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Nutrients (Organic C, P, N, Si) in the Eutrophic River Loire (France) and its Estuary

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The Loire estuary has been surveyed from 1982 to 1985 by 13 isochronous longitudinal profiles realized at low tide. Nutrient (SiO_2, NO_3^-, NH_4^+, PO_4^{3-}, particulate organic carbon or POC) patterns are very variable depending on the season, the estuarine section [river, upper-inner estuary, upstream of the fresh-water–saline-water interphase FSI, the lower-inner estuary characterized by the high turbidity zone (HTZ), the outer estuary] and the river discharge. Biological processes are dominant. In the eutrophied River Loire (summer pigment $> 100\ \mu g\ l^{-1}$), the high algal productivity (algal POC $> 3\ mg\ l^{-1}$) results in severe depletion of SiO_2, PO_4^{3-}, NO_3^-. The enormous biomass (55 000 ton algal POC/year) is degraded in the HTZ where bacterial activity is intense. As a result, there is generally a regeneration of dissolved SiO_2 and PO_4^{3-}, a marked NH_4^+ maximum, while NO_3^- is conservative or depleted when the HTZ is nearly anoxic. Other processes can be considered including pollution from fertilizer plans (PO_4^{3-}, NH_4^+) and from a hydrothermal power plant (NH_4^+). In the less turbid outer estuary, nutrients are generally conservative. Major variations of concentrations are observed in the lowest chlorinity section ($Cl^- < 1\ g\ kg^{-1}$) and also upstream the FSI, defined here as a 100% increase in Cl^-. Nutrient inputs to the ocean are not significantly modified for SiO_2 and NO_3^-, but are increased by 70% and 180% for PO_4^{3-} and NH_4^+ and depleted by 60% for POC. Odd hydrological events, especially some floods, may perturbate or even mask the usual seasonal pattern observed in profiles.

L'estuaire de la Loire a été suivi de 1982 à 1985 par 13 profils longitudinaux synoptiques effectués marée basse. Les éléments nutritifs (SiO_2, NO_3^-, NH_4^+, PO_4^{3-}, carbone organique particulaire ou COP) présentent des profils très divers dans les sections étudiées (rivière, zone fluvio-estuarienne en amont du front de salinité, zone du bouchon vaseux, estuaire externe) qui dépendent de l'élément étudié, de la section, de la saison, et de l'hydrodynamique fluvio-estuarienne. Les processus biologiques semblent ici dominants. La

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rivière est très eutrophe (pigments $>100\,\mu g\,l^{-}$ en été). Il en résulte un appauvrissement saisonnier marqué en SiO_2, NO_3^-, PO_4^{3-}, et une biomasse algale importante ($COP > 3\,mg\,l^{-}$). Cet apport (55 000 t COP algal/an) est dégradé dans le bouchon vaseux, région d'activité bactérienne intense. Il en résulte, en général, un régénération de silice dissoute, de PO_4^{3-} et un pic marqué en NH_4^+, alors que NO_3^- est conservatif ou en défaut par rapport aux dilutions théoriques. D'autres processus peuvent être invoqués, incluant une pollution par des usines d'engrais (PO_4^{3-}, NH_4^+) et une usine hydroélectrique (NH_4^+). Dans l'estuaire externe, beaucoup moins turbide, les nutrients sont en général relativement conservatifs. Les principales variations de concentrations sont observées dans les zones de faibles chlorinités ($Cl^- < 1\ g\,kg^{-1}$) et même en amont du front salin (défini ici comme le doublement des chlorures fluviaux). Les bilans d'apports à l'océan ne sont pas modifiés pour SiO_2 et NO_3^- et sont majorés de 70% et 180% pour PO_4^{3-} et NH_4^+ et minorés de 60% pour le COP. Des épisodes hydrologiques, surtout des crues, peuvent complètement perturber ou occulter les variations saisonnières observées dans les profils.

Introduction

The Loire is probably one of the most eutrophied rivers: total pigments exceeding $200\,\mu g\,l^{-1}$ are commonly found in summer from Orléans to Nantes (Crouzet, 1983; Billen *et al.*, 1986*a*). Estuarine studies have been carried out for more than 20 years in various fields: sedimentology (Gallenne, 1974; Le Douarec, 1978), geochemistry (Diara, 1973; Manickam *et al.*, 1985), and biology (Rincé *et al.*, 1985; Relexans & Etcheber, 1986). In recent years, two sets of interdisciplinary studies have been launched, one by the Conseil Scientifique pour l'Etude de l'Estuaire de la Loire (CSEEL, 1984), which was focused on hydrodynamics but included general water-quality studies and biological surveys, and the other by the French Centre National de la Recherche Scientifique through its GRECO-ICO programme within which studies of nutrients, organic carbon, biomass and biological activities, organic geochemistry, and isotopic tracers have been regularly carried out during the same cruises (June 1982–June 1985) and on the same samples. This paper will give a general introduction to the Loire estuary and consider the following questions: (i) what are the levels and time variations of the major nutrients (carbon, nitrogen, phosphorus and silica) in the eutrophied Loire River; (ii) what is their behaviour in the highly turbid estuary; and (iii) what are the estuarine responses to river geochemical signals?

After summing up the results obtained within the GRECO-ICO, some of which have already been published (Saliot *et al.*, 1984; Billen *et al.*, 1986*a*; Cauwet & Meybeck, 1987), the following nutrients will be considered: NO_3^-, NH_4^+, PO_4^{3-}, total dissolved P, silica, particulate organic carbon (POC). Compared to our previous papers on the Loire, the nutrient (N, P, Si) profiles are presented for the first time, five new estuarine surveys of POC are added, and information on the nutrient inputs from the Nantes City sewage system is added. Phytoplanktonic and bacterial activities are discussed in Relexans *et al.* (1988), and particulate organic components are fully treated by Saliot *et al.* (1988) and organic micropollutants (PCBs, pesticides, etc.) are considered by Marchand *et al.* (submitted). This s probably the first multidisciplinary study carried out on a macrotidal turbid estuary such as the Loire. Previous multidisciplinary works on estuarine chemistry include those on the Amazon (Edmond *et al.*, 1981), the Delaware (Biggs *et al.*, 1983), and the Zaire (Anonimous, 1978).

Numerous studies on the estuarine dynamics of nutrients have been published recently (Edmund *et al.*, 1981; Sharp *et al.*, 1982; Knox *et al.*, 1986) and of organic carbon (Cadée, 1982; Eisma *et al.*, 1982; Biggs *et al.*, 1983; Etcheber, 1983; Etcheber & Relexans, 1983; Mantoura & Woodward, 1983; Tan & Strain, 1983), but few of them, such as Edmond *et al.* (1981) on the Amazon or Biggs *et al.* (1983) on the Delaware, actually considered both organic carbon and nutrients.

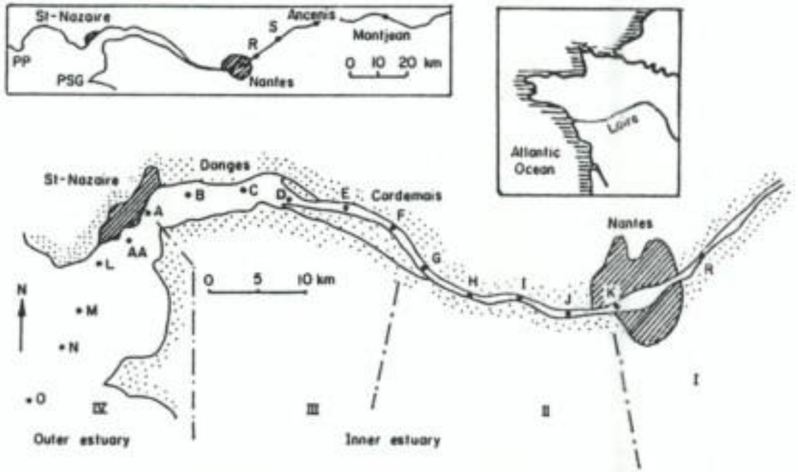

Figure 1. The Loire estuary and its regular sampling stations (K to A). In the outer estuary, the location of stations has changed at each survey, particularly the most oceanic station (O). Nantes city waste water is released on the north and south shores between stations J and K. River samples are usually taken at Ancenis. PP, Pointe de Penchâteau; PSG, Pointe de St Gildas.

Sampling strategies and analyses

Sampling

The study area extends over 150 km from the upstream Montjean gauging station, the last station on the river to the outer estuary downstream of the city of Saint Nazaire and limited by the Pointe de Penchâteau and the Pointe de St Gildas (PP and PSG in Figure 1). The average depth is around 15 m in the outer estuary and decreases to 10 m in the inner estuary from Saint Nazaire to Nantes, where a navigation channel is regularly dredged. Upstream of Nantes, the river is shallower, less than 2 m during the summer period.

Unlike most estuarine studies which are limited to comparing the observed levels of chemical components with the theoretical ones derived from the dilution line, we have focussed our sampling on *isochronous longitudinal profiles* taken at the same period of the tidal cycle, i.e. at low tide ± 30 mn. In particular the fluvio-estuarine zone and the lowest-salinity zone, both found in the upper part of the inner estuary, have been sampled according to a strategy developed in similar estuaries such as the Scheldt (Billen *et al.*, 1986*b*) and the Tamar (Morris *et al.*, 1978). Two kinds of boats were used: a small oceanographic vessel, the *Côte d'Aquitaine*, for the outer estuary, and a rubber boat between Saint Nazaire and Nantes. Upstream of Nantes, river samples were generally taken by hand from the shore, usually at the station of Ancenis (Figure 1). Each survey generally lasted two or three days. Samples were taken by a vertical 5 l Niskin bottle while the boats were drifting, so that the bottle line was always vertical during the sampling operation. This type of sampling is particularly needed in the inner estuary, where water velocities may reach 2–3 $\mathrm{m\,s^{-1}}$ soon after low tide. For each profile, 15–20 stations were sampled; those upstream of Saint Nazaire remained unchanged from June 1982 to June 1985, but outer-estuary stations have various locations according to the salinity pattern. The sampling depth was 1 m below the surface. Occasionally, deep samples at 1 m above the bottom were also taken. It was not always possible to sample coastal oceanic waters ($\mathrm{Cl^- > 19{\cdot}5\,g\,kg^{-1}}$): during some cruises, the maximum sampled salinities did not exceed 15 $\mathrm{g\,Cl^-\,kg^-}$.

In addition to these surveys, which were common to all workers of the GRECO-ICO, other limited surveys were performed at a limited number (generally four) of representative stations, especially for the nutrient organic carbon programme. General information on river and estuarine features during these surveys are given in Appendices 1 and 2; for more details on previous surveys, see Billen *et al.* (1986*a*).

