Nitrogen compounds
Particulate matter
Estuary
Mixing diagram
Bay of Brest

Azote
Diagramme de mélange
Écosystème estuarien
Matière particulaire
Rade de Brest

Seasonal variations in conservative and nonconservative mixing of nitrogen compounds in a West European macrotidal estuary

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ABSTRACT

Seasonal variations in concentrations of DIN (dissolved inorganic nitrogen: nitrate + nitrite, and ammonium), total DON (dissolved organic nitrogen), urea, PON (particulate organic nitrogen), chlorophyll *a*, pheophytin and total suspended matter were measured from September 1983 to July 1984 in a partially mixed, macrotidal estuary (Aulne river, France). Owing to such striking features as the low, although extremely variable annual mean river flow, the high inputs of auxiliary energy originating from tidal action, and the heavy inorganic nitrogen loading caused by the intensive use of the drainage basin for agriculture and cattle rearing, the studied estuary appeared as a typical estuarine system of the West European coastal ecosystems. The major component of freshwater DIN was found to be nitrate nitrogen, whose levels and fluxes varied respectively between 90 µM-N and 0.2 T N d^{-1} in summer to 470 µM-N and 28 T N d^{-1} in winter. Conservative distribution of nitrate along the estuary was generally encountered, except during summer and autumn. Ammonium nitrogen, representing only 1-10% of freshwater DIN, exhibited typical spatial patterns, characterized by high maximum concentrations in the middle of the estuary, which were interpreted as resulting mainly from the biological processes occurring at the water-sediment interface. Estuarine DON levels increased from winter (10 µM-N) to summer (40 µM-N), respectively accounting for 1 to 40% of total dissolved nitrogen, while urea concentrations never exceeded 3 µM-N. Particulate matter distribution was strongly dependent upon tidal action: particulate organic nitrogen concentrations as high as 1,400 µmol N l^{-1} were recorded at the turbidity maximum, under spring-tide conditions. The POC/PON molar ratio decreased from 8.6 during winter to 6.6 during summer when 65-80% of POC came from algal production. Despite intense nitrogen loading, estuarine waters appeared well oxygenated all year round: intense tidal action favours water oxygenation, providing suitable conditions to inhibit the emergence of long-lasting ecological imbalance.

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RÉSUMÉ

Conservativité et non conservativité du mélange des composés de l'azote dans un estuaire macrotidal d'Europe occidentale

Les variations saisonnières de l'azote organique dissous (DIN : nitrate + nitrite, ammonium), de l'azote organique total dissous (DON), de l'urée, de l'azote et du carbone organique particulaire (PON et POC), de la chlorophylle *a* et de la phéophytine, et de la matière totale en suspension (TSM) sont étudiées, pendant la période septembre 1983-juillet 1984, dans un estuaire macrotidal (fleuve Aulne, France). A l'écart des grandes concentrations urbaines, cet estuaire est typique de l'Europe Occidentale du fait : de son débit, faible à l'échelle annuelle mais extrêmement variable aux échelles journalière et saisonnière; du rôle joué par l'énergie auxiliaire dissipée

par les courants de marée sur la distribution des matériaux; et des fortes charges d'azote organique et minéral du bassin versant en raison d'une activité agricole intensive (notamment les élevages). Les apports fluviaux d'azote sont dominés par les nitrates dont concentrations et flux varient respectivement de 90 µM-N et 0,2 T N j^{-1} en été à 470 µM-N et 28 T N j^{-1} en hiver. La distribution des nitrates est conservative en hiver mais non conservative en été et en automne. L'ammonium, qui représente seulement 1 à 10% du DIN dans l'eau douce, révèle une distribution caractéristique « en cloche » avec un maximum dans l'estuaire moyen; ceci est interprété comme résultant principalement d'apports par recyclage à l'interface eau-sédiment. Les teneurs en DON dans l'estuaire varient de 10 µM-N en hiver à 40 µM-N en été, contribuant respectivement à 1 et 40% du stock d'azote total dissous. Les concentrations en urée n'excèdent jamais 3 µM-N. La distribution de la matière particulaire est essentiellement fonction des courants de marée : des teneurs aussi élevées que 1 400 µmol N l^{-1} ont été mesurées dans le bouchon vaseux, en période de vives-eaux. Les rapports moyens POC/PON s'abaissent de 8,6 à 6,6 de l'hiver à l'été où 65 à 80% du POC est d'origine algale. En dépit de la forte charge de cet estuaire en azote nitrique, les eaux restent bien oxygénées tout au long de l'année en raison du brassage périodique des eaux par les courants de marée. Ce type d'estuaire ne présente pas, actuellement, de signe de déséquilibre écologique global et durable.

