KDaltons) obtained by tangential ultrafiltration. During the algal growth peaks, a sharp reduction of nutrients was observed in the dissolved phase: in 1994, consumption of 70% of silica, 50% of ammonium and 40% of soluble phosphorus present before the phytoplanktonic bloom.

The water concentration peaks of suspended matter (SM) and of particulate metals, phosphorus and carbon coincide with those of chlorophyll. The highly significant correlations between pH and chlorophyll ($r = 0.92$, $P < 0.001$), pH and SM ($r = 0.97$, $P < 0.001$) and chlorophyll and SM ($r = 0.93$, $P < 0.001$) confirmed the phytoplanktonic nature of SM and the determining role of pH in the partition of metals, its increase being responsible for the coprecipitation of metal. As a corollary to the increase in the particulate phase, a decrease of 55% was observed for copper and manganese in the 'truly dissolved' phase compared to the concentrations outside bloom periods.

The importance of the colloidal fraction was also shown. During the strong algal growth periods, the proportion of 'colloidal metal' in the dissolved phase ($< 0.22\ \mu$m) reached 60% and the increase in the colloidal fraction was 4 times stronger for copper than for manganese. While manganese seemed to be more associated with macroparticles, copper was more associated with fine colloidal biological particles intrinsic to the phytoplankton.

Introduction

The role of biological matter in the transfer of metallic micropollutants has been widely described in oceans. The correlations between Cd, Ni and Zn with P and Si show that these metals can follow the same biological cycles as nutrients (Yeats & Campbell 1983; Sunda 1991; Sunda & Hunstman 1992).

In sea and continental waters there are also associations between algae and metallic micropollutants: when metals are not directly accumulated by algae, they are often complexed by their extracellular metabolites (Salomons & Mook 1980; Hart 1981; Jardim & Pearson 1984; Seritti et al. 1986; Rudd et al. 1984; Gonzales-Davila 1995).

According to Förstner and Wittman (1983), two important factors involved in the transport of trace metals in continental surface waters are discharge and primary production by biological materials, which shows large seasonal variations. The former is more traditionally studied in rivers and the latter, in lakes.

In lakes, Hamilton-Taylor et al. (1984) and Sigg et al. (1987) have indirectly shown the prominent role of biological matter in the transport of Cu and Zn towards sediments by the excellent correlations between these metals and phosphorus. Salomons and Mook (1980) explained the action of phytoplankton on dissolved metal concentrations by pH increase and by direct assimilation.

In polluted river waters, metals are mainly associated with particulate phase. Their distribution between dissolved and particulate phases is determined by interactions of several types: flocculation, precipitation, coprecipitation, chelation, adsorption on inorganic or organic compounds, etc. ... (Stumm & Morgan 1981; Förstner 1987; Sigg et al. 1992). The predominant process in control of concentrations of most of metals seems to be adsorption on particulate matter of biological origin (Wangersky 1986). Thus, phytoplanktonic blooms, which are mainly dependent on daylight and speed of current, might have an influence on metal partition and hence, on their mode of transport as a function of the seasons, but few studies have described the role of algal biomass in the metal distribution in river waters. However, Pettine et al. (1994) observed a significant positive correlation between orthophosphates and dissolved metals in the river Po, and Admiraal et al. (1995) showed an increase in particulate manganese during the algal blooms due to pH increase resulting from phytoplankton photosynthesis in river Rhine. Moreover, several studies have focused on the role of the colloidal fraction of metallic micropollutants in rivers (Rees & Ranville 1990; Hart et al. 1992).

The location at Marne-Seine confluence, where we measured major phytoplanktonic peaks in 1991 (254 $\mu g \cdot L^{-1}$ and 149 $\mu g \cdot L^{-1}$ of total chlorophyll on May 21 in the river Marne and Seine respectively) (Garban & Ollivon 1995), seemed to be a suitable site for the determination of the role of phytoplankton in pollutant transfer processes in rivers. Therefore, we have studied spring algal blooms in the river Marne directly upstream from its confluence with the river Seine close to Paris, in 1994 and 1995 (Figure 1). We have

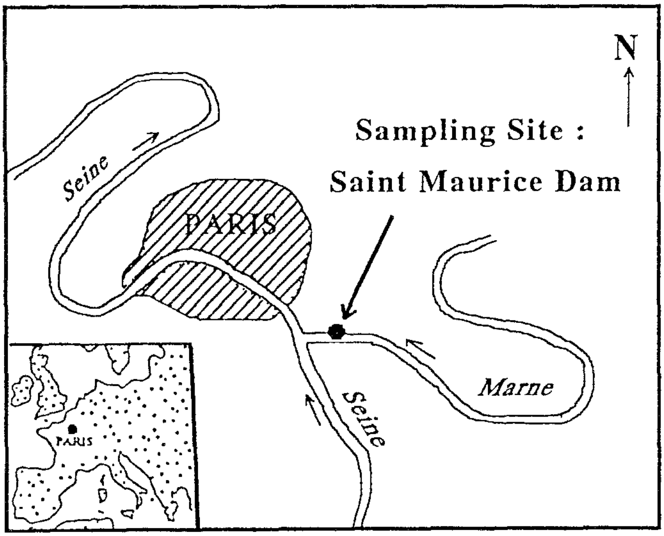

Figure 1. Location of the sampling site on river Marne, at Saint Maurice dam, near Paris (France).

studied the impact of this biological phenomenon on nutrient concentrations and metal distribution in the water column with particular attention to copper and manganese distributions between colloidal (defined from 10 KDaltons to 0.2 μm) and 'truly dissolved' phases (defined as < 10 KDaltons).

Sampling procedures and analytical methods

The river Marne, a tributary of river Seine, is approximately 525 km long and has a median discharge of about 60 $m^3 \cdot s^{-1}$. It drains an agricultural and winegrowing catchment basin (Champagne) upstream, and urbanized suburbs of Paris, downstream.

The sampling site has been chosen 100 m upstream Saint-Maurice dam, 1 Km from confluence with river Seine, where cross section homogeneity is attested by constant conductivity (maximum deviation 0.4%).

As the levels and durations of chlorophyll peaks (expression of algal blooms) are extremely variable according to the years (Dessery et al. 1984), sampling frequency is of main importance in fine analysis of the phenomenon. Dulac et al. (1983) suggested a weekly frequency. For better accuracy, samples were collected twice weekly from April to July during 1994 and 1995, always at 11.00 a.m.

In 1994, the following determinations were carried out on the Marne water: chlorophyll, suspended matter (SM), metals (Cu, Zn and Pb) on raw water (unfiltered); nutrients (ammonium, phosphorus and silica) on 0.45 μm filtered water; Cu, Zn, Pb and particulate organic carbon (POC) on SM.

In 1995, we extended metal determinations to Cr, Ni, Mn and Fe on raw water and SM. In addition, we performed successive filtrations at 0.22 μm and 10 KDaltons (tangential ultrafiltration) on a fraction of sampled water. Cu and Mn in those fractions were determined for the calculation of the colloidal and 'truly dissolved' fractions.

Trace analysis need specific procedures of sampling and storage to minimize sample contamination and adsorption losses (Batley & Gardner 1977). In this way, all the apparatus were tested prior to use after leaching in 0.66% HNO_3 for one week: they provided negligible contamination. All acids used were Merck suprapur quality: 66% HNO_3 (ref 100441), 98% H_2SO_4 (ref 100714), 30% HCl (ref 100318) and were checked frequently for blank levels to the elements to be analyzed. All laboratory handling was carried out under a V 142 A.D.S. hood with laminar flow (filtration of air at 0.3 μm).

Water samples were collected with a stainless steel sampler washed with 6.6% HNO_3, then thoroughly rinsed with Milli-Q water prior to use and in addition rinsed several times on site with river water. Approximately 5 L of water were collected at each sample collection. To minimize contamination single use disposable flasks were used for removal of samples.

On field, immediately after collection, 500 mL were filtered for SM concentration determination using pre-weighed 0.45 μm filters (Gelman): dry weight of SM was determined gravimetrically. Filters were stored at 4 °C until they were dried at 110 °C and weighed at the laboratory. Two samples of 250 mL each, were filtered, for chlorophyll analysis, on 0.45 μm cellulose ester filters (Millipore HAWP). The filters were kept in single use polypropylene tubes, in darkness, at 4 °C, until analysis. Chlorophyll was extracted with 90% aceton then analyzed spectrometrically according to the SCOR-UNESCO method (SCOR-Unesco 1966). Results were means of duplicates (maximum coefficient variation 5%).

