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Seasonal variations of nutrients (NO_3^-, NO_2^-, NH_4^+, PO_4^{3-} and $Si(OH)_4$) and suspended matter in the Rhone delta, France

Nutrients
Suspended matter
Particulate organic carbon
Rhone delta
Mediterranean Sea

Nutriments
Matière en suspension
Carbone organique particulaire
Delta du Rhône
Mer Méditerranée

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ABSTRACT

Nutrient concentrations studied in the upstream Rhone delta showed very different variations according to the season and to the nutrient considered. Nitrate and silicate varied by a factor of 1.6, whereas phosphate and total dissolved phosphorus varied within a wider range, by a factor of 2.1-2.6. The largest variations were observed for ammonia whose concentration varied from 0.011 $mg\,l^{-1}$ in November 1984 to 0.180 $mg\,l^{-1}$ in February 1985. Nutrient concentrations were highest in winter and decreased in spring. In February and the beginning of May 1985 the behaviour of nutrients was practically conservative in the delta, from the river to marine waters. A slight nutrient deficit was observed for low salinity waters for other seasons. An estimation of the annual input of nitrogen/nitrate ($N-NO_3^-$) discharged by the Rhone river was determined from a re-examination of previous data; it was approximately 7.5×10^4 metric tons/year. Rhone river waters showed suspended matter concentrations varying in the range 7-62 $mg\,l^{-1}$. Higher values occurred in October and in November, corresponding to higher river flow values (>2 000 $m^3\,s^{-1}$) due to autumn mediterranean rains. The relationship between suspended matter and particulate organic carbon, expressed in percentage of particulate matter was similar to that observed for most world rivers.

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RÉSUMÉ

Variations saisonnières des éléments nutritifs [NO_3^-, NO_2^-, NH_4^+, PO_4^{3-} et $Si(OH)_4$] et des matières en suspension dans le delta du Rhône

L'étude des variations saisonnières des éléments nutritifs dans la partie amont du delta du Rhône montre des amplitudes de fluctuation très différentes selon l'élément considéré. Alors que les nitrates et la silice montrent une faible amplitude de variation d'un facteur 1,6, les phosphates et le phosphore total dissous varient dans une gamme plus importante (2,1 – 2,6). L'ammonium fluctue plus largement, de 0,011 mg/l en novembre 1984 à 0,180 mg/l en février 1985. Dans l'ensemble les concentrations des éléments nutritifs sont maximales en hiver, puis chutent au printemps. En février et début mai 1985, le comportement des éléments nutritifs, dans le delta et son débouché en milieu marin, est pratiquement conservatif. Un léger déficit est observé pour les autres campagnes pour les eaux de faible salinité. Pour ces années 1984-1985, l'apport en azote/nitrate ($N-NO_3^-$) du Rhône à la Mer Méditerranée serait de $7,5 \times 10^4$ t par an. Le Rhône se situe dans la moyenne des fleuves mondiaux quant à la relation existant entre les matières en suspension et le carbone organique particulaire, exprimé en pourcentage des suspensions. Les teneurs en matières en suspension observées dans le fleuve varient dans une large gamme (7-62 mg/l). Les fortes valeurs rencontrées en octobre et novembre 1984 correspondent à de forts débits du fleuve, associés aux pluies méditerranéennes automnales.

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INTRODUCTION

Although the Mediterranean Sea is a semi-enclosed area, it is considered a good model for studying biogeochemical cycles. The northwestern basin has been the subject of assessment of budget of different chemical species such as nutrients (Bethoux, 1981). In the last few years, several programs have studied the biogeochemistry of the northwestern basin and focused on the impact of inputs from rivers and from the atmosphere (Programs Pelagolion, Écomarge, Dyfamed, Greco Ico, Eros 2000). In this context the Rhone river, which is the largest river entering the Mediterranean Sea, plays a major role in terms of inputs of water, dissolved material and suspended matter originating from natural and anthropogenic riverine and atmospheric mobilization and remobilization of solid materials deposited as sediments into the northwestern basin.

A few previous analyses of nutrients have been performed in the Rhone river by Coste and Minas (1967), Blanc *et al.* (1969), Coste (1974), Coste *et al.* (1977) and Coste *et al.* (1984). In order to complete budgets of matter entering the Mediterranean Sea through the Rone river, we present a study of seasonal variations of nutrients and suspended matter. This study was performed in the river itself and in the Rhone delta to assess the pathway of nutrients within the salinity gradient at some five key hydrological periods.