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INTRODUCTION

This work assesses the seasonal dynamics of dissolved and particulate nitrogen in the macrotidal estuary of the Aulne River (France). In presenting new information about those West European littoral systems which have been hitherto insufficiently documented in spite of their uniqueness, we endeavour to contribute to the knowledge of dynamical processes affecting nutrient mixing in brackish waters. Such typical ecosystems exhibit the following common features: distance from urban and industrial outfalls (Martin *et al.*, 1980; Skeslet, 1986); prevailing use of river drainage basin by intensive agriculture (Tréguer *et al.*, 1985; Riaux-Gobin, 1985); impermeability of soils (mainly crystalline and metamorphic geological composition) which receive heavy and variable rainfalls supplying small river networks (mean individual annual flow not exceeding 50 m^3 s^{-1} for drainage basin below 3,000 km^2) leading in consequence to rapid pollutant transfer in the marine environment (Delmas and Tréguer, 1983); finally, importance of the auxiliary energy dissipated in the coastal zone (intense tidal currents) which results in large extended turbidity maximum area (Bassoulet, 1979; Uncles *et al.*, 1985).

The main questions arising from the studying of such systems are the following: are distributions of dissolved compounds conservative or not? How broad is the range of seasonal variations in nutrient inputs to the adjacent marine ecosystem? How widely do particulate matter levels vary according to the different tidal conditions? In conclusion, are such ecosystems showing evidence of ecological imbalance?

MATERIAL AND METHODS

Description of the studied area

The Aulne River is the main river discharging into the Bay of Brest (Fig. 1), a coastal marine ecosystem

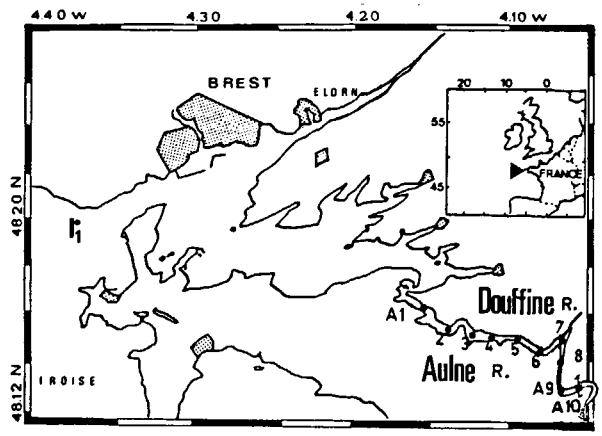

Figure 1

Location of the studied area. The Aulne River is located south of Brest (France, Western Europe). Station A10, Guily-Glas lock, is the limit of the saline tide; station A7 is the oultet of the main tributary (Douffine River); station I1 is located at the Bay of Brest outlet.

Localisation de l'estuaire de l'Aulne, dans la rade de Brest (France, Europe occidentale).

characterized by strong tidal mixing due to the periodical (semidiurnal and fortnightly frequencies) tidal action (average tide height: 4 m). The river drains a 1,660 km^2 area which receives heavy and variable rainfalls (range: 800-1,000 mm per year). Its annual mean flow is 28 m^3 s^{-1}, but large fluctuations of daily water flow occur on a seasonal scale (reaching up to 250 m^3 s^{-1} during high-water flow in winter; decreasing to below 1 m^3 s^{-1} in summer). Salt wedge intrusion is restricted to the lower estuary by the Guily-Glas lock (station A10), 25 km from the mouth of the river (Fig. 1). The depth of the estuary gradually increases from 2.5 m at Guily-Glas to 15 m at the river mouth (Delmas and Tréguer, 1983). Due to seasonal variations in river flow, this estuary appears as a well-mixed system in summer and a stratified system in winter, the stratification being also favoured by neap tide conditions. The flushing time ranges between about 3 and

30 days from high-water to low-water periods (Bassoulet, 1979; SAUM, 1980).