Just after collection, aliquots for determination of nutrients (N, P, Si) were taken with 50 mL polypropylene single use Terumo syringe and filtered extemporaneously through 0.45 μm nylon filters (Shandon, ϕ 25 mm) then placed in 60 mL single use polystyrene flasks; for PO_4, filtered water was acidified with 0.1 mL H_2SO_4. For metals, 50 mL raw water were acidified to less than pH 1 by adding 66% HNO_3. All the flasks were sealed in plastic bags and stored at 4 °C in dark before analysis. Moreover, at the laboratory, flasks for ammonium were frozen within an hour of sampling until analysis.

Two L fluorined bottles were filled up for filtrations at 0.22 μm and 10000 Daltons (tangential ultrafiltration). These operations were performed in laboratory within 4 h from the beginning of collection. Each fraction was acidified with HNO_3 in single use flasks. Cu and Mn in these fractions were determined for the calculation of the colloidal and 'truly dissolved' fractions. To avoid plugging, water was prefiltered through glass fiber filters (Gelman), previously heated in an oven at 400 °C, acid-washed with HNO_3, rinsed with milli-Q water and stored in teflon bomb with milli Q water until use. The 0.22 μm filtration was performed through regenerated cellulose filters (Sartorius SM 116) without binder, washed with suprapur HNO_3 and rinsed with milli-Q water. The fraction obtained, conventionally called 'dissolved', includes the 'truly' dissolved phase and the colloidal phase. Then, it underwent tangential flow ultrafiltration which separated the 'truly dissolved' phase. The ultrafiltration system included a single use polysulfone membrane (Sartorius Sartocon Micro), so as to avoid contaminations. The membrane porosity was about 3 nm (nominal cut-off point 10 KD). A peristaltic pump with a six-roller head led us to use teflon tubings exclusively. Before each use, the complete system (tubings and vessels) underwent a series of washings: washing with 15% sodium hypochlorite solution ('eau de Javel'), followed by a rinse with milli-Q water and successive washings with suprapur acids (HCl, HNO_3) followed by rinsing with milli-Q water until rinsing water blanks and Milli-Q water blanks were in good agreement concerning metals. Unfiltered and filtered water solutions for copper and manganese were analyzed with a GBC 908 electrothermic AAS with a graphite furnace controlled by a GBC programmer (GF 3000). Analyses were performed in triplicate. Detection limits (DL) are calculated from twenty blanks: ($DL_{Cu} = 0.07\ \mu g{\cdot}L^{-1}$, $DL_{Mn} = 0.09\ \mu g{\cdot}L^{-1}$). Average standard deviation ($\pm RSD$) for three replicates Cu and Mn analyses was 1%.

Sediment traps allowed to collect about 20 to 200 g of wet material (5 to 60 g of dry material), depending on hydraulic conditions and SM characteristics. These traps were designed by the CERGRENE (Centre d'Etude et de Recherche pour la Gestion des Ressources Naturelles et de l'Environnement) and described by Estebe et al. (1991). They were composed of plastic cylinders with a 0.1 m^2 circular section and 0.80 m height. There was a honeycomb structure inside to avoid turbulence. The trap was maintained 30 cm below the surface by a float and left in the river for 3–4 days. This time elapsed, trap was brought out of water and SM from the trap was decanted into 'Imhoff' glass cones, then freeze-dried at lab and homogeneized prior to sieving on 200 μm nylon sieve. Determinations were carried out on the sieved fraction (Carre et al. 1980): 500 mg were digested, in single use disposable tubes sealed with teflon screw caps, by 10 mL HNO_3-HCl (6/4, v/v), then placed in an oven at 120 °C for 48 h. This mineralization, which doesn't involve dissolution of silicates, partly preserves the matrix (Agemian & Chau 1976; Welte & Montiel 1985; Carru et al. 1993), and solubilizes adsorbed metal, that is of interest here. This 'aqua regia' digestion method has been widely adopted in Europe and has been used by the Community Bureau of Reference (BCR) of the Commission of the European Communities for provision of reference soils with well established (but not certified) aqua regia soluble contents of several metals in addition to certified 'total contents' (Ure 1996; Gupta et al. 1996). Resulting mixture was centrifuged 20 minutes at 4500 g (Sigma 2–15 centrifuge) and supernatant volume brought up to 40 mL with Milli-Q water. Except Cu and Mn analyzed using a GBC 908 electrothermic AAS, the metals on raw water and supernatants of digested SM were analyzed using flame atomic absorption spectrophotometry (AAS) (GBC 905) or electrothermic AAS (Philips 9200) with a graphite furnace controlled by a PU 9390 electrothermal atomiser. Due to the number determinations, analyzes were routinely performed in duplicate. Background matrix interferences were compensated by the method of proportional additions and addition of matrix modifiers ($NH_4H_2PO_4$ for Pb, $Mg(NO_3)_2$ for Cr, Fe and Mn) (Price 1979; Slavin 1984) and instrumental background correction when appropriate. Blanks were run through for all the procedures and taken into account in the results. All results with AAS type used and detection limits are summarized in Tables 1 and 2. Analytical precision for the range of concentration of our samples was approximately 5% for digested SM and between 5 and 15% for metals in raw water samples (Table 1).

An intercomparison of heavy metal analyses carried out on samples of river Seine water (Huang et al. 1995) has emphasized necessity of identical protocols. Tests were carried out on certified water (SPS-SW1 surface water sample, referensmaterial AB, Sweden). Results are in reasonable-to-good agreement with certified values (Table 3). On certified sample of river sediment (CRM 320 of BCR) tests confirmed the reliability of determinations with aqua regia digestion procedure (Table 3). Results depended mainly on the mineralization method, according to the strength of the attack on the matrix (Carru et al. 1993).

Ammonium and silica were measured spectrophotometrically: Ammonium according to the French AFNOR standard T90-01 with indophenol blue method (Solorzano 1969) and silica after silico-molybdic complex reduction (Voinovitch et al. 1962). Particulate phosphorus was measured in the SM dried at 110 °C, after 0.2 N sulfuric acid digestion (Saunders & Williams 1955).

POC was measured, after carbonate had been destroyed by HCl, using a Carlo Erba elemental analyzer mod 1106 with an autosampler. Oxidation occurs at high temperature (1300 °C) in a catalytic furnace. Organic carbon is analyzed as CO_2 using a catharometric detection. Correlations were calculated by using the software 'Quattro Pro' from Borland, the significance of the correlation was expressed by the coefficient r of Fisher and Yates.

Results

In 1994, the phytoplanktonic bloom as evidenced by chlorophyll results showed a single peak in May at 105 $\mu g \cdot L^{-1}$, much lower than in 1991 (254 $\mu g \cdot L^{-1}$). The average flow of the river Marne was 79 $m^3 \cdot s^{-1}$ from 05/03 to 05/31. Despite this weak peak in 1994, a sharp decrease in concentrations of dissolved nutrients occurred simultaneously with algal growth (Figure 2): silica was reduced by 70%, soluble phosphorus by 40% and ammonium by 50%. This phenomenon, widely described elsewhere, confirmed our previous observations on the river Marne (Billen et al. 1992).

In 1995, the last flood period, relatively weak (324 $m^3 \cdot s^{-1}$), occurred in late April–early May (Figure 3). After this event, four successive chlorophyll peaks were observed at 71, 136, 140 and 245 $\mu g \cdot L^{-1}$. The first peak occurred around May 28, at the end of the high-flow period, with a flow of about 100 $m^3 \cdot s^{-1}$. The next three following peaks occurred from 06/02 to 07/04, with an average flow of 60 $m^3 \cdot s^{-1}$. pH varied around 8 with peaks at 8.3 and 8.45, corresponding exactly with the chlorophyll peaks. Simultaneously an increase of POC concentrations occurred: from 62 to 95% of this POC is attributed to a biogenic origin (Jaïry & Chesterikoff 1977). Chlorophyll peaks also coincided with an increase in SM concentrations, considerably lower than during the flood period during which SM had an allochtonous detrital origin.

During the high-flow period, a metal concentration peak in raw-water was observed on 04/25/95 concomitant with the SM peak which occurred a few days before discharge peak. Subsequently, concentrations decreased and stabilized about 2 weeks after the high-flow peak (Table 2).