Analysis

All samples were filtered within a few hours of sampling on glass-fiber Whatman GF/F filters. After addition of chloroform or $HgCl_2$, samples were kept at 4°C before nutrient analysis by classic colourimetric methods for NO_3^-, NH_4^+, PO_4^{3-}, and SiO_2. Total dissolved P was determined for some profiles after digestion with sulfuric acid at 110°C for 1 h. Particulate organic carbon (POC) and dissolved organic carbon (DOC) was analyzed after filtration on pre-ignited Whatman GF/F filters. DOC samples were kept in sealed vials and preserved with $HgCl_2$; for details, see Saliot *et al.* (1984) and Cauwet (1984). Chlorophyll-*a* and phaeopigments were determined using the equations and procedure of Lorenzen (1967). Prior to September 1983, the acidification of samples was too weak and the phaeopigments were overestimated; therefore, for these surveys, only the total pigments (chlorophyll-*a* + phaeopigments) have been considered.

Unusual hydrological events

Altogether, 13 general or limited surveys have been carried out over three years in various months of the year (Appendices 1 and 2). However, we were surprised to find the following unusual hydrological events which resulted in an unusual physico-chemical structure of the estuary (resulting concentrations measured during these events are generally well identified in seasonal variations):

(i) 22–24 May 1983, river discharge = 3500 $\mathrm{m^3\,s^{-1}}$ (exceptionally high compared to 700 $\mathrm{m^3\,s^{-1}}$ for the average May value);

(ii) 18 November 1983, 220 $\mathrm{m^3\,s^{-1}}$ (much lower discharge than the average 800 $\mathrm{m^3\,s^{-1}}$ for this month);

(iii) 13 June 1984, 1200 $\mathrm{m^3\,s^{-1}}$ (twice the average June discharge); and

(iv) 13–17 June 1985, 650 $\mathrm{m^3\,s^{-1}}$, normal river discharge but occurring three weeks after a major flood rarely observed in May (4200 $\mathrm{m^3\,s^{-1}}$ on 17 May) which swept all suspended matter from the inner estuary to the outer estuary.

General features of the Loire estuary

The following section is a summary of the general investigations carried on the estuary from 1982 to 1985 through the GRECO-ICO study and this is compared to previous

studies (Gallenne, 1974; Le Douarec, 1978; Manickam, 1982; CSEEL, 1984; Rincé *et al.*, 1985).

A highly eutrophied river

The Loire river (110 000 $\mathrm{km^2}$, 838 $\mathrm{m^3\,s^{-1}}$ from 1866 to 1981) has a high-water stage from January to March ($Q > 1350\,\mathrm{m^3\,s^{-1}}$) and a low-water stage from July to September ($Q < 400\,\mathrm{m^3\,s^{-1}}$). The water residence times within the estuary from Nantes to Saint Nazaire are between 1 and 10 days, depending on river discharge. Inorganic detrital suspended matter in the river is generally low (20 $\mathrm{mg\,l^{-1}}$) in summer, when the river is very shallow and light can easily penetrate through the whole water column. Unlike other French major rivers (Rhône, Garonne, Seine, Oise), the Loire waters are not continuously stirred up by canal boats nor exposed to turbid water inputs during summer from glacial melt (Rhône). According to Crouzet (1983), the median P–PO_4^{3-} value is 0·16 $\mathrm{mg\,l^{-1}}$ at the lowest survey station of the Loire, and the 90% percentile is near 0·66 $\mathrm{mg\,l^{-1}}$; the corresponding yearly averages of chlorophyll-*a* are around 80 $\mathrm{\mu g\,l^{-1}}$ with summer maximum values exceeding 200 $\mathrm{\mu g\,l^{-1}}$. Such a high pigment value is very rare in major world rivers and the values found in the Loire are the highest in the world for a river of this size, closely followed by the lower Rhine in which the average chlorophyll-*a* content is around 50 $\mathrm{\mu g\,l^{-1}}$ with a summer maximum of 100 $\mathrm{\mu g\,l^{-1}}$ (Friedrich & Viehweg, 1984).

A turbid estuary

As in many other macrotidal estuaries (Allen *et al.*, 1980), the Loire estuary is characterized by a marked increase in suspended matter concentration (SMC) from the river (yearly average SMC = 50 $\mathrm{mg\,l^{-1}}$) to the turbidity maximum where the maximum SMC exceeds 1000 $\mathrm{mg\,l^{-1}}$ at some periods. In the bottom of the navigation channel, a layer of fluid mud is commonly found in which the SMC is over 20 $\mathrm{g\,l^{-1}}$.

The high turbidity zone (HTZ) is here defined as a doubling of river SMC, and its position varies according to river discharge and tidal coefficient (Gallenne, 1974). During the summer river low stage ($Q < 200\,\mathrm{m^3\,s^{-1}}$), the HTZ extends from Donges (station C in Figure 1) up to the city of Nantes (station R). After a major flood ($Q > 3000\,\mathrm{m^3\,s^{-1}}$), the suspended sediments are flushed out in the outer estuary downstream of Saint Nazaire (station A). At intermediate river-water discharges, the HTZ is found between Saint Nazaire (station L) and Cordemais (station F) on neap tides and between Saint Nazaire and Tougas (station J) on spring tides. The range of SMC found on our 13 profiles (low tide), reported in Figure 2(a), clearly confirms Gallenne's work (1974). On the basis of median values, bottom samples commonly have twice as much SMC as do surface ones; the maximum SMC found 1 m above the bottom is 10 $\mathrm{g\,l^{-1}}$, i.e. a value close to the fluid-mud definition. In the outer estuary, the SMC drops rapidly downstream of Saint Nazaire (station A). The HTZ was not always found: in May 1983, during a major flood, the HTZ was hardly evidenced; in June 1985, three weeks after another major flood, the HTZ was not observed at all in the inner estuary. This very unusual profile has not been taken into account for the SMC range reported in Figure 2(a).

Multiple estuarine limits

The fresh water–seawater interface (FSI) is here defined as the doubling of river chlorinity, generally around 20 $\mathrm{mg\,l^{-1}}$. The chlorinity ranges found during our 13 surveys at low tide in the estuary are compared to the corresponding SM profiles in Figure 2(b). The FSI is found between stations C (February 1983) and G (June 1982), depending on the hydrological conditions (see Figure 1 for locations). At low tide, during or soon

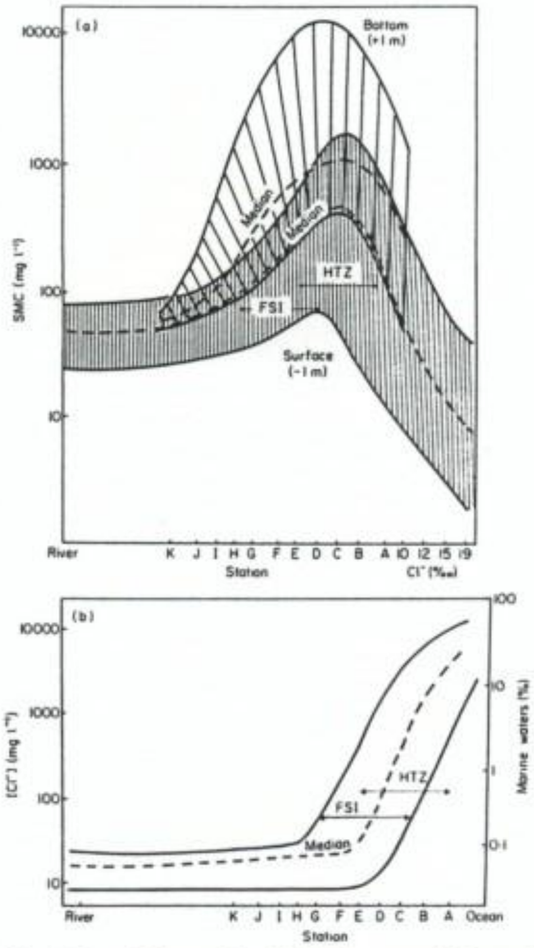

Figure 2. General characteristics of the Loire estuary. (a) Range of suspended matter concentration (SMC) for surface and bottom samples at low tide. The high turbidity zone (HTZ) is defined as a 100% increase in river SMC. The June 1985 profile is not taken into account here. (b) The chlorinity range observed in surface samples during the low-tide isochronous surveys. The freshwater–saline-water interphase (FSI) is defined as a 100% Cl^- increase.

after the winter and spring floods, the inner estuary is filled with fresh or slightly brackish waters, and the proportion of seawater at Saint Nazaire (station A) is only a few percent, while during the summer drought this proportion rises to 40%. At high tide, the measured salinity was much higher in June 1984 where the variation in chlorine content between low tide and high tide was: station E, 13·4–460 mg l^{-1}; C, 350–4800 mg l^{-1}; A, 3800–10 900 mg l^{-1}. However, at identical salinities, the water chemistry was very similar while SMC was somewhat lower for the high-tide profile. According to Le Douarec's study (1978) on the saline structure of the estuary, the FSI horizontal movement during a tidal cycle extends from 5 to 22 km depending on the spring–neap cycle. During the June 1984 survey the FSI movement was 10 km. As commonly observed in other macrotidal estuaries, the HTZ generally begins upstream of the FSI, but the maximum SMC is found 20–40 km downstream of the FSI, except for the June 1982 survey.

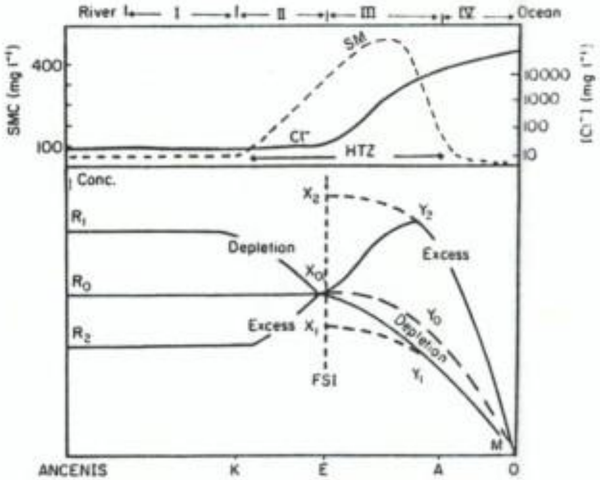

Figure 3. The Loire estuary. Schematic longitudinal profiles of dissolved components. FSI, freshwater–saline-water interphase; RoXoYo, conservative behaviour in all estuarine sections (XoYoM is the ' classic ' theoretical dilution); R1(R2), depletion (excess) in the fluvio-estuarine zone; XoY1 (XoY2), depletion (excess) in the inner and/or outer estuary. When computing net fluxes to the ocean, the theoretical continental end-members, X1 and X2, are computed on the basis of Y1 and Y2 concentrations and the corresponding chlorinities.

As a result of the SMC and salinity profiles, we have characterized the major Loire estuarine sections at low tide as per most previous authors (see also Figure 3):

(i) *The fluvio-estuarine section:* from Ancenis to station K. In this stretch, the river velocity is lowered and the water level is tidally influenced, but the SMC remains unchanged.

(ii) *The upper inner estuary:* from station K downstream Nantes to the FSI, generally found near Cordemais (station E). There is a marked increase in SMC, but still no saline influence.