MATERIAL AND METHODS

Sampling sites

Since the erection of the Assouan dam on the Nile river, the Rhone river has become the major river entering the Mediterranean Sea, with an average annual water flow of 1 570 $m^3 s^{-1}$. It enters the sea through a complex deltaic system, the left branch of which (or Grand Rhone) collects approximately 90 % of the total Rhone flow. The hydrological regime of the river is mainly influenced by: *a*) rains of oceanic origin, predominating from January to March; *b*) waters originating from the melting of alpine ice-fields, leading to spring high waters; *c*) rains of mediterranean origin, occurring roughly from October to December, bringing large and sudden variations of the river flow.

Five sampling cruises were carried out from October 1984 up to May 1985 (Fig. 1). This permitted collection of samples belonging to different key hydrological periods (Tab. 1). For example, the water flow varied from 1300 $m^2 s^{-1}$ in May 1985 to 2431 $m^3 s^{-1}$ in November 1984.

Analytical methods

Nutrients

The water was filtered through pre-combusted glass fibre Whatman GF/F filters (0.7 µm pore size) and kept at T<4°C after addition of chloroform. Nutrient determination was carried out in the land-based laboratory within a few days. References for methods, limits of detection and precision are reported in Table 2.

Suspended matter (SM), particulate organic carbon (POC)

These parameters were measured on particulate matter collected from the filtration of water through pre-combusted Whatman GF/F glass fibre filters, rinsed several times with distilled water. SM was determined by weighing the filters before and after filtration. POC was measured after decarbonation of particulate matter by phosphoric acid using a Leco analyzer.

RESULTS AND DISCUSSION

Nutrients in the river

Nutrient data obtained in the riverine zone are given in Table 3. The riverine station corresponds to the minimum salinity value encountered, here less than 33 mg l^{-1}. The position of this station varies between Barcarin and Port Saint Louis du Rhone (Fig. 1),

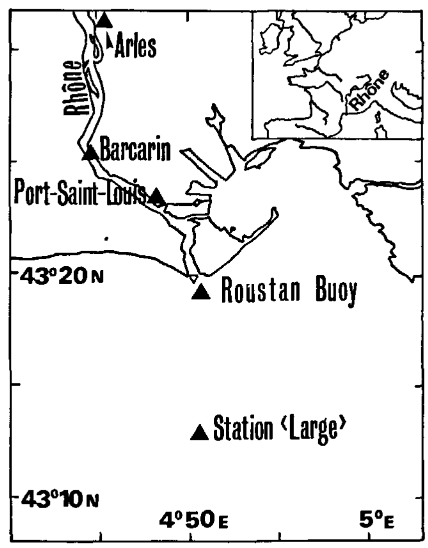

Figure 1
Rhone delta; location of sampling sites.
Carte des stations de prélèvements occupées dans le delta du Rhône en 1984-1985.

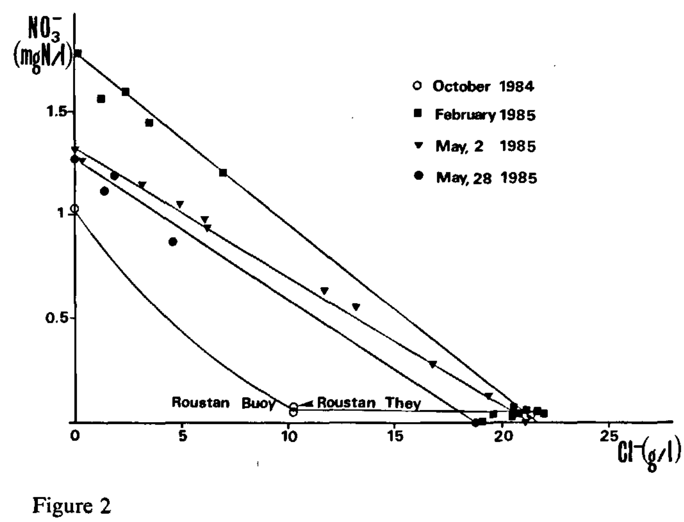

Figure 2
Relationship between nitrate ($N-NO_3^-$) and chlorinity.
Relation entre nitrates ($N-NO_3^-$) et chlorinité.

Table 1

General characteristics of the five sampling cruises carried out in the Rhone delta in the period 1984-1985: date, river flow and characteristics of reference riverine and marine stations.