The suspension traps enabled us to collect settling material every 3 to 4 days and to determine particulate metals, organic carbon (POC) and phosphorus in these suspensions (Table 2). Traps are likely not to capture smallest fractions carried by the river, but still, they give an average aliquot of SM carried for a few day time more representative than a ponctual sampling. Representative sampling by the traps used in this study has been confirmed by controlled field experiments (Taconet et al. 1995). Thus, if we assume that SM collected in suspension traps and SM carried in the river (filtered through 0.45 μm) are nearly the same material, from the quantity of SM carried in the river ($mg \cdot L^{-1}$) and the metal contents in the suspensions ($\mu g \cdot g^{-1}$) (Table 2), the particulate metal concentrations ($\mu g \cdot L^{-1}$) in the river water can be easily calculated (Figure 5). These results are overall more reliable than those

Table 1. Metal concentrations ($\mu g{\cdot}L^{1}$) in raw water, during the flood period from April 14 to May 19, 1995 and during 'algal blooms' from May 26 to July 4, 1995 and total chlorophyll concentrations ($\mu g{\cdot}L^{-1}$).

Dates	Cr^a	Cu^b	Fe^c	Mn^b	Ni^a	Pb^a	Zn^c	Discharge	Chloro
	$\mu g{\cdot}L^{-1}$	$\mu g{\cdot}L^{-1}$	$\mu g{\cdot}L^{-1}$	$\mu g{\cdot}L^{-1}$	$\mu g{\cdot}L^{-1}$	$\mu g{\cdot}L^{-1}$	$\mu g{\cdot}L^{-1}$	$m^3.s^{-1}$	$\mu g{\cdot}L^{-1}$
DL	0.2	0.07	10	0.09	0.2	0.2	1.5		
RSD %	15%	1%	5%	1%	10%	10%	10%		5%
Flood period									
04/14/95	2.1 ± 0.3	12.4 ± 0.1	366 ± 18	NA	0.38 ± 0.04	27 ± 3	9.4 ± 0.9	164	11.2 ± 0.5
04/18/95	1.7 ± 0.2	0.98° ± 0.01	140 ± 7.5	NA	0.28 ± 0.03	0.2° ± 0.02	3.6 ± 0.4	97	7.7 ± 0.2
04/21/95	0.5° ± 0.1	7.32 ± 0.07	190 ± 10	NA	0.33 ± 0.03	27 ± 3	10.6 ± 1	129	8.6 ± 0.2
04/25/95	1.6 ± 0.2	8.36 ± 0.08	1650 ± 75	NA	0.97 ± 0.09	32 ± 3	22.6 ± 2	272	31.5 ± 1.5
04/28/95	1.3 ± 0.2	7.22 ± 0.07	997 ± 5	NA	0.77 ± 0.08	20 ± 2	26 ± 3	324	17.2 ± 0.8
05/02/95	1.4 ± 0.2	6.37 ± 0.06	378 ± 18	NA	0.49 ± 0.05	7.2 ± 0.7	9.5 ± 0.9	263	13.1 ± 0.6
05/09/95	0.7 ± 0.1	3.88 ± 0.04	234 ± 10	NA	0.31 ± 0.03	1.3 ± 0.1	9 ± 0.9	171	13.0 ± 0.6
05/12/95	0.7 ± 0.1	6.16 ± 0.02	281 ± 15	NA	0.33 ± 0.03	1.4 ± 0.1	6.6 ± 0.6	162	10.8 ± 0.5
05/16/95	0.7 ± 0.1	4.31 ± 0.04	277 ± 13	NA	0.25 ± 0.02	1.3 ± 0.1	5.6 ± 0.6	128	9.9 ± 0.5
05/19/95	0.7 ± 0.1	3.88 ± 0.04	252 ± 12	NA	0.28 ± 0.03	1.7 ± 0.1	6 ± 0.6	120	14.3 ± 0.7

Table 1. (Continued).

Dates	Cr[a] $\mu g \cdot L^{-1}$	Cu[b] $\mu g \cdot L^{-1}$	Fe[c] $\mu g \cdot L^{-1}$	Mn[b] $\mu g \cdot L^{-1}$	Ni[a] $\mu g \cdot L^{-1}$	Pb[a] $\mu g \cdot L^{-1}$	Zn[c] $\mu g \cdot L^{-1}$	Discharge $m^3.s^{-1}$	Chloro $\mu g \cdot L^{-1}$
Phytoplanktontic blooms period									
05/26/95	0.8 ± 0.1	9.04 ± 0.09	214 ± 10	36.4 ± 0.4	0.56 ± 0.05	1.1 ± 0.1	8.9 ± 0.9	104	65.7 ± 3.2
05/30/95	0.7 ± 0.1	4.74 ± 0.05	259 ± 12	23.2 ± 0.2	0.25 ± 0.02	2.7 ± 0.2	9.3 ± 0.9	94	71.3 ± 3.5
06/02/95	0.4 ± 0.1	4.44 ± 0.04	326 ± 15	72.3 ± 0.7	0.38 ± 0.04	1.4 ± 0.1	9.8 ± 0.9	73	31.4 ± 1.6
06/06/95	0.2 ± 0.1	4.12 ± 0.04	223 ± 10	30.4 ± 0.3	0.36 ± 0.04	1.4 ± 0.1	9.5 ± 0.9	59	22.7 ± 1.1
06/09/95	0.7 ± 0.1	6.22 ± 0.06	405 ± 20	63.2 ± 0.6	1.30 ± 0.13	2.2 ± 0.2	9.6 ± 0.9	74	136 ± 7
06/13/95	0.8 ± 0.1	4.86 ± 0.05	289 ± 15	39.8 ± 0.4	0.46 ± 0.05	2.2 ± 0.2	9.2 ± 0.9	57	39.7 ± 2
06/16/95	1.1 ± 0.2	3.89 ± 0.04	256 ± 12	24.3 ± 0.2	0.41 ± 0.04	10 ± 1	8.3 ± 0.8	64	28.4 ± 1.4
06/20/95	1.1 ± 0.2	4.46 ± 0.04	255 ± 12	24.3 ± 0.2	0.31 ± 0.03	11 ± 1	7.7 ± 0.8	71	140 ± 7
06/23/95	1.3 ± 0.2	3.78 ± 0.4	181 ± 10	16.8 ± 0.2	0.36 ± 0.04	9.4 ± 1	7.6 ± 0.8	50	35.5 ± 1.8
06/27/95	0.8 ± 0.1	4.67 ± 0.05	267 ± 12	23.6 ± 0.2	0.23 ± 0.02	1.8 ± 0.2	12 ± 1	57	245 ± 12
06/30/95	0.8 ± 0.1	4.65 ± 0.05	227 ± 10	29.2 ± 0.3	0.36 ± 0.04	1.7 ± 0.2	6 ± 0.6	44	140 ± 7
07/04/95	0.7 ± 0.1	4.04 ± 0.05	186 ± 10	123 ± 1.2	0.21 ± 0.02	1.9 ± 0.2	6 ± 0.6	60	68.5 ± 3.4

N.A. Not analyzed.

° unexplained weak values.

[a] Electrothermic AAS (Philips 9200) with a graphite furnace controlled by a PU9390 electrothermal atomiser.

[b] Electrothermic AAS (GBC 908) with a graphite furnace controlled by a GBC programmer (GF 3000).

[c] Flame atomic absorption spectrophotometry (AAS) (GBC 905).

Table 2. Metal and phosphorus contents of 'trapped' suspended-matter, expressed in $\mu g \cdot g^{-1}$, particulate organic carbon (POC) in % and suspended-matter (SM) concentrations in $mg \cdot L^{-1}$ at St Maurice Dam in the river Marne during flood period from April 14 to May 19, 1995 and during ≪ algal blooms ≫ from May 26 to July 4, 1995. Values corresponding to phytoplanctonic peaks are noted in bold characters.

	Cr^a $\mu g \cdot g^{-1}$	Cu^b $\mu g \cdot g^{-1}$	Fe^b $\mu g \cdot g^{-1}$	Mn^b $\mu g \cdot g^{-1}$	Ni^a $\mu g \cdot g^{-1}$	$Pb^{a)}$ $\mu g \cdot g^{-1}$	Zn^b $\mu g \cdot g^{-1}$	Phosphorus $\mu g \cdot g^{-1}$	Chlorophyll $\mu g \cdot g^{-1}$	SM $\mu g \cdot g^{-1}$	POC %
Detection limit (DL)	1	3	8	6	1	2	2	5			
Flood period											
Dates											
04/14/95	25	39	19633	410	21	67	201	763	11.2	29.3	NA
04/18/95	22	46	20383	444	21	55	256	933	7.7	14.1	NA
04/21/95	26	79	20111	433	23	208	327	1075	8.6	20.1	NA
04/25/95	20	40	15244	375	18	88	192	690	31.5	173	NA
04/28/95	22	32	14045	335	21	90	165	485	17.2	153	NA
05/02/95	15	35	14313	335	14	34	132	495	13.5	61.4	NA
05/09/95	20	30	18143	406	20	35	170	638	13.0	35.3	5.2
05/12/95	47	38	16740	416	NA	53	178	930	10.8	26.4	NA
05/16/95	48	55	14980	436	NA	73	249	1060	9.9	21.9	5.5
05/19/95	45	59	21300	435	NA	81	251	1130	14.3	22.1	NA
05/23/95	52	52	16520	498	NA	88	235	1080	17.8	22.9	7.1
05/26/95	49	43	17140	604	NA	83	321	1210	65.7	20.4	7.2

Table 2. (Continued).