(iii) *The lower inner estuary:* from station E to Saint Nazaire (station A). The SMC is maximum and the seawater influence is effective (from a few percent to 40%).

(iv) *The outer estuary:* downstream Saint Nazaire. The SMC drops dramatically from a few hundred mg l^{-1} to a few mg l^{-1} as the seawater proportions gradually raise to 100%. The external limit of this section varies according to the river discharge and may extend well over the PP–PSG line in Figure 1.

General profiles of SMC, O_2, pH, temperature and Cl^- clearly exemplify these overall features [see June 1982 in Saliot *et al.* (1984); March and September 1983 in Billen *et al.* (1986*a*); and June 1985 in Figures 7 and 10, this paper).

Variable stratification

Our objective was to study the estuarine longitudinal structure at low tide on the basis of surface samples only. It was postulated that vertical gradients were negligible relative to longitudinal variations. As concerns the suspended matter, the range in inner-estuary surface waters is commonly 1–20 while, at a given station, the vertical range is usually less than 2 from Nantes to Cordemais and less than 4 from Cordemais to Saint Nazaire, if the fluid-mud layer is not considered. According to Le Douarec (1978), the saline stratification is small or non-existent at the lowest river discharge ($Q < 350\ \mathrm{m^3\ s^{-1}}$), and at the average discharge during spring-tide periods. The stratification is marked during the high discharges ($Q > 1500\ \mathrm{m^3\ s^{-1}}$), particularly on spring tides where a salt wedge may develop.

In our low-tide profiles, vertical gradients of chlorinity are usually less than 200% in the inner estuary and may reach 200% near Saint Nazaire. In the outer estuary, salinity gradients are variable: from 200–500% near Saint Nazaire to less than 10% at the most saline station. For example, in June 1984, the most marine station had a chlorinity of 17·7 g $\mathrm{Cl^-\ kg^{-1}}$ in surface waters and 18·7 g $\mathrm{Cl^-\ kg^{-1}}$ in bottom waters, while at the center of the outer estuary the chlorinities were 7·7 and 16·7 g $\mathrm{kg^{-1}}$, respectively.

As concerns the dissolved oxygen which is highly variable along the estuary in some summer cruises, vertical gradients were also moderate. In September 1983, five vertical profiles have been taken at station A, E, G, J and K: the E profile was the only one where an appreciable O_2 gradient was found (from 2·85 mg $\mathrm{l^{-1}}$ in surface waters to 1·2 mg $\mathrm{l^{-1}}$ in bottom waters). In June 1984, nine profiles were taken (A–G, I and J): the maximum gradient was observed at station B (5·07–3·7 mg $\mathrm{l^{-1}}$).

A summer oxygen depletion

During summer, a marked dissolved oxygen depletion curve was observed (see full discussion in Relexans *et al.*, 1988), reaching 0·5 mg $\mathrm{l^{-1}}$ (surface samples) between Donges and Cordemais (stations C, D, E) as in June 1982 (Saliot *et al.*, 1984) or in September 1983 (Billen *et al.*, 1986*a*). In winter, the oxygen levels were nearly constant along the estuary as in March 1983 (O_2 always > 9 mg $\mathrm{l^{-1}}$; Billen *et al.*, 1986*a*). The pH variability was nearly inverse to the O_2 one (Relexans *et al.*, 1988). In the lower inner estuary, the pH values were almost constant at around 7·8 ± 0·2 throughout the year, while in the fluvio-estuarine zone and the upper-inner estuary the pH ranged from 7·6 in winter to 9·4 in summer (as in September 1983), and at the most saline station, the pH was slightly higher than that near Donges (8·0 ± 0·2).

The 0_2 and pH variations are closely connected (Saliot *et al.*, 1984; Billen *et al.*, 1986*a*; Relexans *et al.*, 1988). In the river, during summer, phytoplankton productivity is extremely high and results in O_2 oversaturation and very high pH. In the inner estuary, as soon as the SMC increases, the bacterial decomposition of the river planktonic material overtakes the production, and both O_2 and pH decrease. Downstream of Donges (station C), the decrease in SMC, and therefore of bacterial activity (Billen *et al.*, 1986*a*; Relexans *et al.*, 1988), and the mixing with oxygenated oceanic waters restores the oxygen levels in the estuary, while pH values reach oceanic levels of close to 8·2.

An important human pressure

The city of Nantes collects sewage water from a total of about 600 000 people on both sides of the estuary. On the north shoreline, waters undergo primary treatment (Tougas station) and are then re-injected into the estuary between stations J and K. On the south shoreline, waters undergo primary and secondary treatments (Petite Californie station), and are then re-injected close to those from the north shoreline. The Saint Nazaire waters are collected and injected without treatment near station A. According to a recent industrial census (CSEEL, 1984; Rincé *et al.*, 1985), there are two major nutrient point sources in the estuary which arise from two N-fertilizer plants: GardiLoire and Grande Paroisse both release their waste waters near station B, upstream of Saint Nazaire. Another fertilizer plant (including super phosphate products), the 'Générale des Engrais', is located near station I. Other industrial activities concern mainly the metal industry, near stations I and D, and a major refinery at Donges (station C). A major thermal electric power plant using fuel and coal is located at Cordemais between stations E and F. The treatment of its water intake by chlorine could be responsible for the slight increase in $\mathrm{Cl^-}$ (from 20 to 25 mg $\mathrm{l^{-1}}$) which is often observed upstream of the FSI, between stations E and F.

Continental and oceanic end-members

The definition of end-members is a must in any classic estuarine study in order to determine the theoretical dilution lines with chlorinity. In the Loire estuary, most studies have followed this scheme (See Rincé *et al.*, 1985). Our approach since June 1982 has been different: we have considered the longitudinal variations of surface-water chemistry in the whole estuary at low tides. This is particularly appropriate to the Loire in which more than half the inner estuary may not be influenced by salt-water intrusion and will remain characterized by marked water-quality variations (pH, dissolved oxygen and suspended matter). The continental end-member chosen for reference in this work is the FSI defined previously and generally found at 30–50 mg $\mathrm{Cl^-\ l^{-1}}$; it corresponds to $\mathrm{Cl^-}$ levels much lower than the previous limit of salt intrusion (250 mg $\mathrm{Cl^-\ l^{-1}}$) set up in the Loire for practical purposes (Le Douarec, 1978: Rincé *et al.*, 1985), i.e. for the drinking-water intake of Nantes. The oceanic end-member is not easy to determine either: in most of our surveys, the most saline station was only 80–90% marine, according to chlorinities. As will be seen later, the dissolved concentrations measured at these stations can be extrapolated to obtain those of oceanic water characterized by a chlorinity of 19·5 g $\mathrm{kg^{-1}}$.

Our interpretation of measured dissolved components in the Loire estuary will be decomposed in three parts: (i) in the fluvio-estuarine section, and in the upper part of the inner estuary, only the isochronous longitudinal profiles are considered; (ii) in the lower part of the inner estuary, where the salt-water proportion exceeds 1‰, the oserved concentration profile is compared to the theoretical isochronous profile obtained from the continental end-member taken at the FSI and from the oceanic end-member; and (iii) in the outer estuary, usually between 5 and 19·5 g $\mathrm{Cl^-\ kg^{-1}}$, the interpretation is more classically done by reference to the theoretical dilution line (concentration versus chlorinity plot). In this latter case the samples may not all be taken at the same period of the tidal cycle.

The complex behaviour of a given dissolved component in the fluvio-estuarine section and in the inner estuary is detailed in Figure 3: starting from various river levels (R1), there may be an increase (R2), decrease (R1) or a conservative behaviour in the upper-inner estuary as soon as the suspended matter level increases. The continental end-member (Xo) is the concentration effectively measured at the FSI. In the lower-inner estuary and in the outer estuary from the FSI to the oceanic station M, a theoretical dilution profile (Xo–Yo–M) can be drawn, which separates excess (Xo–Y2–M) and depletion (Xo–Y1–M) patterns. At downstream stations where maximum excess or depletion is noted, the observed profiles generally correspond to theoretical dilutions (Y2–M and Y1–M); they correspond to higher (A2) or lower (A1) continental end-members. Actual

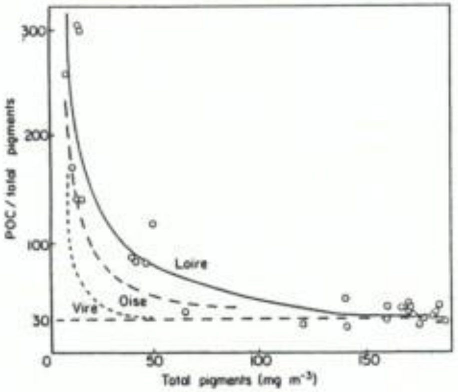

Figure 4. Evolution of the particulate organic carbon (POC) to total chlorophyll pigment [chlorophyll + phaeopigments, Lorenzen (1967)] ratio versus the total pigments in the Loire river (O) compared to two other French rivers (from Dessery *et al.*, 1984). Algal blooms are characterized by a similar ratio (POC/pigments–30).

budgets of chemical constituents to the ocean are computed by multiplying these excess (X2) or depleted (X1) contents by the river discharge.

Nutrient levels in the Loire River

Organic carbon

The particulate matter carried by the river can be divided into four parts: (i) detrital inorganic matter, (ii) non-algal organic matter, (iii) autochtonous calcite particles, and (iv) phytoplanktonic organic material. The phytoplanktonic material is characterized by the ratio POC/total-pigments = 30, where POC is the particulate organic carbon and total pigments are the sum chlorophyll-*a* + phaeopigments based on Lorenzen equations (Billen *et al.*, 1986*a*). This ratio is similar to those found in other French rivers such as the Vire, the Oise (Dessery *et al.*, 1984), and the Garonne, where POC/chlorophyll-*a* = 35, based on the SCOR-Unesco equations (Relexans & Etcheber, 1982). Khalanski (1984) has also calculated a similar ratio in the Loire, considering the specific ratio of each algal group. Figure 4 illustrates the relation between the POC/pigments ratio and the total pigment levels from the winter low-productivity levels (pigments $<10\,\mu g\,l^{-1}$) to the summer planktonic blooms (pigments $>100\,\mu g\,l^{-1}$).

The amount of calcite in suspended matter (SM) has been studied by Manickam (1982) and Manickam *et al.* (1985): there is a marked seasonal variation with a winter minimum of 4% $CaCO_3$ and a summer maximum of up to 35% (dry weight basis). This variation is most probably caused by the river's seasonal pH cycle due to eutrophication, as is common in hard-water eutrophied lakes. If it is assumed that the lowest winter $CaCO_3$ content (about 4%) is related to the detrital particles eroded from the lower Loire basin, a region rich in carbonate rocks, the autochtonous $CaCO_3$ content ranges from 0 in winter to about $10\,mg\,l^{-1}$ in summer when it could constitute 25% of the inorganic SM.