Caractéristiques des cinq campagnes de prélèvement réalisées en 1984-1985 dans le delta du Rhône : date, débit du fleuve, propriétés de la station fluviale et de la station marine étudiées.

Sampling cruise	River flow ($m^3 s^{-1}$)	Riverine station pk (km)	Riverine station Cl^- (mg/l)	Riverine station T°C	Marine station pk (km)	Marine station Cl^- (g/l)	Marine station T°C
October 3-4, 1984	2 134-2 332	Barcarin 316	33.0	14.9	Roustan buoy 332	21.5	-
November 29, 1984	2 431	Barcarin 316	18.5	10.3	River mouth 330	0.024 5	10.9
February 23-25, 1985	1 570-1 285	Barcarin 316	18.8	4.2	Station "large" 342	20.86	11.5
May 2, 1985	1 300	Port Saint Louis 318.5	19.2	13.9	Roustan buoy 332	21.0	12.6
May 28, 1985	1 760	Port Saint Louis 320	23.8	17.0	Roustan buoy 331.5	17.8	17.5

pk: kilometric point: distance from the city of Lyon.
Cl^-: chlorinity.
T°C: temperature.

Table 2

Characteristics of analytical methods used for the determination of nutrients.

Caractéristiques des méthodes de dosage employées pour la détermination des éléments nutritifs

Nutrient	Reference	Limit of detection (mgl^{-1})	Precision %	for a concentration of ($-mg\,l^{-1}$)
NO_3^-	*E-P-A	0.001 (N)	5	0.5 (N)
NO_2^-	Reference AFNOR T90013 11/1985	0.001 (N)	10	0.010 (N)
NH_4^+	Reference AFNOR T90015 08/1975 (indophenol method)	0.002 (N)	5	0.100 (N)
P_{ortho}	Reference AFNOR T90023 09/1982	0.001 (P)	3	0.100 (P)
P_{total}	Reference AFNOR T90023 09/1982 (mineralisation persulfate)	0.002 (P)	5	0.100 (P)
$Si(OH)_4$	Industrial Method No. 7-68W	0.02 (Si)	5	1.0 (Si)

*E-P-A: Methods for chemical analysis of water and wastes. Environmental Protection Agency, 1971. Cincinnati, Ohio, USA.

Table 3

Chemical characteristics of Rhone river surface waters collected at the riverine reference station in the period 1984-1985: Cl^-: chlorinity; NO_3^-: nitrate; NO_2^-: nitrite; NH_4^+: ammonia; PO_4^{3-}: phosphate; P: total phosphorus; $Si(OH)_4$: silicate; n.d.: not determined.

Caractéristiques physico-chimiques des eaux du Rhône collectées au point fluvial lors des prélèvements réalisés en 1984-1985: Cl^-: chlorinité; NO_3^-: nitrates; NO_2^-: nitrites; NH_4^+: ammoniac; PO_4^{3-}: phosphates; P: phosphore total; $Si(OH)_4$: silice; n.d.: non déterminé.

Riverine reference Station	Cl^- (mgl^{-1})	NO_3^- ($mgNl^{-1}$)	NO_2^- ($mgNl^{-1}$)	NH_4^+ ($mgNl^{-1}$)	PO_4^{3-} ($mgPl^{-1}$)	Total P ($mgPl^{-1}$)	$Si(OH)_4$ ($mgSil^{-1}$)
Barcarin 4.10.84	33.00	1.04	n.d.	0.050	0.068	n. d.	1.40
Barcarin 29.11.84	18.50	1.86	n. d.	0.011	0.205	0.209	1.53
Barcarin 25.02.85	18.80	1.87	0.018	0.180	0.146	0.150	2.27
Port St Louis 2.05.85	19.20	1.29	0.019	0.065	0.148	0.152	1.41
Port St Louis 28.05.85	23.80	1.24	0.017	0.058	0.092	0.098	1.72

according to the river flow. These data lead to the following comments: seasonal variations show very different ranges from one nutrient to another. Nitrite shows fairly constant and low concentrations representing less than 1.5 % of nitrogen/NO_3^-. Nitrate and silicate show a narrow seasonal variation range, characterized by factors of 1.60 and 1.65 respectively. Phosphate and total phosphorus have a wider variation range (2.13-2.56). Ammonia has the widest variation range, from $0.011\ mg\,l^{-1}$ in November 1984 up to $0.180\ mg\,l^{-1}$ in February 1985, corresponding to a factor of 16.