	Cr^a μg·g^{-1}	Cu^b μg·g^{-1}	Fe^b μg·g^{-1}	Mn^b μg·g^{-1}	Ni^a μg·g^{-1}	Pb^a) μg·g^{-1}	Zn^b μg·g^{-1}	Phosphorus μg·g^{-1}	Chlorophyll μg·g^{-1}	SM μg·g^{-1}	POC %
Phytoplanctonic blooms period											
30/05/95	38	91	22078	542	64	140	432	1335	71.3	14.9	8.3
02/06/95	40	80	20578	477	76	156	329	1275	31.4	12.5	5.7
06/06/95	40	83	24462	586	48	188	382	1365	22.7	16.3	6.7
09/06/95	**34**	**60**	**19679**	**441**	**36**	**156**	**264**	**1313**	**136**	**26.5**	**6.4**
13/06/95	42	69	24806	556	48	256	312	1258	39.7	17.9	4.8
16/06/95	36	82	24634	520	30	140	298	1335	28.4	15.6	4.0
20/06/95	**40**	**84**	**24093**	**546**	**36**	**156**	**284**	**1435**	**140**	**25.5**	**7.0**
23/06/95	38	83	25406	599	38	164	308	1513	33.5	13.9	5.0
27/06/95	**120**	**87**	**25243**	**618**	**156**	**152**	**311**	**1513**	**245**	**30.3**	**6.9**
30/06/95	**36**	**77**	**21924**	**513**	**32**	**184**	**277**	**1395**	**140**	**20.2**	**6.0**
04/07/95	36	94	21599	573	32	180	390	1630	68.5	21.1	6.1

N.A. Not analyzed.

RSD 5%.

[a] Electrothermic AAS (Philips 9200) with a graphite furnace controlled by a PU9390 electrothermal atomiser.

[b] Flame atomic absorption spectrophotometry (AAS) (GBC 905).

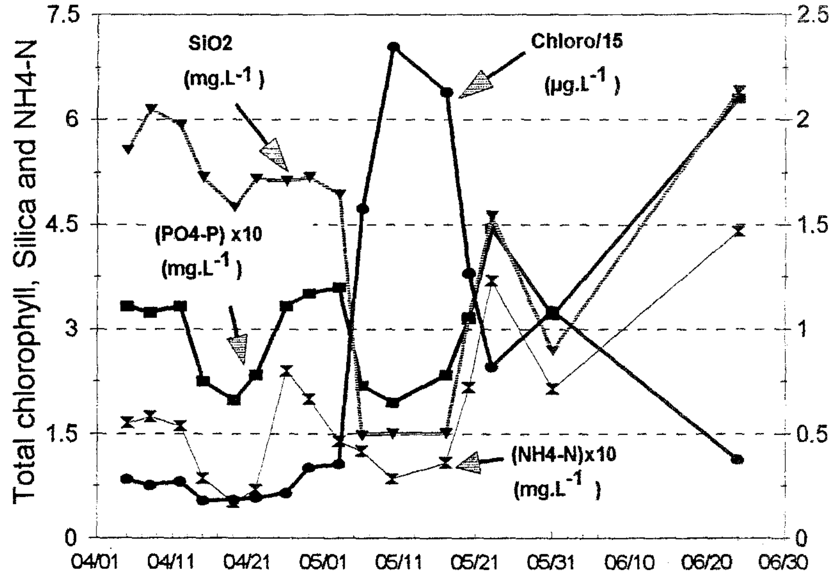

Figure 2. (-●-) Total chlorophyll and soluble nutrients (⧗) ammonium, (-■-) phosphorus and (-▼-) silica concentrations in river Marne at Saint Maurice dam in spring 1994. Total chlorophyll concentrations ($\mu g \cdot L^{-1}$) are divided by 15, phosphorus and ammonium concentrations ($mg \cdot L^{-1}$) are ten fold higher than measured values.

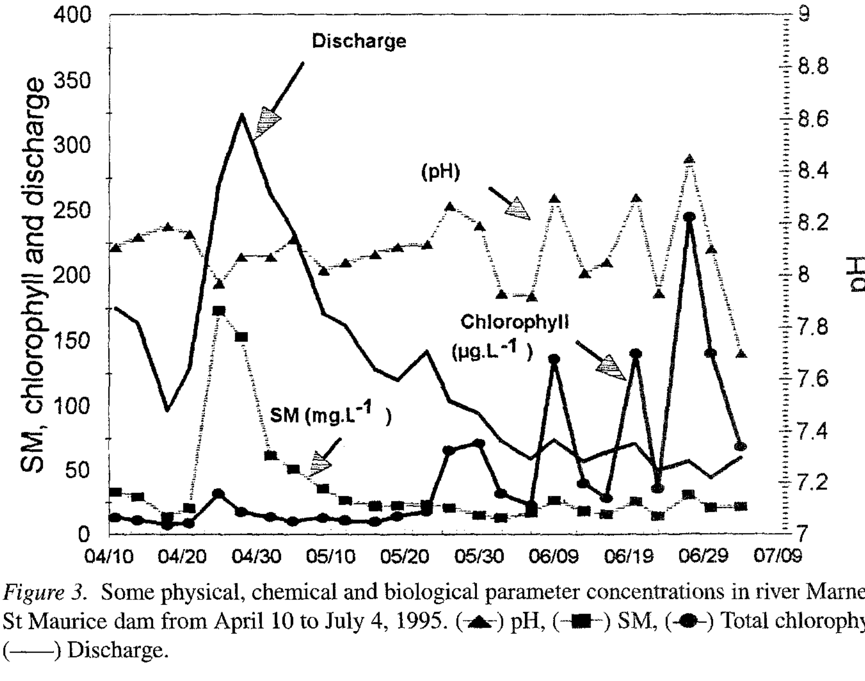

Figure 3. Some physical, chemical and biological parameter concentrations in river Marne at St Maurice dam from April 10 to July 4, 1995. (-▲-) pH, (-■-) SM, (-●-) Total chlorophyll, (——) Discharge.

Table 3. Metal concentrations in reference surface water (SPS-SW1 referensmaterials AB, Sweden) and metal contents in reference river sediment (CRM 320 of the commission of the European communities, BCR (Community bureau of reference)).

	Cu	Fe	Mn	Ni	Pb	Zn
SPS-SW1						
Certified values	20 ± 1	20 ± 1	10.0 ± 1.0	9.8 ± 0.1	5.1 ± 0.1	19 ± 1
●	23 ± 0.2	21 ± 1	9.2 ± 0.1	9.6 ± 0.9	5.0 ± 0.5	20 ± 2
CRM320						
Certified values	44.1 ± 1.0	48500◆	930◆	75.2 ± 1.4	42.3 ± 1.6	142 ± 3
*	42.0 ± 2.6	32000 ± 640		55.0 ± 4.3	30.0 ± 2.6	124 ± 5
◈	42.8 ± 2.1	42800 ± 2100	973 ± 48	62.3 ± 3.1	40.0 ± 2.0	139 ± 75

● concentrations $\mu g \cdot L^{-1}$ (mean of triplicate).
* 'well determined' values after aqua regia digestion ($\mu g \cdot g^{-1}$) BCR.
◈ contents after aqua digestion ($\mu g \cdot g^{-1}$) (mean of triplicate).
◆ BCR values calculated from oxide contents.

obtained by difference between the unfiltered and filtered water (Carru et al. 1994).

Both in 1994 and 1995, a significant increase in particulate metal concentrations was observed during algal blooms. In 1994, concentrations of particulate Cu, Zn and Pb increased approximately threefold (Figure 4). In 1995, when a wider range of metals was studied, particulate metal concentrations with a logarithmic scale as shown on Figure 5, which highlights all the variations, generally tracked down the chlorophyll concentrations. The increases were very marked during the last two chlorophyll peaks when concentrations were more than two fold higher. Furthermore, during phytoplanktonic bloom period, some metal behaviours are identical as for Fe and Mn, Cr and Ni or Cu and Zn; Pb is more atypic. In addition, during the period of high biological activity, we observed concentration curves for particulate carbon and phosphorus which varied in the same way as those of SM and chlorophyll (Figure 6).