The algal POC is highly variable, ranging from $0{\cdot}5\,mg\,l^{-1}$ in winter to more than $5\,mg\,l^{-1}$ in summer. The unusual hydrological events are definitely out of the seasonal

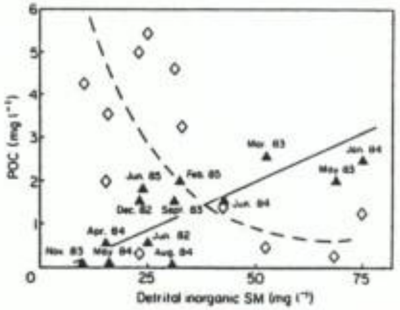

Figure 5. The Loire river. Algal POC (◇) and non-algal POC (▲) variations with detrital inorganic suspended matter (corrected for autochthonous river $CaCo_3$).

variations: May 1983 and June 1984, low algal levels; November 1983, high algal levels (see also Figure 13). The non-algal POC is maximum in winter ($\simeq 3\,mg\,l^{-1}$) and minimum in summer ($<0{\cdot}5\,mg\,l^{-1}$) and is roughly correlated (Figure 5) to the inorganic detrital suspended matter which has been calculated: the total organic matter is estimated to be 2·5 times the POC level, then the Autochtonous $CaCO_3$ content is estimated from seasonal variation (Manickam *et al.*, 1985), taking into account a detrital $CaCO_3$ content of 4‰. The direct correlation between non-algal POC and inorganic detrital material supports the assumption of similar origin—the terrestrial erosion. A weak inverse relation is observed between algal POC and detrital SM [Figure 5]. As in many other rivers (Meybeck, 1982), the POC level in SM is inversely related to the detrital inorganic SM, with a minimum 3·0‰ for the highest SM in winter and during major floods. This minimum value is attributed to the terrestrial organic detritus.

The dissolved organic carbon (DOC) in the river varies from 2·4 to $7{\cdot}8\,mg\,l^{-1}$, and is higher during the high-water stage (Cauwet & Meybeck, 1987), probably as a result of soil leaching by surface runoff. The total organic carbon (TOC), computed as the sum of DOC and POC separately measured, presents a limited annual variation, but its components are actually very variable.

Nutrients (N, P, Si) levels in the river

The average nutrient levels (water-discharge weighted) are: DOC, $5{\cdot}08\,mg\,l^{-1}$; POC, $2{\cdot}62\,mg\,l^{-1}$; N-NO_3^-, $2{\cdot}56\,mg\,l^{-1}$; N-NH_4^+, $0{\cdot}038\,mg\,l^{-1}$; N-NO_2^-, $0{\cdot}015\,mg\,l^{-1}$; dissolved organic N, $0{\cdot}9\,mg\,l^{-1}$; P-PO_4^{3-}, $0{\cdot}079\,mg\,l^{-1}$; total dissolved P, $0{\cdot}11\,mg\,l^{-1}$; dissolved SiO_2, $9{\cdot}8\,mg\,l^{-1}$. The average corresponding water discharge is $1050\,m^3\,s^{-1}$ compared to $850\,m^3\,s^{-1}$ for the long-term average. Inorganic N, phosphate and SiO_2 levels are close to the previous estimates of Manickam (1982), to the median values (1971–80) of the Loire water authority (AFBLB, 1971–1985), to data of the Nantes interdisciplinary study (CSEEL, 1984) and of Rincé *et al.* (1985). These levels are quite similar. When compared to the world average of pristine rivers (Meybeck, 1982), the Loire River is very similar as concerns the silica and the organic carbon content, four times richer in phosphorus, and about 20 times richer in nitrate! Orthophosphate, i.e. phosphomolybdate reactive P, represents about 80% of the dissolved P; nitrite and ammonia are negligible compared to nitrate, but organic nitrogen is about 25% of the total dissolved N.

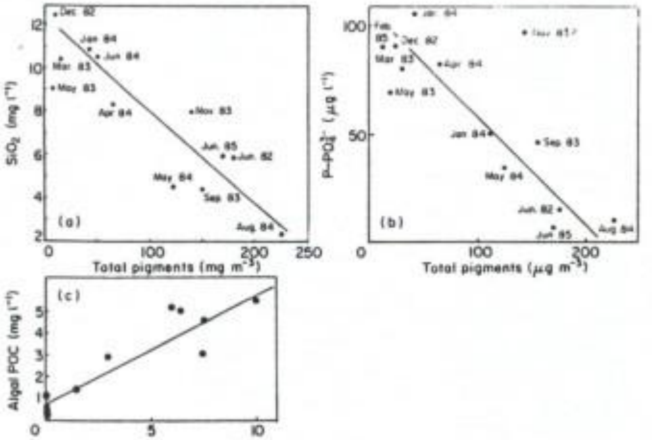

Figure 6. The Loire river. Nutrient variations with total pigments. (a) Silica content; (b) phosphate; (c) algal POC *vs.* estimated silica depletion.

While dissolved silica and orthophosphate exhibit a definite inverse relationship with total chlorophyll pigments [Figure (6a, b)], the nitrate correlation is much weaker. If it is assumed that the average silica level in the river is around 12 mg l^{-1} when no biological uptake is taking place (winter maximum value), the corresponding theoretical SiO_2 depletion is directly correlated to 'algal POC' [Figure 6(c)]. When the depletion is zero, the small remaining POC may be attributed to algae groups other than diatoms.

Nutrient behaviour in the fluvio-estuarine section and in the inner estuary

Particulate organic carbon

The concentrations of POC in estuarine waters are highly variable and may reach 30 mg l^{-1}. The POC concentration depends primarily on the amount of suspended matter (SM), and then on the origin and age of the particulate material (Billen *et al.*, 1986*a*). Most recent POC profiles fall within the previously observed POC variations (Figure 7) which are characterized by a very low and constant POC level in the HTZ and variable river and oceanic end-members according to the algal productivity of these waters.

The June 1985 profile appears to be completely out of the normal range (Figure 7): the POC levels are much higher throughout the estuary, particularly in the lower-inner estuary (stations A–E) where POC does not fall below 10%. This pattern was quite unexpected. Actually, the bulk of estuarine particulate matter was completely flushed out by a previous major flood in May 1985, and the HTZ was not observed. Thus, the SM did not limit light penetration as in other profiles (Billen *et al.*, 1986*a*; Relexans *et al.*, 1988), and the whole estuary was highly productive from the river to Saint Nazaire. The POC/total-pigment ratio, which is usually high (100–300) in the HTZ characterizing the lower-inner estuary, was betwen 30 and 50 from station K to A, a level close to that of algal blooms.

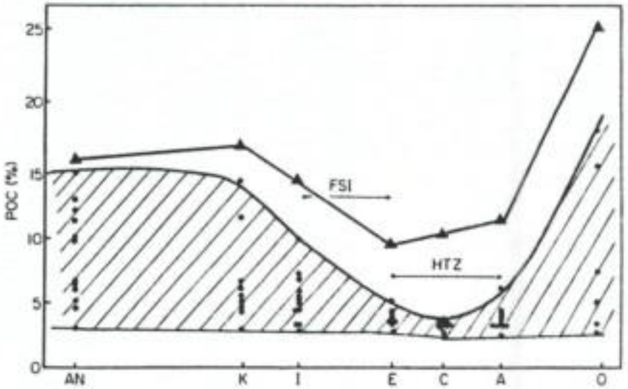

Figure 7. The Loire estuary. Longitudinal isochronous profiles of the POC content in suspended matter, all surveys. The June 1985 pattern (▲) in the outer estuary is completely outside the common range. AN, Ancenis (river station); O, most oceanic station.

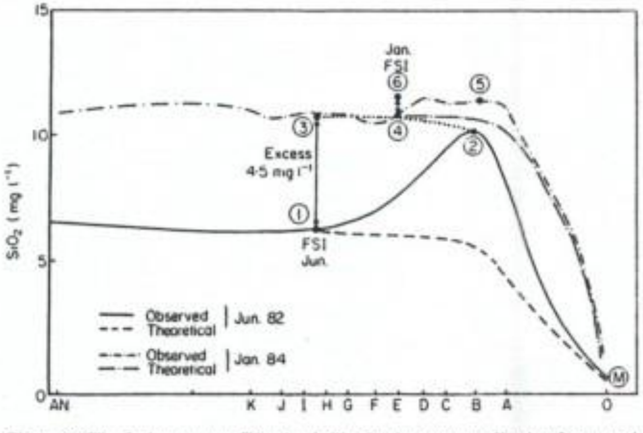

Figure 8. The Loire estuary. Dissolved silica isochronous profiles (surface samples) in June 1982 and June 1984. FSI, freshwater–saline-water interphase. Excess values (1)–(3) and (4)–(6) are computed on the basis of (2) and (5) contents observed at station B. – – –, Theoretical variations downstream from FSI. See Figure 3 for explanation.

Silica

There is practically no change between the riverine values taken at Ancenis or Montjean, and those found at the FSI. In the inner estuary, when the river silica is high in winter, the estuarine profile follows a theoretical profile, as defined in Figure 3. Such a typical pattern is observed in January 1984 (Figure 8): the dilution from the continental end-member (4) to the ocean (0), is very close to the observed variation between (5) and (0). The corresponding excess between (6) and (4) is only about 0·5 mg SiO_2 l^{-1}, i.e. less than 10%. A different pattern is noted in spring and summer, when the river silica is depleted due to diatom uptake: an excess is generally observed downstream of the FSI as in June 1982 (Figure 11), the excess (3) to (1) is 4·5 mg $SiO_2\,l^{-1}$, i.e. the corresponding silica level in the continental end-member (11 mg l^{-1}) is similar to the one observed in winter. It must be noted that the maximum excess is usually observed at the maximum SM in the lower-inner estuary, where the O_2 level is strongly depleted due to high bacterial respiration (Relexans *et al.*, 1988).

Considering all the available profiles established during complete surveys at about 15 stations, it is noted that: (i) when there is no river silica depletion in late spring, such as in May 1983 and June 1984, there is little or no estuarine excess; and (ii) in some summer surveys, the observed excess is quite moderate with regard to the very low river silica levels, as in August 1984 and June 1985. The complete pattern of silica behaviour from a set of seven profiles shows that silica is conservative in one, in excess in five and slightly depleted in one profile.

Orthophosphate

The pattern of $P\text{–}PO_4^{3-}$ in the Loire estuary is more complex and is commonly characterized by several maxima. The first excess is noted in the upper-inner estuary, i.e. upstream of the FSI, and the second one, which usually corresponds to the HTZ is observed in the lower inner estuary, between Donges and Saint Nazaire. The first excess does not always occur, but is well marked during the lowest river stage, as in June 1982 and May 1983 (Figure 9); it begins downstream of station K, i.e. at the disposal site of Nantes city sewage waters (Tougas and Petite Californie). In June 1982, this excess, (1)–(2) in Figure 9, coincides with a downstream increase in SM, while in May 1983 there is no corresponding change in SM. When the river discharge is higher, moderate peak values are sometimes observed in the same section, as in January 1984 (stations K–J) and in March 1984 (stations H–G). Moreover, well-marked depletions can be observed on many profiles, such as those of January 1984 and March 1983 in the fluvio-estuarine section when the SMC increased.