With the exception of nitrite, nutrients exhibit higher concentrations in winter, followed by a decrease in spring.

Pathway of nutrients in the Rhone river delta

In order to study the fate of nutrients during freshwater/seawater mixing where strong chemical gradients should control how and at what rate nutrients are transported to the sea, other samples were collected and analyzed from the riverine reference station up to the river mouth (Roustan They), to Roustan Buoy or even to station "Large", 12 km off the river mouth (corresponding to a chlorinity$>18\ g\,l^{-1}$).

Figures 2, 3 and 4 show the variations of nitrate, phosphate and silicate concentrations as a function of chlorinity. With respect to the extreme riverine and marine reference points, nitrate shows a conservative pathway during the mixing process in May 2, 1985

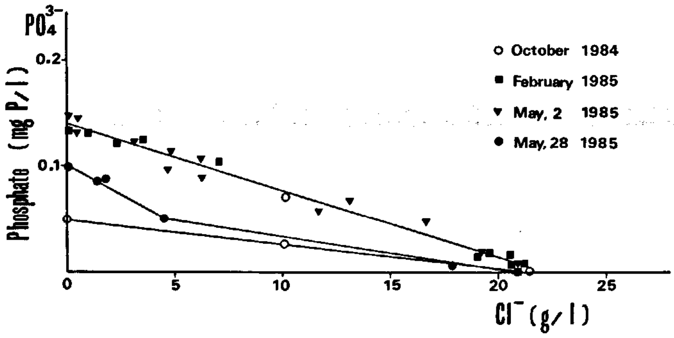

Figure 3
Relationship between phosphate ($P-PO_4^{3-}$) and chlorinity.
Relation entre phosphates ($P-PO_4^{3-}$) et chlorinité.

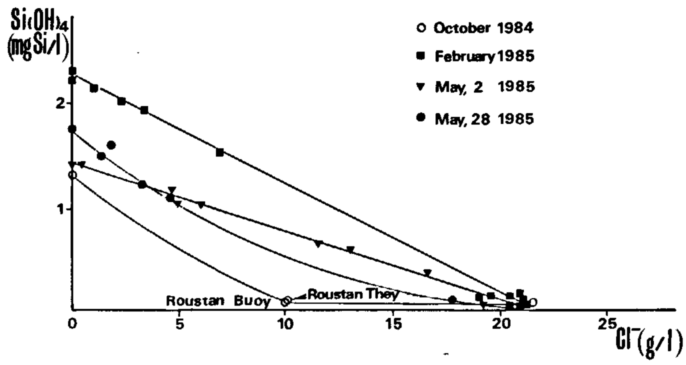

Figure 4
Relationship between silicate ($Si-Si(OH)_4$ and chlorinity.
Relation entre silice ($Si-Si(OH)_4$) et chlorinité.