Tangential ultrafiltration enabled us to determine Cu and Mn concentrations in the 'truly dissolved' (< 10 KD) and colloidal phases at the time of blooms and thus to calculate the proportion of colloidal metals in dissolved phase < 0.2 μm, predominant during phytoplanktonic peaks. Colloïdal Cu concentrations ranged from 0.35 to 1.30 $\mu g \cdot L^{-1}$. A proportion of 20 to 60% of Cu usually considered with dissolved fraction was in colloïdal form. Colloïdal Mn varied from 8 to 90% of total dissolved Mn. The fraction of colloïdal Mn ratio was influenced by phytoplankton activity: 62, 50

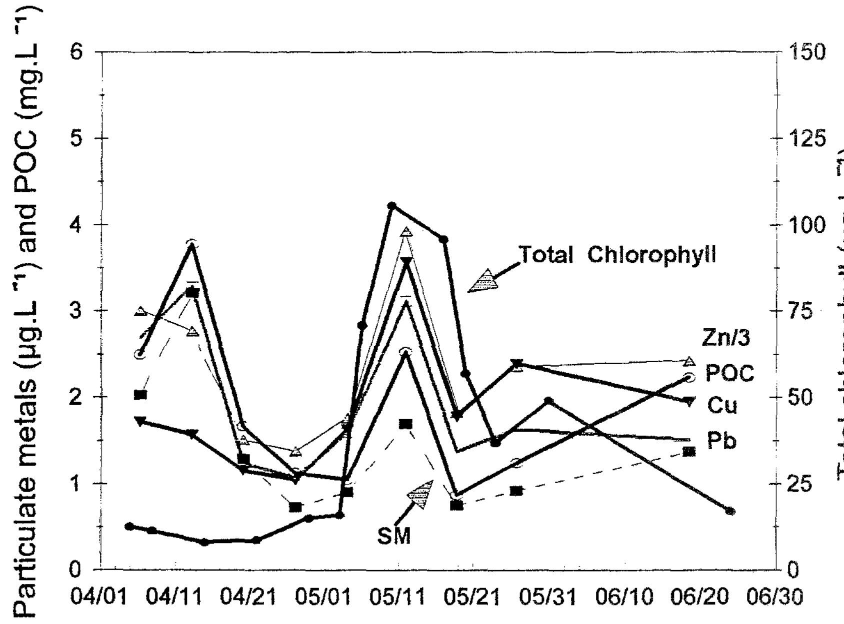

Figure 4. (-●-) Total chlorophyll, particulate heavy metals (-△- Zn, -▼- Cu, -□- Pb), (-■-) SM and (-○-) organic carbon concentrations in river Marne at St Maurice dam (1994). Zn concentrations are divided by 3.

and 62%, respectively concomitant with the three peaks in chlorophyll with intermediate values around 22% when chlorophyll concentrations were lower (Tables 4 and 5). Increase in colloïdal fraction corresponded to a decrease in the truly dissolved forms (Table 6). Cu and Mn distributions are detailed elsewhere (Jaïry et al. in press).

Discussion and conclusion

During the two spring periods studied, we showed the impact of algal blooms on the distribution of nutrients essential to algal growth: reduction of the concentrations of ammonium, dissolved phosphorus and silica, increase in particulate phosphorus and carbon, overall increase in SM. An increase of particulate matter, including phytoplankton, observed during the phytoplanktonic blooms also included an increase in particulate metal concentration. Correlations between the particulate metals studied and chlorophyll were significant (Table 7). However, since particulate metal concentrations in $\mu g{\cdot}L^{-1}$ had been calculated from the contents in the trapped suspensions in $mg{\cdot}g^{-1}$, evaluation of the impact of phytoplanktonic development on

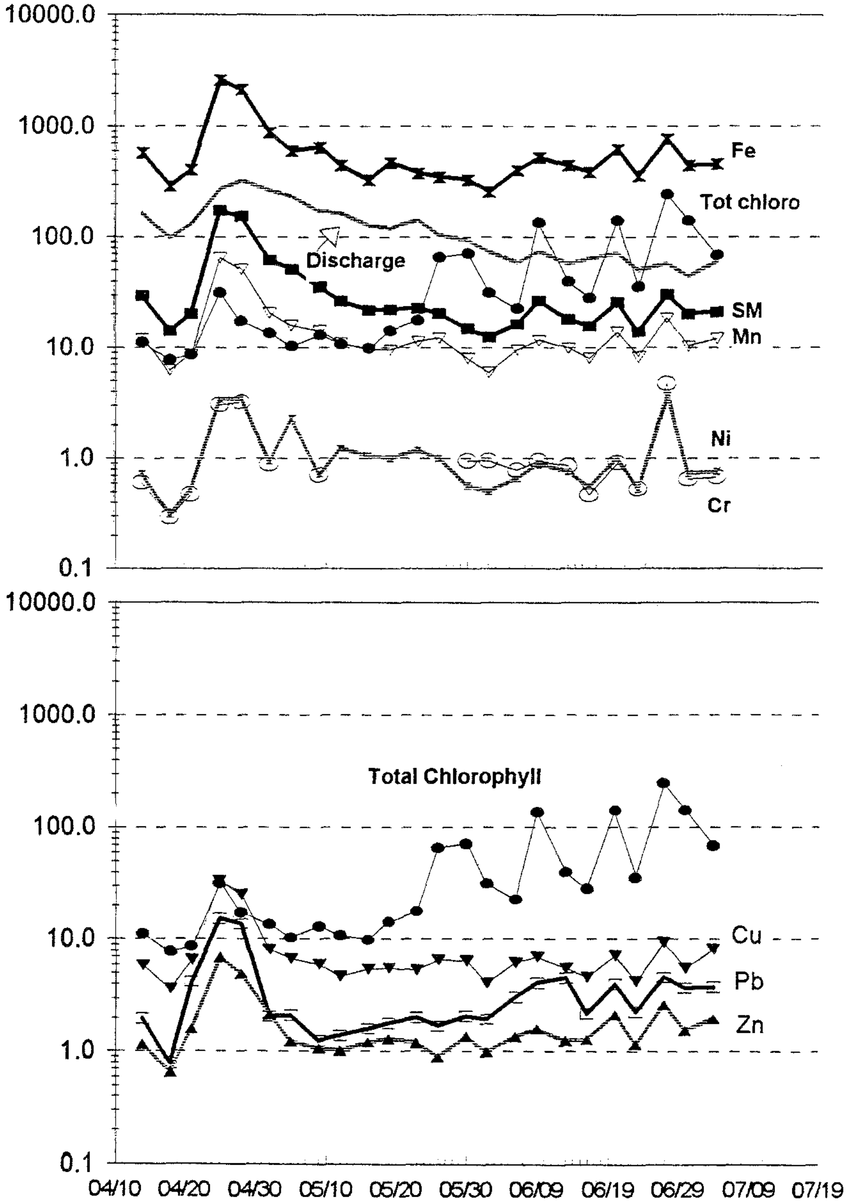

Figure 5. Metal concentrations in raw water (-○- Ni, ⧗ Fe, -▽- Mn, ⧗ Cr, -□- Pb, ▼ Cu, ▲ Zn), (determined after 'aqua regia' digestion of trapped SM and calculated in $\mu g \cdot L^{-1}$), (-■-) SM, (-●-) total chlorophyll and (——) discharge in the river Marne at St Maurice dam from April 10 to July 4, 1995, displayed on logarithmic scale.