Downstream of the salt-water intrusion (FSI), the $P\text{–}PO_4^{3-}$ profiles generally show one or two zones of maximum concentration, as in June 1982: see (2)–(3) and (4)–(5) in Figure 9, compared to the theoretical dilution profile (2)–(0). The profiles are usually related to the high turbidity zone which is generally located between stations A–D. However, there are noted exceptions in June 1982 [excess (4)–(5) in Figure 9] and in June 1985 (Figure 10) where excess P is not related to high turbidities.

When considering all the detailed profiles realized from June 1982 to June 1985, the phosphate content shows a very variable behaviour in the upper-inner estuary upstream of the FSI (three excess, one depletion, three erratic profiles), and systematic excess in the lower-inner estuary.

Nitrate

In the upper-inner estuary, nitrates are usually constant, like silica, from the river station (Ancenis) to the FSI.

In the lower-inner estuary, the nitrate behaviour can be conservative (March 1983) or depleted (December 1982) (Figure 11). This pattern is very different from the one observed for phosphates, but it is not possible to attribute a definite behaviour to any season: depletions are noted in June 1982, December 1982, and September 1983. It is not always easy to assess whether nitrate is conservative or not, as in May 1983, but an excess was never found.

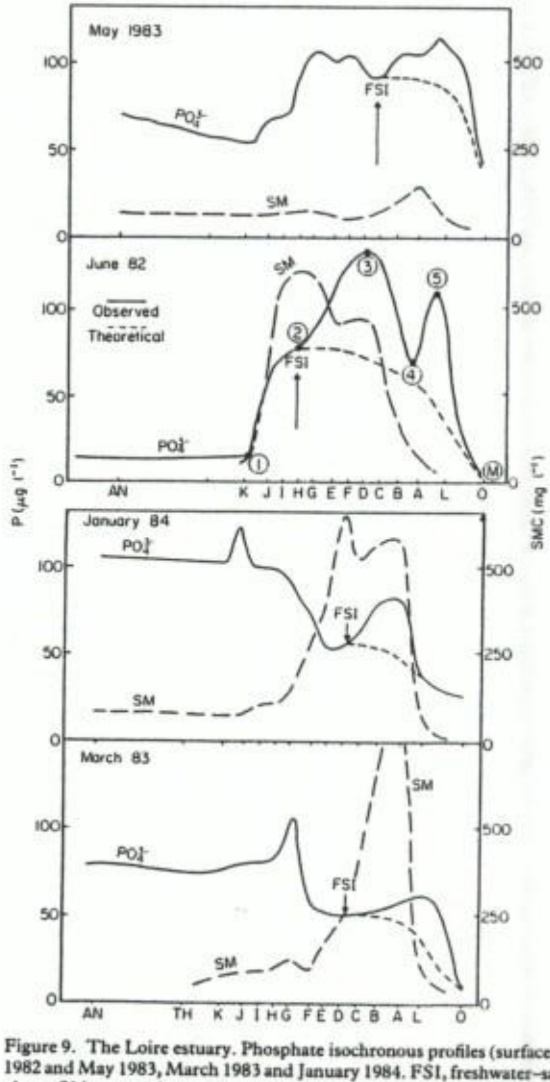

Figure 9. The Loire estuary. Phosphate isochronous profiles (surface samples) in June 1982 and May 1983, March 1983 and January 1984. FSI, freshwater–saline-water interphase, SM, suspended matter profile. Theoretical dilution profiles (---) are computed downstream of the FSI. Marked variations are commonly observed, as in June 1982, upstream of the FSI, (1)–(2), or downstream, (3)–(4)–(5). AN, Ancenis (river station); O, most oceanic station.

Ammonia and nitrite

Unlike phosphate, ammonia is not highly variable in the fluvio-estuarine section, but in the upper-inner estuary pronounced maxima may be found near stations E and/or G (Figure 12). The ammonia pattern in the lower-inner estuary is characterized by one or

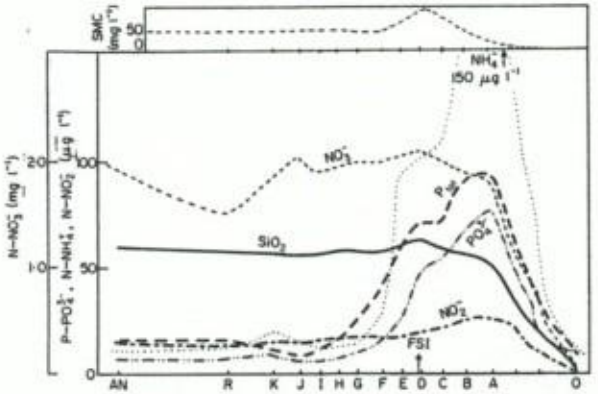

Figure 10. The Loire estuary. Comparison of the nutrient isochronous profiles (surface samples) in June 1985, during a rare eutrophication event in the inner estuary characterized by low SMC. FSI, freshwater–saline-water interphase. From Saint Nazaire (station A) to the most oceanic station (O), nutrient patterns are close to the theoretical dilution.

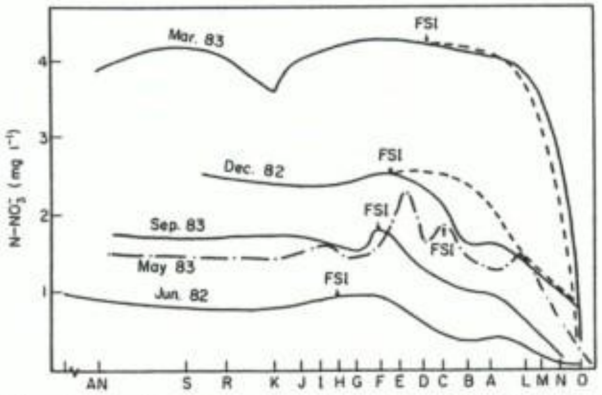

Figure 11. The Loire estuary. Nitrate isochronous profiles (surface samples) at five surveys. FSI, freshwater–saline-water interphase. – – –, Theoretical variations from FSI.

two maxima (as in March 1983 and September 1984) near station E or station A, or both; the maxima generally coincide with the HTZ. However, in June 1985, in the absence of any HTZ (SM < 90 mg l^{-1} throughout the whole estuary), a marked NH$_4^+$ increase is noted at station F and a maximum is observed near Saint Nazaire (stations B–A, Figure 10). In May 1983 (Figure 12), NH$_4^+$ was low and variable throughout the estuary; this pattern was the only one of its kind to be found.

Nitrite profiles have seldom been carried out since NO$_2^-$ is never a major nitrogen species. The June 1985 profile (Figure 10) shows a marked NO$_2^-$ excess downstream of the FSI, parallel to the major NH$_4^+$ maximum.

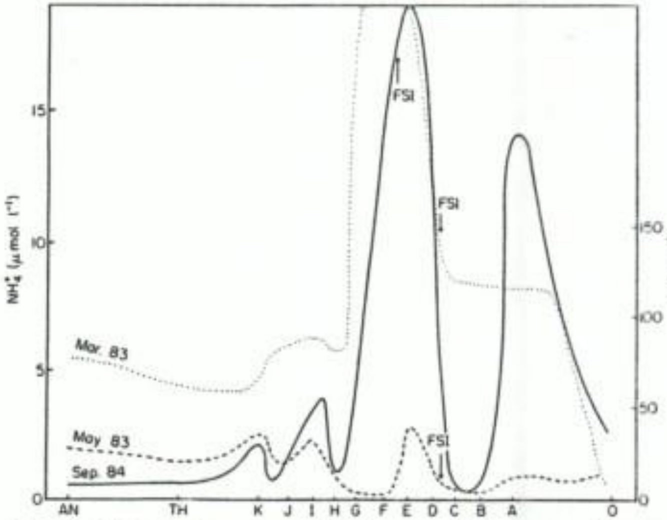

Figure 12. The Loire estuary. Ammonia isochronous profiles (surface samples) at three surveys. Nantes city waste waters are injected between stations K and J. Cordemais coal and fuel power plant is between F and E, and the fertilizer plant is between B and A.

Nutrient behaviour in the outer estuary

The outer estuary, west of Saint Nazaire (Figure 1), is characterized by higher chlorinities (the proportion of seawater at low tide at Saint Nazaire is between 10 and 40‰), lower turbidities, and greater depths. Primary production of marine phytoplankton generally exceeds bacterial activity and restores the O$_2$ balance (Relexans *et al.*, 1988).

Particulate organic carbon

The variation of particulate organic carbon (in percent of SM) exemplifies the seasonal cycle in the outer estuary (Figure 13). In winter (as in January 1984 and March 1983), the estuarine particulate material poor in organic matter (POC 3‰) is flushed into the outer estuary by the highest river discharge; the SM at the most oceanic station has the same level of POC as the one found in the inner estuary, as already found by Billen *et al.* (1986*a*). In spring, the coastal planktonic bloom and the settling of estuarine material are responsible for very high POC levels which may reach 20‰. A maximum content of 26‰ was measured at one station during the June 1985 survey and the POC/total-pigment ratio was 39. Considering the dilution of estuarine particulate material in the outer estuary, Relexans *et al.* (1988) found that the coastal plankton is generally characterized by a similar ratio (around 50).

Some deviations from the usual seasonal variation are caused by the unusual hydrological events which have been described above. In May 1983 and June 1984, the outer estuary was highly turbid as in winter (SM 10–50 mg l^{-1}) due to late-spring river floods. As a result, the POC level in SM was much lower than usual (around 3%).

Nutrients

The behaviour of nutrients in the outer estuary has not been detailed as for the other estuarine sections: generally, only two or three stations have been sampled between Saint

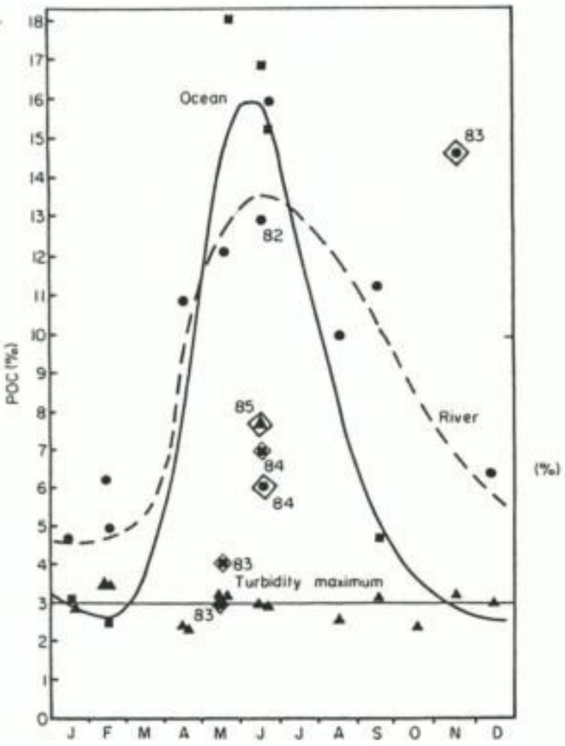

Figure 13. The Loire estuary. Seasonal evolution of the total POC content of suspended matter in the river (●), the HT Zone (▲), and at the most oceanic station (■) (surface samples for all surveys). ◇, unusual hydrological events in the river (November 1983, May 1983, June 1984) and in the estuary (June 1985). All surveys, from June 1982 to June 1985, have been plotted.