through the whole chlorinity range and, in February 1985, so far as measurements are available, through the chlorinity range 0-7 $g\,l^{-1}$. In contrast, data obtained at the end of May 1985 and in October 1984 suggest a loss in nitrate in the low chlorinity range resulting from uptake reactions related to other processes other than mixing, such as uptake by deltaic biota or removal to the sediment interface.
A reasonable number of points in the 0-20 $g\,l^{-1}$ chlorinity range suggests a conservative pathway for phosphate in February and beginning of May with a close value observed for the slope of the two mixing curves. The limited number of samples obtained for other cruises in the medium chlorinity range does not permit conclusions concerning a conservative pathway. A slight deficit is observed at the end of May 1985 in the 0-5 $g\,l^{-1}$ chloronity range, as previously observed for nitrate. The same trends are encountered for silicate.
These data confirm previous observations by Blanc *et al.* (1969) and Coste *et al.* (1977) suggesting a quasi-conservative behaviour of nutrients in the Rhone delta. Chlorophyll *a* concentrations were slightly higher at the end than at the beginning of May 1985 (3.2-19.4 $\mu g\,l^{-1}$ in the river, 2.5-10.5 $\mu g\,l^{-1}$ in marine waters and 0-6 $\mu g\,l^{-1}$ in the river; 1.9-4.3 $\mu g\,l^{-1}$ in marine waters respectively). The higher biological activity revealed by the chlorophyll *a* and total pigment concentrations encountered at the end of May, indicators of the pressure of the biological utilization of primary nutrients, N, P, Si (Sharp *et al.*, 1984; Church, 1986) could explain the change of behaviour of nutrients leading to the observed deficit, whereas chlorophyll *a* concentrations are in the same range in October 1984 (0.8-1.6 $\mu g\,l^{-1}$ in the river; 1.6 $\mu g\,l^{-1}$ in marine waters) and in February 1985 (0-1.9 $\mu g\,l^{-1}$ in the river; 0-1.6 $\mu g\,l^{-1}$ in marine waters).
A tentative assessment of the Rhone river inputs to the Mediterranean Sea necessitates considering chemical species concentrations as a function of river discharge at a given time point. A serious difficulty here is the great variability of the river flow as measured on a daily, weekly, or monthly basis. Such a budget has been established by Coste in 1974 for Rhone inputs of nitrate and phosphate for the year 1968. This period was characterized by more marked seasonal variations than those observed by Parde (1925) over forty years. Comparing values obtained for nitrate during the five periods sampled with those reported by Coste shows that our values are higher by 26 % in February, by 55 % in November, the yearly average being 40 % higher. This suggests that during the period 1984-1985 where river discharge values were similar in winter and in spring but higher in autumn than mean values over a 40-year period, the annual input of the Rhone river in nitrogen/nitrate ($N-NO_3^-$) could be estimated at a 40 % higher level than that evaluated by Coste, *i.e.*, approximately 7.5×10^4 metric tons $N-NO_3^-$.
Phosphate concentrations are approximately twice those reported by Coste (1974). The comparison here is only possible for three months and does not allow any yearly extrapolation. Nevertheless, it could be possible to use the mean value of N/P atomic ratios from concentrations in nitrate and phosphate as shown in Table 3. This gives a ratio of 26:5 with a coefficient of variation of 25 %. According to this hypothesis, the tentative evaluation of annual phosphate input would be 6.45×10^3 metric tons $P-PO_4^{3-}$. This estimation is 35 % higher than that proposed by Coste in 1974: 4.8×10^3 tons $P-PO_4^{3-}$. We can note that the value of the N/P atomic ratios, 26:5, is close to that given by Coste (1974) (25:6) with a coefficient of variation of 55 % and to that given by McGill (1965), 23:4 with a coefficient of variation of 15.2 % for the Ligurian Sea.

Suspended matter and particulate organic carbon

Riverine waters show suspended matter concentrations varying from 7 $mg\,l^{-1}$ at the beginning of May 1985 up to 62 $mg\,l^{-1}$ in November 1984, as measured at the riverine reference station (Tab. 4). High values encountered in October and in November correspond to higher flow values ($>2\,000\ m^3\,s^{-1}$), associated with autumnal mediterranean rains. Suspended matter concentrations of surface waters show generally slight variations in the river between Barcarin and waters influenced by dilution with seawater (chlorinity $> 1\ g\,l^{-1}$). These variations illustrated in Figure 5 are as follows: *a*) 23-34 $mg\,l^{-1}$ (mean $= 29 \pm 17$ %) in October 1984; at this season much higher concentrations, up to 84 $mg\,l^{-1}$ have been observed between Arles and pK 310, probably related to local influences such as

Table 4

Chemical characteristics of Rhone river surface waters collected at the riverine reference station in the period 1984-1985; SM: suspended matter in mgl^{-1}; POC: particulate organic carbon; POC/SM (%): percentage of suspended matter in organic carbon; Chl a: chlorophyll a in μgl^{-1}.

Caractéristiques chimiques des eaux du Rhône collectées au point fluvial lors des prélèvements réalisés en 1984-1985; SM : matières en suspension en mgl^{-1}; POC : carbone organique particulaire; POC/SM (%) : pourcentage des matières en suspension en carbone organique; Chl *a* : chlorophylle *a* en μg/l.

Riverine reference Station	SM (mg/l)	POC (mgC/l)	POC/SM (%)	Chl *a* (μg/l)
Barcarin 4.10.84	23.0	0.68	2.96	1.60
Barcarin 29.11.84	62.0	2.96	4.75	12.30
Barcarin 25.02.85	12.6	1.01	8.05	1.04
Port St Louis 2.05.85	7.0	0.41	5.75	0
Port St Louis 28.05.85	16.0	0.74	4.49	3.64

erosion of river banks or inputs from human activities; *b*) 42-68 mg l^{-1} (mean: 55±23 %) in November 1984; *c*) 11-13 mg l^{-1} (mean: 12±10 %) in February 1985; *d*) 6-8 mg l^{-1} (mean: 7±15 %) in early May 1985 and *e*) 11-25 mg l^{-1} (mean: 18±42 %) in last May 1985.