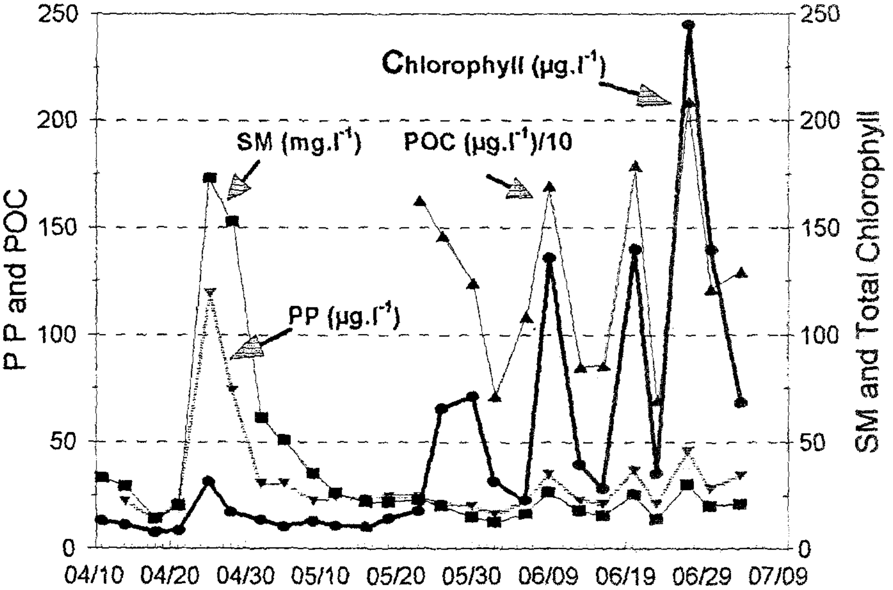

Figure 6. (▼) Particulate phosphorus (PP) and (▲) particulate organic carbon (POC) concentrations in $\mu g \cdot L^{-1}$ of raw water compared with (■) SM and (●) total chlorophyll in river Marne at St Maurice dam, from April 10 to July 4, 1995 (for comparison, POC concentrations are divided by 10).

metal partition requires verification that the increase in SM is due to the phytoplankton alone.

In the Seine watershed rivers, spring algal communities consist in 80% of diatoms where Cyclotella is the predominant species (50 à 80%) (Dessery et al. 1984; Chesterikoff et al. 1985).

Diatoms are cylindric or rod cells which diameters range from 10 to 300 μm and thus they are totally collected with the 0.45 μm filtered SM.

Contribution of diatoms in SM concentration can be easily estimated from the amount of algal cells per L and the dry weight of diatoms: in the river Marne a linear relationship between algal population and total chlorophyll may be established from data by Chesterikoff et al. (1985) during spring algal blooms with total chlorophyll > 100 $\mu g \cdot L^{-1}$:

$$\text{Total chlorophyll } (\mu g \cdot L^{-1}) = 5 \times \text{Algal population } (10^6 \text{ cell} \cdot L^{-1})$$

Furthermore in another study on the river Marne, Billen et al. (1992) assumed that 1 μg of that pigment corresponds to 0.06–0.16 mg of dry matter. These two relations give cell weights ranging from 300 to 800 $pg \cdot cell^{-1}$ which are in good agreement with diatoms dry weights from about 164 to 1,400 $pg \cdot cell^{-1}$

Table 4. Concentrations of Cu in dissolved (a) < 0.2μm, (b) < 10 KD, (c) particulate (calculated from trapped suspended-matter) and (d) colloidal (= a–b) parts, expressed in $\mu g \cdot L^{-1}$; colloidal percentage in dissolved part (e) and total chlorophyll values (f) during 'algal blooms' from May 30 to July 4, 1995. K_{Cu} concentration in < 10 KD water, expressed in $L \cdot Kg^{-1}$ (phytoplanktonic peaks are noted in bold characters).

Cu	(a)	(b)	(c)	(d)	(e)	(f)	
Dates	fraction	fraction	particulate	colloidal	%	tot.	K_{Cu}
	< 0.2 μm	< 10 KD	in digested	(a)–(b)	colloidal	chloro	
			SM (Trap)		in (a)		
	$\mu g \cdot L^{-1}$	$\mu g \cdot L^{-1}$	$\mu g \cdot g^{-1}$	$\mu g \cdot L^{-1}$	%	$\mu g \cdot L^{-1}$	$L \cdot Kg^{-1}$
05/30/95	1.70 ± 0.01	1.35 ± 0.01	91 ± 4	0.35 ± 0.02	21	71	6.77 10^{-5}
06/02/95	2.65 ± 0.03	2.11 ± 0.02	80 ± 4	0.54 ± 0.05	20	31	3.77 10^{-5}
06/06/95	1.50 ± 0.01	1.06 ± 0.01	83 ± 4	0.34 ± 0.02	23	23	7.12 10^{-5}
06/09/95	**2.07 ± 0.02**	**0.80 ± 0.01**	**60 ± 3**	**1.27 ± 0.03**	**61**	**136**	**7.54 10^{-5}**
06/13/95	2.30 ± 0.02	1.70 ± 0.01	69 ± 3	0.60 ± 0.03	26	40	4.08 10^{-5}
06/16/95	2.12 ± 0.02	1.71 ± 0.01	82 ± 4	0.41 ± 0.03	19	28	4.77 10^{-5}
06/20/95	**2.06 ± 0.02**	**1.12 ± 0.01**	**84 ± 4**	**0.94 ± 0.03**	**46**	**140**	**7.51 10^{-5}**
06/23/95	2.42 ± 0.02	1.99 ± 0.02	83 ± 4	0.43 ± 0.04	18	36	4.19 10^{-5}
06/27/95	**2.13 ± 0.02**	**0.93 ± 0.01**	**87 ± 5**	**1.20 ± 0.03**	**56**	**245**	**9.35 10^{-5}**
06/30/95	**2.26 ± 0.02**	**0.96 ± 0.01**	**77 ± 4**	**1.30 ± 0.03**	**58**	**140**	**7.97 10^{-5}**
07/04/95	2.02 ± 0.02	1.50 ± 0.01	94 ± 5	0.52 ± 0.03	26	69	6.27 10^{-5}

given in the literature (Lund 1965; Reynolds et al. 1982 and Hamilton-Taylor et al. 1984). From these results, to the increase of chlorophyll measured during algal peaks corresponds a phytoplanktonic mass which is in good agreement with SM increase measured (Table 8).

Biologic nature of SM present during algal blooms is confirmed by POC analyses. In 1995 from 62 to 95 % of POC have a biological origin at the very time of the four chlorophyll peaks (Jaïry & Chesterikoff 1997).

In 1994, a linear relationship between SM and chlorophyll pigments was determined using a linear regression. The linear coefficient is 0.235 $mg \cdot \mu g^{-1}$ (Garban & Ollivon 1995) comparable to that calculated during a study of eutrophication of the river Marne in 1991 (0.24 $mg \cdot \mu g^{-1}$ chlorophyll pigments) (Billen et al. 1992). This coefficient is a function of the algal species found in the river but it seems a little too high to result from the direct contribution of the algal biomass alone to the SM. Therefore, we may hypothesize that there is a contribution of precipitation of carbonates and/or hydroxides due to the high pH values associated with the phytoplanktonic production: values of 10 to 20 $mg \cdot L^{-1}$ of precipitated $CaCO_3$ are common in the river

Table 5. Concentrations of Mn in dissolved (a) < 0.2μm, (b) < 10 KD, (c) particulate (calculated from trapped suspended-matter) and (d) colloidal (= a–b) parts, expressed in $\mu g \cdot L^{-1}$; colloidal percentage in dissolved part (e) and total chlorophyll values (f) during ≪ algal blooms ≫ from May 30 to July 4, 1995. K_{Mn} = ratio of Mn content in trapped suspended matter to Mn concentration in < 10 KD water, expressed in $L \cdot Kg^{-1}$ (Phytoplanktonic peaks are noted in bold characters).

Mn Dates	(a) fraction < 0.2 μm $\mu g \cdot L^{-1}$	(b) fraction < 10 KD $\mu g \cdot L^{-1}$	(c) Particulate in digested SM (Trap) $\mu g \cdot g^{-1}$	(d) colloidal (a)–(b) %	(e) % colloidal in (a) $\mu g \cdot L^{-1}$	(f) tot. chloro $L \cdot Kg^{-1}$	K_{Mn}
05/30/95	10.0 ± 0.1	4.00 ± 0.04	542 ± 27	6.00 ± 0.14	60	71	13.6 10^{-5}
06/02/95	17.4 ± 0.2	9.48 ± 0.09	477 ± 24	7.94 ± 0.29	46	31	5.03 10^{-5}
06/06/95	11.3 ± 0.1	10.6 ± 0.1	586 ± 29	0.71 ± 0.20	6	23	5.52 10^{-5}
06/09/95	**10.2 ± 0.1**	**3.90 ± 0.04**	441 ± 22	**6.34 ± 0.14**	**62**	**136**	**11.3 10^{-5}**
06/13/95	18.4 ± 0.2	11.4 ± 0.11	556 ± 28	6.90 ± 0.31	38	40	4.85 10^{-5}
06/16/95	14.5 ± 0.1	13.3 ± 0.13	520 ± 26	1.20 ± 0.23	8	28	3.92 10^{-5}
06/20/95	**9.0 ± 0.1**	**4.5 ± 0.04**	546 ± 27	**4.50 ± 0.14**	**50**	**140**	**12.1 10^{-5}**
06/23/95	16.1 ± 0.2	11.5 ± 0.11	599 ± 30	4.62 ± 0.31	29	35	5.20 10^{-5}
06/27/95	**9.1 ± 0.1**	**3.46 ± 0.03**	618 ± 30	**5.61 ± 0.13**	**62**	**245**	**17.9 10^{-5}**
06/30/95	**13.5 ± 0.1**	**8.76 ± 0.09**	**513 ± 26**	**4.67 ± 0.19**	**35**	**140**	**5.86 10^{-5}**
07/04/95	28.3 ± 0.3	3.74 ± 0.04	573 ± 29	24.5 ± 0.3	87	68	15.3 10^{-5}