Nazaire and a line between Pointe de St Gildas and Pointe de Penchâteau (PSG–PP, Figure 1), although the 19·5 g Cl l^{-1} value is generally not found within this limit at low tide. When station A at Saint Nazaire is chosen as an upstream reference on which a theoretical dilution line is based, most nutrients (SiO_2, PO_4^{3-}, NO_3^-, NH_4^+) are conservative in the outer estuary.

Two intensive surveys (seven and nine stations) were done in May 1983 and June 1985. In May 1983, the SM was between 10 and 50 mg l^{-1}, and was mostly inorganic. Within the PSG–PP limit it was not possible to find surface chlorinities higher than 15 g kg^{-1} and all nutrients presented a general dilution pattern from station A to the oceanic station. However, minor variations are observed: nitrates are slighly depleted, phosphates are in some excess, and the oceanic theoretical end-member for silica is zero. In June 1985, SMC was between 2 and 10 mg l^{-1} and was mostly organic with chlorinities reaching 20 g l^{-1}. The behaviour of SiO_2, PO_4^{3-}, NO_3^- and NH_4^+ was nearly conservative with the exception of PO_4^{3-} and NO_3^- slightly depleted at the very oceanic stations, possibly due to plankton uptake.

Phosphate is probably the most reactive nutrient in the outer estuary, but its variations are very limited compared to those found in the inner estuary. Maximum values for the whole estuarine system have been measured twice at the nearest station west of Saint Nazaire (station AA in Figure 1) in June 1982 and March 1983; from these stations seaward PO_4^{3-} was found to be conservative.

The oceanic end-members have been calculated by extrapolation of the concentrations found at the most marine station (between 15 and 20 g Cl^- kg^{-1}); the average values for their seven surveys in the outer estuary were: 160 µg N–NO_3^- l^{-1}, 33 µg N–NH_4^+ l^{-1} 165 µg Norg. l^{-1}, 17 µg P–PO_4^{3-} l^{-1}, 26 µg P_{tot} l^{-1}, and 0·5 mg SiO_2 l^{-1}. These levels are close to those measured by Delmas and Treguer (1983) in the Rade de Brest (Britanny) before the spring algal bloom: 280 µg inorg. N l^{-1}, 19 µg P l^{-1}, 0·3 mg SiO_2 l^{-1} for salinities between 32·5 and 34·5%.

Discussion

Particulate organic carbon behaviour

The POC pattern in the estuary is complex due to its three different origins: (i) riverine plankton, living and detrital ('algal POC'), which is rich in pigments; (ii) terrestrial POC detritus ('non-algal POC') mostly carried by the river during floods (POC 3%) which probably constitute the bulk of resistant POC found in deposited estuarine muds (POC 2·5%) from which most of the particles of the HTZ are derived (POC 3%), and (iii) marine planktonic POC which is relatively abundant in coastal waters during spring (POC up to 20%). According to the relative abundance of these three forms, four POC patterns were observed during the first 12 surveys (Figure 14). A fifth pattern had to be added after the last survey, in June 1985; due to the absence of the HTZ, the whole estuary, from Nantes to the outer estuary included, was highly productive (Figure 14).

Generally, the non-algal POC levels downstream of the turbidity maximum located in the lower-inner estuary follows the settling and dilution behaviour of the inorganic SM, i.e. the non-algal POC content (in percent of SM) is constant at around 3%. A similar behaviour was noted for chlorophyll pigments immediately downstream of the turbidity maximum (Billen *et al.*, 1986*a*).

Although most authors did not pay much attention to the POC variations along estuaries, the literature data seem to confirm the Loire POC pattern; a similar minimum in the HTZ is noted in most cases. Etcheber (1983) found a range of 1·5–14·6% in the Garonne river (France) and a nearly constant POC level (1·5%) in the HTZ of the Gironde estuary. A similar decrease in levels from the river to the HTZ are noted for the Delaware [9% and 2·3%, respectively, according to Biggs *et al.*, (1983)], for the Ems [6·1% and 2·8 ± 0·2%, Eisma *et al.* (1982)] and for the Tamar [5% and 2·0–2·5%, Morris *et al.* (1982)].

The difference between algal and non-algal POC was not considered by Wollast and Peters (1978) on the Scheldt estuary, nor by Sharp *et al.* (1982) on the Delaware estuary, but permanganate oxidizability and POC profiles presented by these authors are very similar to some of those found in the Loire. However, the high variability in the POC pattern is peculiar to the latter estuary. The major processes which may regulate the POC variations in the Loire are: primary production (river and outer estuary), bacterial

TABLE 1. The average composition of the Nantes' waste water

Sampling Location	Concentration ($mg\,l^{-1}$)							
	DOC	POC	SMC	$N-NO_3$	$N-NH_4^+$	$P-PO_4^{3-}$	SiO_2	N_{org}
Tougas	25	30	100	3·0	2·7	4·4	20·5	15
Petite Californie	10	1·6	5	12	0·4	7·6	20	1·5

process is probably of limited importance. It could however explain the rare phosphate decrease (as in January 1984, see Figure 9) observed upstream of the FSI when the suspended matter concentration starts to increase.

Desorption may explain the important maximum observed in the HTZ, particularly in its downstream part, usually near station B or A, when the chlorinity increases from 500 to 5000 mg kg^{-1}. Desorption is also invoked by van Bennekom *et al.* (1978) for the Zaire. Actually, in the Loire, this process is probably of minor importance with regards to the others: when the SM is relatively low (100 mg l^{-1}), either of organic nature as in June 1985, or of inorganic nature as in May 1983, the dissolved-nutrient maxima are as marked as those observed for the highest turbidities.

The waste waters of Nantes are injected into the upper-inner estuary, between stations K and J. They have been sampled three and five times; their average composition is given in Table 1.

The water discharge is estimated to be 1·5 $m^3\,s^{-1}$ for Tougas and 1 $m^3\,s^{-1}$ for Petite Californie (Saunier *et al.*, 1982). When compared to the river discharge at low stage (around 200 $m^3\,s^{-1}$), these waste waters can only influence the estuarine water quality if their concentrations are about 100 times higher than those found in the fluvio-estuarine section, near station K. This is not the case for silica and nitrate, but is so for phosphate. Therefore, the sharp increase of PO_4^{3-} in some surveys between stations K and J (see June 1982 in Figure 9) may well be attributed to this input. According to Rincé *et al.* (1985), the total P input from Nantes city is estimated to be around 450×10^6 g $year^{-1}$, mostly as phosphate and organic P; this is about 20% of the river Loire load, upstream of Nantes. The waste water N flux is only 1·5% of that of the river (Rincé *et al.*, 1985). These urban inputs from Nantes do not affect the estuarine nutrients budget presented here which is based on measured values at the FSI, i.e. for downstream from the city. Urban wastes are often thought to be responsible for marked nutrient maxima in estuaries, as for ammonia in the Clyde (Mackey & Leatherland, 1976) and for phosphate in the Hudson (Simpson *et al.*, 1975). In the Hudson estuary, the impact of New York City (population estimated at 15 million people by the present authors) is likely to be much greater than that of Nantes on the Loire estuary: the ratio of sewage-water-discharge/river-discharge is ≃0·3% in the Loire, compared to ≃11% in the Hudson! The marked phosphate increase in the Tamar is also attributed by Morris *et al.* (1981) to the waste waters released from Plymouth city.

Major nitrogen inputs from fertilizer plants are located near Saint Nazaire, between stations A and B, and at Basse Indre, near station I. They are estimated by the CSEEL (1984) to comprise around 800×10^6 g N $year^{-1}$, which is minor compared to the river N flux (around 60×10^9 g $year^{-1}$). However, this statement is questionable when considering, for instance, the high ammonia and phosphate maximum observed in June 1985 between stations B and A, when the whole estuary was characterized by high phytoplanktonic production in the absence of any HTZ. Rincé *et al.* (1985) also attribute a phosphate maximum observed in February 1982 to the fertilizer plant.

The well-marked increase of ammonia which was observed at each survey at station E (in June 1982, it was measured at station F, but this sample was taken more than 1 h after low tide) is most probably linked to the Cordemais power plant located between stations E and F.

Diffusion from pore waters and/or stirring of deposited sediments can be a major source of silicate and phosphate in macrotidal estuaries (Wollast & DeBroeu, 1971; Callender & Hammon, 1982). Higher levels of nitrite and ammonia are also often found as a result of denitrification in the sediment (Knox *et al.*, 1986). In the Chesapeake Bay, the regeneration of silica from sediments is estimated to be five times that of the river input (D'Elia *et al.*, 1983). In the Loire estuary, diffusion from pore waters may be important for silica, phosphate and ammonia in adjacent salt marshes which generally support reed vegetation, and are connected to the inner estuary between stations A and H (Diara, 1983). Stirring of the fluid-mud layer, very much enriched in dissolved nutrients as for silica, may also play a major role here (Gouleau, in prep.).

Two chemical processes have been quoted for the phosphate excess commonly found in estuaries. The hydrolysis of hydroxyapatite has been described for the Mississippi by Fox *et al.* (1986): the particulate hydroxyapatite is partially hydrolysed to release HPO_4^{2-} and Ca^{2+}, the dissolved P budget to the Gulf of Mexico would be increased by 40%! This excess is observed between 2 and 14‰, i.e. at salinities similar to those where a maximum phosphate is found in the Loire estuary. Although not studied, this process could be responsible for the phosphate maximum observed here in the Loire, and in the Gironde by Philipps (1980). In the Weser estuary, Rehm (1985) found that particulate P was directly linked to particulate iron. In anoxic conditions, a P release may be expected in the Loire where it could occur in sediment pore waters.

Finally, short-term variations in the dissolved concentrations of river nutrients are likely to produce scattering and artefacts of depletion or excess, as in the Tamar (Morris *et al.*, 1981). Such scattering has been clearly shown by van Bennekom *et al.* (1978: Figure 11) in the phosphate dilution curves determined five days apart in the Zaire estuary. In the Loire river, the seasonal pattern of nutrients based on monthly samples (Guillaud, 1983*a*; CSEEL, 1984) is quite constant, while the average water residence time in the estuary is of the order of one week. Therefore, river variations are not likely to be responsible for the marked maxima and minima observed in estuarine profiles.