Suspended matter concentrations measured at the Roustan Station are slightly higher than those observed in the river itself. This could be easily explained by intense mixing of surface and bottom waters and resuspension of fine sediments at the river mouth by strong winds such as the Mistral. Bottom waters in the river are characterized by higher suspended matter loads than observed in surface waters. The increase of suspended matter load in bottom water varies between 1.5 and 2.5 for all samples with the exception of early May, where a remarkable stratification of waters is observed, leading to very turbid bottom waters. The maximum increase observed is 7.4.

Higher values of particulate organic carbon (POC), >1.5 mg l^{-1}, are also observed in autumn. POC can be expressed as a percentage of the suspended material. This percentage varies from 4.49 % at the end of May

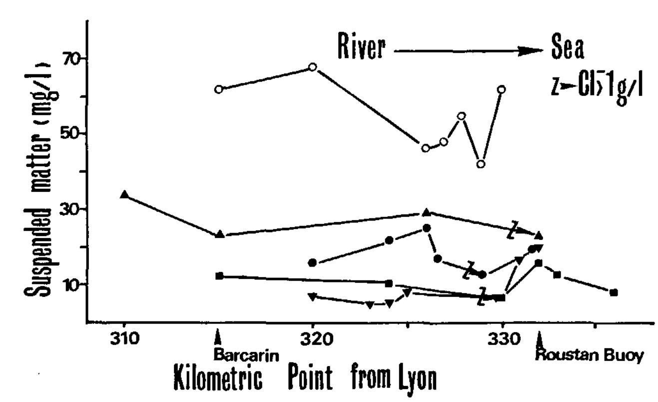

Figure 5

Distribution of suspended matter concentrations in the Rhone delta as a function of pk, kilometric point, i.e. *distance from Lyon.*

Répartition des concentrations en matières en suspension dans le delta du Rhône, en fonction du point kilométrique compté à partir de Lyon (pk).

to 8.05 % in February, whereas this percentage has been found to vary in the range 0.5-40 % for lowland rivers worldwide (Meybeck, 1982). Figure 6 illustrates the relationship between suspended matter load and organic carbon content in suspended matter (POC in %). Variation of POC content results, as in most large rivers, from two opposite trends: the decrease of POC % with suspended matter load and the increase of suspended matter with water discharge, the latter process being dominant.

The Rhone river belongs to the mean variation range of POC % versus suspended matter relationship as determined for world rivers by Meybeck (1982). As an exception, note that values representative of marine waters collected in February 1985 are outside the mean variation range window. This is not surprising as the mean variation range window has been established from river waters and not from coastal marine waters. The existence of a relation between suspended matter POC content and suspended matter load could help in evaluating transport budgets for different organic chemical species associated mainly with suspended matter such as hydrocarbons or pesticides (Marchand *et al.*, 1986; Saliot *et al.*, in press) using the suspended matter concentration, a routinely determined parameter in most river monitoring programs.

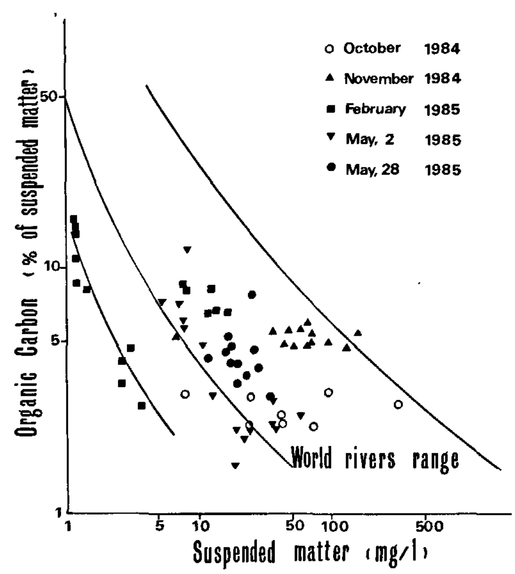

Figure 6

Relationship between organic carbon as a percentage of suspended matter and suspended matter concentration.

Relation entre le carbone organique exprimé en pourcentage des matières en suspension et la concentration en matières en suspension.

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