Table 6. Distribution of Cu and Mn mean percentages in each phase: < 10 KD, colloidal and particulate during 'algal blooms' period according to total chlorophyll values: *(a)*: < 50 $\mu g \cdot L^{-1}$, *(b)*: > 50 $\mu g \cdot L^{-1}$. The evolution is the difference between *(b)* and *(a)* values: it shows that 'truly dissolved' Cu and Mn decrease during algal growth meanwhile colloidal and particulate metals increase.

	Truly dissolved % of total	Colloidal % of total	Particulate (trapped SM) % of total
Cu (Chloro < 50 $\mu g \cdot L^{-1}$) $^{(a)}$	50	13	37
Cu (phytoplanctonic blooms) $^{(b)}$	23	29	48
(evolution) $^{(b-a)}$	*(−27)*	*(+16)*	*(+11)*
Mn (Chloro < 50 $\mu g \cdot L^{-1}$) $^{(a)}$	47	18	35
Mn (phytoplanctonic blooms) $^{(b)}$	21	22	57
(evolution) $^{(b-a)}$	*(−26)*	*(+4)*	*(+22)*

Table 7. Correlation coefficient (r) between particulate metal concentrations (determined after 'aqua regia' digestion of trapped SM and calculated in $\mu g \cdot L^{-1}$), SM and discharge in river Marne, in (a) flood period, from April 14 to May 9 1995 and during (b) 'algal blooms' period from May 30 to July 4, 1995 (r values > 0.8 are noted in bold characters, negative r values are in italics).

a–r values, $n = 7$ (flood period, from April 14 to May 9, 1995)

	Cr	Cu	Fe	Mn	Ni	Pb	Zn	SM
Cr	1							
Cu	**0.96**	1						
Fe	**0.98**	**0.99**	1					
Mn	**0.98**	**0.99**	**1.00**	1				
Ni	**1.00**	**0.95**	**0.98**	**0.98**	1			
Pb	**0.97**	**0.97**	**0.96**	**0.96**	**0.97**	1		
Zn	**0.98**	**0.99**	**0.99**	**0.99**	**0.97**	**0.98**	1	
SM	**0.99**	**0.98**	**1.00**	**1.00**	**0.99**	**0.96**	**0.98**	1
Discharge	**0.85**	0.79	**0.84**	**0.83**	**0.86**	0.75	0.78	**0.87**

b–r values, $n = 11$ (phytoplanktonic blooms period, from May 30 to July 4, 1995)

	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Tot. Chloro	SM
Cr	1								
Cu	**0.81**	1							
Fe	**0.84**	**0.92**	1						
Mn	**0.87**	**0.96**	**0.98**	1					
Ni	**0.98**	0.72	0.74	0.78	1				
Pb	0.55	0.67	**0.80**	0.79	0.45	1			
Zn	0.72	**0.92**	**0.82**	**0.89**	0.67	0.69	1		
Tot. Chloro	**0.83**	**0.85**	**0.87**	**0.87**	0.77	0.64	0.74	1	
SM	0.74	**0.89**	**0.95**	**0.94**	0.64	**0.82**	**0.84**	**0.90**	1
Discharge	*−0.17*	*−0.10*	*−0.20*	*−0.21*	*−0.07*	*−0.35*	*0.07*	*−0.09*	*−0.10*

Loire (Meybeck et al. 1988). Besides, secondary phenomena of adsorption on biological membranes or emission of complexing products causing the production of 'flocks' cannot be excluded (Mouchet 1986).

In contrast, over the whole set of samples taken in the river Marne at its confluence in June 1995, outside the high-flow periods, the relationship SM/chlorophyll pigments established by the linear regression equation was compatible with a phytoplanktonic contribution alone, a significant correla-

Table 8. Δ chloro is the increase in total chlorophyll during 3 algal peaks in 1995; N is calculated from relation: N cells = chlorophyll/5 from Chesterikoff *et al.* (1985); phytoplanktonic cell weight (PCW) is calculated from diatoms weight ranging from 300 to 800 pg·cell^{-1} and N cells; Δ SM is the increase of suspended matter at the same date.

Dates	Δ chloro	N	PCW phytoplanktonic cell weight	Δ SM
	μg·L^{-1}	cells·L^{-1}	mg·L^{-1}	mg·L^{-1}
06/09/95	114	22.8 10^6	6.8–18.2	10.2
06/20/95	112	22.4 10^6	6.7–17.8	9.9
06/27/95	210	42 10^6	12.5–33.5	16.4

tion ($r = 0.89$, $n = 12$, $P < 0.001$) was found between the two parameters, with a linear coefficient of 0.073 mg·μg^{-1} of chlorophyll pigments. This coefficient was in the same order of magnitude as those calculated from steady state measurements in the river Marne upstream of Trilport in 1982 (0.096) (Chesterikoff et al. 1983), and in the river Seine at Porcheville in 1990 (0.075) (Chesterikoff et al. 1990).

During the period from 05/30/95 to 07/04/95, variations in SM concentration seemed due mainly to variations in phytoplanktonic concentration, and had no connection with the small fluctuations in flow. In fact, during the bloom period, the correlation coefficient r between SM and chlorophyll was 0.90 ($n = 11$, $P < 0.001$). However, there was no correlation between SM and flow ($r = -0.10$; $n = 11$), in contrast to the high-flow period between 04/14 and 05/09 when SM had an allochtonous detrital origin ($r = 0.87$; $n = 8$, $P < 0.01$). Whereas, particulate metals correlated with flow and SM during this high-water period but, during the bloom period, they correlated with chlorophyll and SM, and no more with the flow rates (Table 7).

The highly significant correlations between pH and chlorophyll ($r = 0.92$; $n = 8$, $P < 0.001$), pH and SM ($r = 0.97$; $n = 8$, $P = < 0.001$) and chlorophyll and SM ($r = 0.93$; $n = 8$, $P < 0.001$) confirmed the link between these parameters (Table 9). During phytoplanktonic blooms from 06/06 to 06/30/95 pH was modified and SM increase was accompanied by an increase of the particulate metal content.

Phytoplanktonic development consumes the dissolved carbon dioxide in the water, and thus causes a significant increase in pH (Chesterikoff et al. 1991; Wolf et al. 1988, cited by Bubb & Lester 1991) and the influence of pH on the adsorption of metals on particulate phase is now widely accepted in the literature (Sigg 1987; Tessier et al. 1989; Tessier et al. 1990; Serpaud

Table 9. Correlation coefficient (r) between Cu concentrations in different parts, but particulate, and SM, total chlorophyll and POC during 'algal blooms' period from June 6 to 30, 1995. Idem for Mn (r vales > 0.8 are noted in bold characters, negative r values are in italics – $n = 8$).

$n = 8$	SM	Tot. Chloro	POC	Cu < 0.2 μm	Cu < 10 kD	Cu colloid.
SM	1					
Tot. Chloro	**0.93**	1				
POC	0.73	0.66	1			
Cu < 0.2 μm	*−0.03*	0.13	*−0.56*	1		
Cu < 10 KD	*−0.79*	*−0.73*	***−0.83***	0.41	1	
Cu colloidal	**0.82**	**0.87**	0.52	0.23	*−0.79*	1
pH	**0.97**	**0.92**	0.65	0.08	*−0.69*	0.79

$n = 8$	SM	Tot. Chloro	POC	Mn < 0.2 μm	Mn < 10 kD	Mn colloid.
SM	1					
Tot. Chloro	**0.93**	1				
POC	0.73	0.66	1			
Mn < 0.2μm	*−0.76*	*−0.69*	***−0.95***	1		
Mn < 10 KD	***−0.96***	***−0.88***	***−0.81***	**0.82**	1	
Mn colloidal	0.50	0.49	*−0.04*	0.09	*−0.49*	1
pH	**0.97**	**0.92**	0.65	*−0.74*	***−0.91***	0.46

et al. 1994; Eyrolle et al. 1993). Admiraal et al. (1995) results support that statement on manganese partition in the river Rhine. They showed that, during the algal blooms, manganese was essentially in particulate form (> 0.45μm), and suggested that phytoplanktonic synthesis, by its increase in pH, favoured the manganese precipitation in the river.