River carbon budget

By combining the river-water discharge and the levels of the various forms of organic carbon found during the 13 surveys, a seasonal budget of the river input of carbon to the estuary can be proposed (Table 2). Although the algal POC level (in percent of SM and in mg l^{-1}) is at its maximum in summer, its flux (in kg s^{-1}) is higher in spring. The non-algal POC flux is maximum in winter. DOC is always the dominant form of organic carbon input into the estuary. If it is assumed that the minimum 4% content observed in winter (Manickam *et al.*, 1985) can be attributed to calcite particles derived from land erosion, the yearly average autochthonous calcite levels correspond to 0·4 mg C l^{-1}, i.e. twice the allochthonous calcite (0·17 mg C l^{-1}), and dominates throughout summer.

The input of highly labile organic carbon from the Nantes City sewers to the estuary is estimated to be about 3×10^9 g $year^{-1}$, i.e. only 5% of the river load of algal POC.

Actual nutrient input to the ocean

The nutrient input to the ocean presented here is based on only a dozen surveys over three years which are, moreover, slightly biased towards higher discharges; it is only a first

TABLE 2. Seasonal budgets of the riverine inputs of carbon into the Loire estuary (1982–85)[a]

	Jan.–Mar.	Apr.–Jun.	Jul.–Sep.	Oct.–Dec.	Year	
					mg l^{-1}	t year^{-1}
Suspended matter						
Total (mg l^{-1})	28	44	41	41	35·5	1175
(kg s^{-1})	50	48	16	35		
Inorganic SM[e] mg l^{-1}	24·5	34	30	33	29	960
Detrital PIC[c] (mg l^{-1})	0·15	0·20	0·18	0·20	0·175	5·8
Autochthonous PIC[c] (mg l^{-1})	0	0·4	0·7	0·5	0·4	13
Algal POC[d]						
(mg l^{-1})	0·62	2·6	3·1	2·1	1·65	55
(% SM)	2·15	5·9	7·55	5·0	4·65	
(kg s^{-1})	1·15	2·85	1·2	1·8	1·75	
Non-algal POC						
(mg l^{-1})	0·84	1·3	1·5	1·5	1·05	38
(% SM)	3·0	3·0	3·0	3·0		
(kg s^{-1})	1·5	1·45	0·58	1·3	1·2	
DOC						
(mg l^{-1})	5·65	5·05	4·1	5·45	5·3	175
(kg s^{-1})	10·4	5·6	1·7	4·7	5·6	
TOC (mg l^{-1})	7·08	8·95	8·7	9·05	8·1	268
River discharge[b] ($m^3 s^{-1}$)	1840	1100	390	860	1050	
Algal POC/TOC (%)	8·8	29	36	24	21	

[a] Based on 13 surveys at all seasons.
[b] Mean seasonal discharge of the 13 surveys.
[c] Based on the Manickam $CaCO_3$ survey (1982), see text.
[d] Assuming POC = 30 × total pigments.
[e] Total SM − 2·5 total POC.

attempt. Due to the various non-conservative behaviours of nutrients, the actual inputs to the ocean are calculated on the basis of nutrients levels and chlorinities measured not at the FSI but at station A (Saint Nazaire), assuming that nutrients are generally conservative in the outer estuary. The marine water proportion at station A is moderate: average value 20%, extreme values 1·4% (March 1983) and 52% (May 1984) for 11 surveys at low tide. It is also postulated that surface nutrient concentrations at a given salinity are not much different from those found in deeper waters of the estuary (when a saline stratification occurs) at similar salinities. The actual continental reference value is based on concentrations observed at station A and computed as explained in Figure 3. When comparing the average dissolved loads measured in the river to the actual load to the ocean for all available surveys, additional fluxes of phosphates (+70%) and ammonia (+180%) are found, while silica and nitrate fluxes do not present any significant increase and the POC flux is 60% depleted (Table 3).

Conclusions

(1) In the highly eutrophied Loire River, dissolved silica and phosphate, and to a lesser extent nitrate, are regulated by phytoplankton uptake. The particulate carbon levels are also closely linked to this season cycle: algal POC is maximum in summer, together with PIC due to $CaCO_3$ precipitation. Non-algal POC is directly related to inorganic detrital material, both originating from soil erosion occurring in winter.

TABLE 3. Actual inputs of Loire nutrients to the ocean

	Nutrient					
	POC	DOC	SiO_2	P-PO_4^{3-}	N-NH_4^+	N-NO_3^-
Average river flux ($\times 10^9$ g year^{-1})	90	175	410	3·3	1·6	90
Estimated continental flux to ocean ($\times 10^9$ g year^{-1})	35		370	5·55	4·5	90
No. of surveys considered	13		11	11	11	9
Actual flux—river flux ($\times 10^9$ g year^{-1})	−55[d]	NS[a]	*NS*	+2·25	+2·9	0
Total anthropic input ($\times 10^9$ g year^{-1})	1·4[e]	1·4[e]	0·8[c]	0·5[c]	2·0[b]	

[a] Cauwet (pers. comm.).
[b] Rincé *et al.* (1985).
[c] Nantes city only.
[d] Assuming all algal POC is degraded in the inner estuary.
[e] CSEEL (1984).

(2) The behaviour of dissolved nutrients in the estuary here observed at low tide is highly variable from one nutrient to another, from one estuarine section to another, and also from one survey to another. The major process involved is the degradation of the enormous amount of algal POC inherited from the river (yearly average 1·65 mg l^{-1} or 55 000 t year^{-1}) which regenerates silica, phosphate and ammonia in the most turbid section of the estuary, while nitrate is conservative or depleted. In the outer estuary, the nutrients' behaviour is much more conservative. Such high variability in nutrient patterns has seldom been described in estuarine systems, although this is sometimes due to the paucity of surveys, particularly during or after peculiar hydrological and/or biological events.

(3) The non-conservative patterns are mostly observed in summer during the low river water stage. The additional fluxes (water discharge-weighted) are estimated to be of the order of +70% for PO_4^{3-} and +180% for ammonia, on an annual basis. These increases are much less than those expected from concentration profiles in which the theoretical continental end-member can exceed, in summer, the measured river contents by a factor of 2 (silica), 5 (PO_4^{3-}), or 10 (NH_4^+). Nitrate, the least variable nutrient, is often depleted due to possible denitrification. However, nitrate and silica annual budgets to the ocean are not significantly affected by estuarine processes.

(4) Very careful attention must be given to the upper-inner estuary, upstream of the FSI, here defined as a 100% Cl^- increase: the phytoplankton degradation may occur 20 km upstream of the FSI as soon as the suspended matter increases. Similar patterns have been found in the Amazon by Edmond *et al.* (1981) upstream of the FSI. However, major nutrient excess and dissolved oxygen depletion are found in the HTZ, generally at low tide 10–15 km downstream of the FSI, in the lower-inner estuary ($0{\cdot}3 < Cl^- < 1{\cdot}5$ g l^{-1}).

(5) Since the major changes in water chemistry (POC content of SM, nutrient levels, pH, dissolved oxygen, etc.) are observed in the lower salinity region which extends over a 50-km stretch, the classical approach (Liss, 1976; Aston, 1979) based only on

the concentrations *vs.* salinity relationship cannot be applied and must be replaced by longitudinal isochronous profiles (Edmond *et al.*, 1981; Morris *et al.*, 1978).

(6) The interpretation of longitudinal profiles is often difficult due to various anthropogenic inputs from urban and industrial (fertilizer plants) origins. An unexpected source of ammonia and Cl^- is found at Cordemais where an important electrical power plant is located. However, some of these anthropogenic inputs are probably of secondary importance when compared to natural processes.

(7) Unusual hydrological events (major floods in summer, drought in December) may cause marked deviations from the usual seasonal or longitudinal patterns.

(8) The biogeochemical characterization of the Loire estuary is highly dependent on River's hydrodynamic factors. In winter, during major floods, the inner estuary may not be characterized by a HTZ since all suspended matter is flushed into the outer estuary, a pattern similar to that of river deltas, such as the Rhône river. A rare event occurred one month after an unusual late-spring (May 1985) flood and during a neap-tide period: the whole estuary was characterized by very low suspended matter content (SMC < 100 mg l^{-1}), but highly organic due to a planktonic bloom continuously observed from the river to the ocean, a pattern closer to that found in the U.S. east-coast estuaries, and only observed here once out of 13 surveys.

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References

AFBLB Annuaires de qualité des eaux des rivières et canaux. Agence Financière de Bassin Loire Bretagne, Orléans.

Allen, G. P., Salomon, J. C., Bassoullet, B., Du Penhoat, Y. & De Grand Pre, C. 1980 Effects of tides on mixing and suspended sediment transport in macrotidal estuaries. *Sedimentary Geology* **26**, 69–90.

Anonymous 1978 *Netherlands Journal of Sea Research* **12**, 3–4.

Aston, S. R. 1979 Estuarine chemistry. In: *Chemical Oceanography, Vol. VII* (Riley, J. P. & Chester, R., eds). New York: Academic Press, pp. 362–440.

Bennekom, A. J. van, Krijgsman van Hartingsveld, E., Der Veer, G. C. M. van & Voorst, H. F. J. van 1974 The seasonal cycle of reactive silicate and diatoms in the Dutch Wadden Sea. *Netherlands Journal of Sea Research* **8**, 174–207.

Bennekom, A. J. van, Berger, G. W., Helder, W. & DeVries, R. T. P. 1978 Nutrient distribution in the Zaire estuary and river plume. *Netherlands Journal of Sea Research* **12**, 296–323.

Biggs, R. B., Sharp, J. H., Church, T. M. & Tramontano, J. M. 1983 Optical properties, suspended sediments, and chemistry associated with the turbidity maximum of the Delaware estuary. *Canadian Journal of Fisheries and Aquatic Science* **40** (Suppl. 1), 172–179.

Billen, G., Cauwet, G., Dessery, S., Meybeck, M. & Somville, M. 1986*a* Origines et comportement du carbone organique dans l'estuaire de la Loire. *Rapport P.-V. Réun. Cons. Int. Exploration de la Mer* **186**, 375–391.

Billen, G., Lancelot, C., De Becker, E. & Servais, P. 1986*b* The terrestrial–marine interface: modelling nitrogen transformations during its transfer through the Scheld river system and its estuarine zone. In: *Marine Interface Ecohydrodynamics*. (Nihoul, J. C. J., ed.). *Elsevier Oceanographic Series* 42, 429–452.

Cadée, G. C. 1982 Tidal and seasonal variation in particulate and dissolved organic carbon in the Western Dutch Wadden Sea and Marsdiep tidal inlet. *Netherlands Journal of Sea Research* **15**, 228–249.

Callender, E. & Hammond, D. E. 1982 Nutrient exchange across the sediment-water interface in the Potomac river estuary. *Estuarine, Coastal and Shelf Science* **15**, 395–413.

Cauwet, G. 1984 Automatic determination of dissolved organic carbon in sea water in the subppm range. *Marine Chemistry* **14**, 97–309.

Cauwet, G. & Meybeck, M. 1987 Seasonal fluctuations of carbon levels in a temperate river, Loire river (France). In: *Transport of Carbon and Minerals in World Major Rivers. Part IV. Mitt. Geol. Paläont. Inst., Univ. Hamburg, SCOPE/Unep Sonderband*, **64**, 349–357.