Classically, the separation threshold between the particulate and the dissolved phases is fixed as 0.45 μm, and increasingly often 0.22 μm, but we have shown that the dissolved fraction contains a major proportion of colloidal material. In our study using tangential ultrafiltration we could catch the 'truly dissolved' phase < 10 KD in which we analyzed copper and manganese. This enabled us to calculate distribution coefficient K_{metal} respectively between the particulate phase and the dissolved fraction < 10 KD.

$$K_{metal} = \frac{mental\ content\ (trapped\ SM)}{metal\ concentration\ (<\ 10\ KD)} = \frac{\mu g \cdot Kg^{-1}}{\mu g \cdot L^{-1}} = L \cdot Kg^{-1}$$

Table 10. Correlation coefficient (r) between the distribution coefficients K_{Cu} and K_{Mn} and total chlorophyll, pH and particulate organic carbon (POC) calculated during the 'algal blooms' period from June 9 to June 30, 1995 (K_{metal} = ratio of metal content in trapped suspended matter to concentration in < 10 KD water)(r values for $n = 7$).

r values	$n = 7$			r values	$n = 7$		
	K_{Cu}	tot.chloro	pH		K_{Mn}	tot.chloro	pH
K_{Cu}	1.00			K_{Mn}	1.00		
Tot.chlorophyll	0.97	1.00		Tot.chlorophyll	0.91	1.00	
pH	0.88	0.91	1.00	pH	0.95	0.91	1.00
POC	0.90	0.93	0.99	POC	0.95	0.93	0.99

K_{Cu} and K_{Mn} are calculated from respective values in Tables 4 and 5.

Maxima values are obtained during algal blooms.

For the period from 06/09/95 to 06/30/95, we obtained highly significant correlations between these distribution coefficients K_{Cu} and K_{Mn} and chlorophyll, pH and POC, confirming the role of algae and pH in the partition of these metals (Table 10).

In consequence, we were able to verify that at the time of algal peaks there was a decrease in the 'truly dissolved' concentration (reduction of 54% of truly dissolved Cu compared to concentrations outside bloom periods and 55% reduction for Mn) (Figure 7 and 8).

By studying algal activity, we obtained different distributions between the particulate (trapped), colloidal and 'truly dissolved' phases. Moreover, the distribution between the three phases was different for Cu and Mn. Increase of colloidal fraction was four times greater for Cu than for Mn (Table 6).

From data presented in Tables 1, 2, 4 and 5, correlation matricies (Table 9) show that during phytoplanktonic blooms, colloidal form of Cu was associated with algae ($r = 0.87$; $n = 8$, $P < 0.01$) and pH ($r = 0.79$, $n = 8$, $P < 0.05$), whereas for Mn there was no significant correlation of colloidal form with chlorophyll but an inverse correlation of the 'truly dissolved' Mn (< 10 KD) with chlorophyll ($r = -0.88$; $n = 8$, $P < 0.01$) and pH ($r = -0.91$; $n = 8$, $P < 0.01$). During these high algal growth periods when pH increases, it seemed that manganese was associated with macroparticles, pH variation being decisive in this state change. Copper was more associated with colloids, thus to the fine colloidal biological particles directly associated with phytoplankton. This study has enabled us to demonstrate the impact of the algal growth. Concerning increase in metal concentrations in particulate and colloidal phases during phytoplanktonic peaks, it is an expression of the important role played by this biological phenomenon in the transfer of metallic micropollutants and their settling.

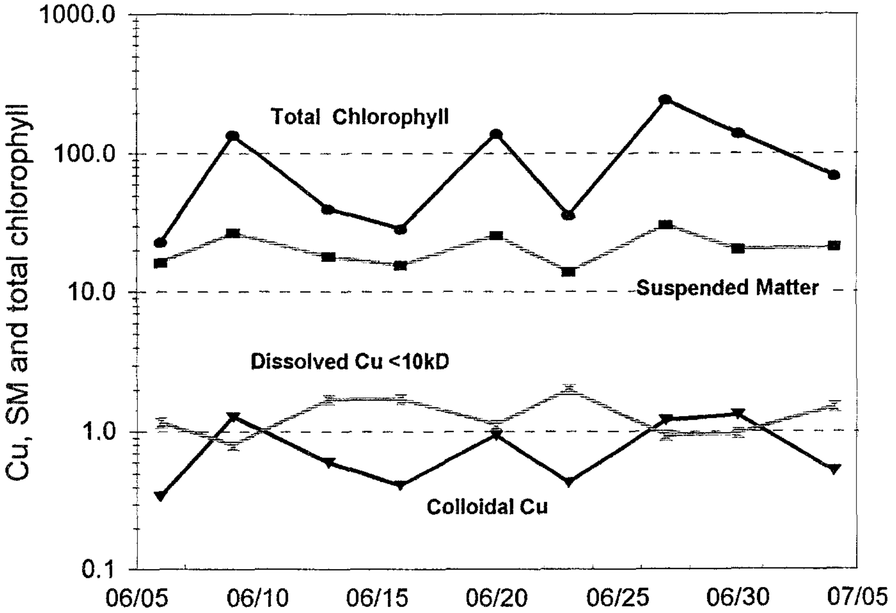

Figure 7. (✕) Truly dissolved (< 10 KD) copper, (-▼-) colloidal copper, (-■-) SM and (-●-) total chlorophyll concentrations in the river Marne at St Maurice dam, during phytoplanktonic blooms from June 6 to July 4, 1995, displayed on logarithmic scale.

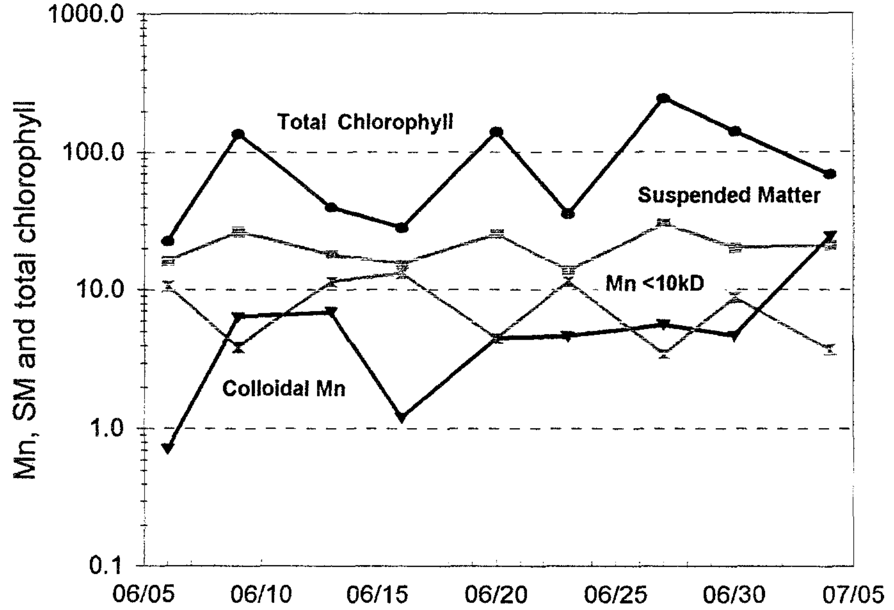

Figure 8. (✕) Truly dissolved (< 10 KD) manganese, (-▼-) colloidal manganese, (-■-) SM and (-●-) total chlorophyll in the river Marne at St Maurice dam, during phytoplanktonic blooms from June 6 to July 4, 1995, displayed on logarithmic scale.

The importance of the colloidal fraction in the metal transport has been shown. The role of pH is determinative in the precipitation of metals, but contribution of direct assimilation by algae remains to be investigated. This is very specific of the metal precised, as demonstrated by differences in distribution of the copper and manganese between the phases studied. Research in hand on the organic forms of these metals in the different phases should clarify their respective affinities.

Acknowledgements

This work was supported by grants from the PIREN-Seine Research Programme of the CNRS (France). We would like to thank the Service de la Navigation de la Seine for giving us access to field sites.

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