Crouzet, P. 1983 L'eutrophisation de la Loire. *Water Supply* **1**, 131–144.

CSEEL 1984 Comité Scientifique pour l'Environnement de l'Estuaire de la Loire. Rapport final. *Rapports Science et Technogie CNEXO No. 55*.

D'Elia, C. F., Nelson, D. M. & Boynton, W. R. 1983 Chesapeake Bay nutrients and plankton dynamics: III. The annual cycle of dissolved silicon. *Geochimica et Cosmochimica Acta* **47**, 1945–1955.

Delmas, R. & Treguer, P. 1983 Evolution saisonnière des nutriments dans un ecosystème eutrophe d'Europe occidentale (La Rade de Brest). Interactions marines et terrestres. *Oceanologica Acta* **6**, 345–355.

Dessery, S., Dulac, C., Laurenceau, J. M. & Meybeck, M. 1984 Evolution du carbone organique particulaire 'algal' et 'détritique' dans trois rivières du Bassin Parisien. Archiv Hydrobiol. **100**, 235–260.

Diara, M. 1983 Echanges hydrologiques et sédimentologiques entre l'.estuaire de la Loire et ses zones marginales. Thèse de 3ème Cycle, Université de Nantes.

Edmond, J. M., Boyle, E. A., Grant, B. & Stallard, R. F. 1981 The chemical mass balance in the Amazon plume. I: the nutrients. *Deep Sea Research* **28A**, 1339–1374.

Eisma, D., Cadée, G. C., Laane, R. & Kalf, J. 1982 Preliminary results of Aurelia and Navicula cruises in the Rhine and Ems estuaries, Jan.–Feb. 1982. *Mitt. Geol. Paläont. Inst., Hamburg, SCOPE/Unep Sonderband*, **52**, 633–653.

Etcheber, H. 1983 Biogéochimie de la matière organique en milieu estuarien: comportement, bilan, propriétés. Cas de la Gironde. Thèse Doctorat d'Etat, Bordeaux.

Etcheber, H. & Relexans, J. C. 1983 Nature et répartition de la matière organique particulaire sur le plateau continental au large de l'estuaire de la Gironde. *Ann. Institut Oceanogr., Paris* **59**, 5–19.

Fox, L. E., Sager, S. L. & Wofsy, S. C. 1986 The chemical control of soluble phosphorus in the Amazon estuary. *Geochimica et Cosmochica Acta* **50**, 783–794.

Friedrich, G. & Viehweg, M. 1984 Recent development of the phytoplankton and its activity in the Lower Rhine. *Verhandlung Int. Vereiningung Limnologie* **22**, 2029–2035.

Gallenne, B. 1974 Les accumulations turbides de l'estuaire de la Loire. Etude de la crème de vase. Thèse de 3ème Cycle. Université de Nantes.

Guillaud, J. F. 1983 La qualité des eaux dans l'estuaire de la Loire. Unpublished report, CNEXO-COB, Ste Anne du Portzic.

Kaul, L. W. & Froelich, Jr, P. N. 1984 Modeling estuarine nutrient geochemistry in a simple system. *Geochimica et Cosmochimica Acta* **48**, 1417–1433.

Khalanski, M. 1984 Evaluation de la biomasse phytoplanctonique des eaux courantes par le dosage de la chlorophylle. *Verhandlung Int. Vereiningung Limnologie* **22**, 2010–2019.

Knox, S., Whitfield, M., Turner, D. R. & Liddicoat, M. I. 1986 Statistical analysis of estuarine profiles. III. Application to nitrate, nitrite and ammonium in the Tamar estuary. *Estuarine, Coastal and Shelf Science* **22**, 619–636.

Le Douarec, P. 1978 L'intrusion saline dans l'estuaire de la Loire. Thèse de 3ème Cycle, Université de Nantes.

Liss, P. S. 1976 Conservative and non-conservative behaviour of dissolved constituents during estuarine mixing. In: Estuarine Chemistry (Burton, J. D. & Liss, P. S., eds). London: Academic Press, pp. 93–130.

Lorenzen, C. J. 1967 Determination of chlorophyll and phaeopigments: spectrophotometric equations. *Limnology and Oceanography* **6**, 343–346.

Lucotte, M. & D'Anglejan, B. 1983 Forms of phosphorus and phosphorus-iron relationships in the suspended matter of the St Lawrence estuary. *Canadian Journal of Earth Science* **20**, 1880–1890.

Mackay, D. W. & Leatherland, T. M. 1976 Chemical processes in an estuary receiving major inputs of industrial and domestic wastes. In: *Estuarine Chemistry* (Burton, J. D. & Liss, P. S., eds). London: Academic Press, pp. 185–218.

Manickam, S. 1982 Etude hydrologique et sédimentologie de la zone de transition entre la Loire fluviale et l'estuaire. Thèse de 3ème Cycle, Université de Nantes.

Manickam, S., Barbaroux, L. & Ottmann, F. 1985 Composition and mineralogy of suspended sediment in the fluvio-estuarine zone of the Loire river, France. *Sedimentology* **32**, 721-741.

Mantoura, R. F. C. & Woodward, E. M. S. 1983 'Conservative behaviour of riverine dissolved organic carbon in the Severn estuary: chemical and geochemical implications. *Geochimica et Cosmochimica Acta* **47**, 1293-1310.

Marchand, M., Tronczinski, J., Caprais, J. C., Marty, J. C., Scribe, P., Saliot, A. Transport of organic pollutants in estuarine environment. Levels, behaviour and fluxes of hydrocarbons and halogenated hydrocarbons in the Loire estuary. *Estuarine, Coastal and Shelf Science* (submitted).

Appendix 2. Nutrient levels (mg l^{-1}) at key stations in the Loire estuary (surface waters, low tide)

	Jun. 1982	Nov.–Dec. 1982	Feb.–Mar. 1983	May 1983	Sept. 1983	Nov. 1983	Jan. 1984	Apr. 1984	May 1984	Jun. 1984	Aug. 1984	Feb. 1985	Jun. 1985
River		—[e]		—[e]						—[e]			—[e]
SiO_2	6·3	12·3	10·5	10·2	5·35	8·07	10·9	8·40	4·50	10·6	2·15	10·5	6·04
$N–NO_3^-$	0·81	2·48	3·82	1·47	1·68	2·72	2·80		2·80	1·82		3·76	1·95
$N–NH_4^+$	0·013	0·049	0·062	0·024	0·008	0·11	0·106		0·039	0·018		0·056	0·010
$P–PO_4^{3-}$	0·015	0·090	0·080	0·069	0·046	0·097	0·105	0·083	0·035	0·105	0·010	0·091	0·007
POC	6·0	1·9	3·0	2·3	6·2	3·05	3·7	2·4	3·1	3·0	5·45	2·42	6·8
Freshwater–saline water interphase[a]													
Station	G	D	C	C[d]	E	H–I	D	H–I[b]	H–I[b]	D		H–I	D
SiO_2	6·15	12·35	10·45	8·76	5·57	See	11·3	8·4	4·3	10·9		10·7	6·15
$N–NO_3^-$	0·91		4·16	0·132	1.57	below	3·5		2·80	1·74		3·49	2·0
$N–NH_4^+$	0·03		0·113		0·27		0·26		0·070	0·024		0·10	0·10
$P–PO_4^{3-}$	0·073	0·175	0·048	0·096	0·060		0·057	0·32	0·059	0·115		0·108	0·051
POC	6·8	9·55	12·5	3·56	29·2		21·1	2·45	5·15	4·0		3·95	6·25
Maximum turbidity[a]													
Station	D	C	A	A	C	H–I[b,c]	B	C[c]	C[c]	C	H–I[c]	A[e]	D
SiO_2	9·65	15·5	11·1	7·50	5·8	7·32	11·2	7·1	4·2	10·6	4·95	8·2	See FSI
$N–NO_3^-$	0·55	2·18	4·10	1·26	1·09	4·44	3·57			1·89			
$N–NH_4^+$	0·115	0·063	0·11	0·013	0·008	0·14	0·17			0·053		0·15	
$P–PO_4^{3-}$	0·13	0·093	0·055	0·105	0·091	0·123	0·081	0·085	0·024	0·13	0·050	0·085	
POC	8·15	21·55	30·4	5·30	29·2	29·0	17·7	4·45	51·0	17·7	7·5	8·6	
Cl	850	540	300	1450	1370	25	213	4580	2700	350		3330	
Oceanic reference[a]													
SiO_2	1·0		1·16	0·57	1·7		1·48			0·51			0·59
$N–NO_3^-$	0·075		0·52	0·145	0·125		0·60			0·00			0·010
$N–NH_4^+$	0·025		0·00		0·045		0·22			0·032			0·008
$P–PO_4^{3-}$	0·020		0·015	0·045	0·041		0·028			0·035			0·003
POC	0·42		1·32	0·78	0·47		0·37			0·385			0·52
Cl^-	17 500		18 100	15 270	16 650		15 900			17 750			19 700

Where oceanic references are missing, sampling was limited to the inner estuary.

[a] See Appendix 1 and Figure 1 for exact location and characteristics.

[b] Exact FSI and HTZ not located, see Appendix 1.

[c] Still upstream of the FSI!

[d] Wrongly reported at station E in Billen *et al.* (1986).

[e] Odd hydrological event in river or in estuary, see text.

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Algal and Microbial Processes Involved in Particulate Organic Matter Dynamics in the Loire Estuary

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Keywords: biomass; estuaries; heterotrophic activity; ETS activity; particulate organic carbon (POC); pigments; primary production

Algal and bacterial biomass and activities have been studied in the Loire estuary (France) by means of particulate organic matter proteins and chlorophyll pigments determination, electron transport system activity measurement, ^{14}C-bicarbonate incorporation and tritiated thymidine incorporation determination. These data collected throughout the estuary in various hydrological conditions allow to characterize two opposite typical situations: (i) During winter and early spring, when discharge increases beyond 1000 m^3 s^{-1}, heterotrophic activity always dominates over primary production but remains moderate because of low temperature and non-biodegradable quality of organic carbon; (ii) at drought situations, phytoplankton production develops in the river causing increases of pH and oxygen concentration. In these situations, accumulation of phytoplanktonic material in the highly turbid inner estuary results in very high heterotrophic activities causing pH decrease and complete depletion of dissolved oxygen.

Budgets of POC show that the anthropogenic inputs contribute only for less than 5% to the organic load of the inner estuary.

Introduction

Estuaries constitute a major interface between land and ocean. Biogeochemical processes occurring in such environments greatly affect the fate of material originating upstream (Head, 1976; Reuter, 1981). This influence is particularly important for organic material: depending on estuarine conditions, production of autochthonous material or degradation of allochthonous matter will dominate. Major chemical conditions (pH, redox conditions) are directly dependent on this autotrophic/heterotrophic balance. Therefore, studies of primary production and heterotrophic activities in estuaries are important for correctly assessing the river inputs to the ocean as well as for understanding the conditions

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