Sampling and filtrations

Ten stations along a transect (Fig. 1) were monitored from September 1983 to July 1984 on seven occasions representative of the seasonal cycle previously described for the adjacent marine ecosystem: the Bay of Brest (Quéguiner and Tréguer, 1984). The research vessel was moored at station A_1 and transects between A_1 to A_{10} were conducted within two hours near high tide slack water, using a fast-moving rubber boat.

Surface and bottom waters were collected at each station using acid precleaned 5-1 Niskin samplers. During the transects, sampling and fixation were performed immediately on the rubber boat, while filtrations were carried out on board the research vessel. Filtered water samples were stored in acid precleaned glass bottles, previously washed with deionized water; suspended matter samples were stored in glass Petri dishes and immediately frozen (−20°C).

Analytical methods

Temperature measurements were made using Richter and Wiese thermometers (precision: ±0.01°C) at station A_1 and laboratory thermometers (precision: ±0.1°C) at other stations. Chlorosity (Cl l^{-1}) and salinity (g kg^{-1}) were determined according to the Mohr-Knudsen method (precision: ±0.01 Cl l^{-1}). Oxygen concentrations were determined by the Winkler method (precision: ±0.02 ml O_2 l^{-1}).

Nutrient and dissolved organic matter concentrations were made after filtration on precombusted (at 450°C for one hour) Whatman GF/C glass fibre filters. Samples for ammonium determinations were immediately fixed on board and measurements performed using the method of Koroleff (1969) (precision: ±0.05 µM-N). A Technicon AutoAnalyzer II was used for the determination of nitrate+nitrite (precision at the 10 µM-N level: ±0.01 µM-N, Tréguer and Le Corre, 1975) and urea (precision: ±0.05 µM-N, Aminot and Kérouel, 1982). Total dissolved organic nitrogen (DON) was measured following the photooxidation method (Armstrong *et al.*, 1966) under conditions described by Le Jehan and Tréguer (1984) (blanks: <0.1 µM-N, photooxidation efficiency: 0.86-0.96, precision: ±1 to ±2 µM-N respectively at 10 and 50 µM-N levels).

For total suspended matter (TSM) determination, 50 to 1,000 ml water were filtered on pre-weighed Whatman GF/C filters and measurements were performed by further weighing (precision: ±0.05 mg l^{-1}). For particulate organic carbon (POC) and nitrogen (PON), 50 to 1,000 ml water were filtered on precombusted Whatman GF/C filters and further measurements were made using a Hewlett Packard HP185 CHN analyzer (precision: ±5%). 50 to 200 ml water were filtered on Whatman GF/C filters for chlorophyll *a* and pheophytin using the fluorimetric method of Yentsch and Menzel (1963): the 6-ml acetonic extract was acidified by 0.015 ml HCl 1N according to Hafsaoui (1984).

River flow data were obtained from the *Service Hydrologique Centralisateur Loire-Bretagne* (Nantes, France). Values of the tidal coefficient, ranging between 20 (neap tide minimum) and 120 (spring tide maximum), were obtained from the *Service Hydrographique et Océanographique de la Marine* (Brest, France).

RESULTS

Winter situation

Measurements conducted on 6 and 10 April 1984 are representative of winter conditions (respective freshwater flows: 56 and 34.6 m^3 s^{-1}, and temperatures: 8-10°C). The first transect was conducted under mid-tide conditions (tidal coefficient, t. c.: 69), the second during neap tide (t. c.: 43). The flushing time is estimated to be respectively 5 and 7 days for the first and second cruises.

Nitrate+nitrite dilution plots are similar for both cruises, as shown in Figure 2*a* which indicates conser-

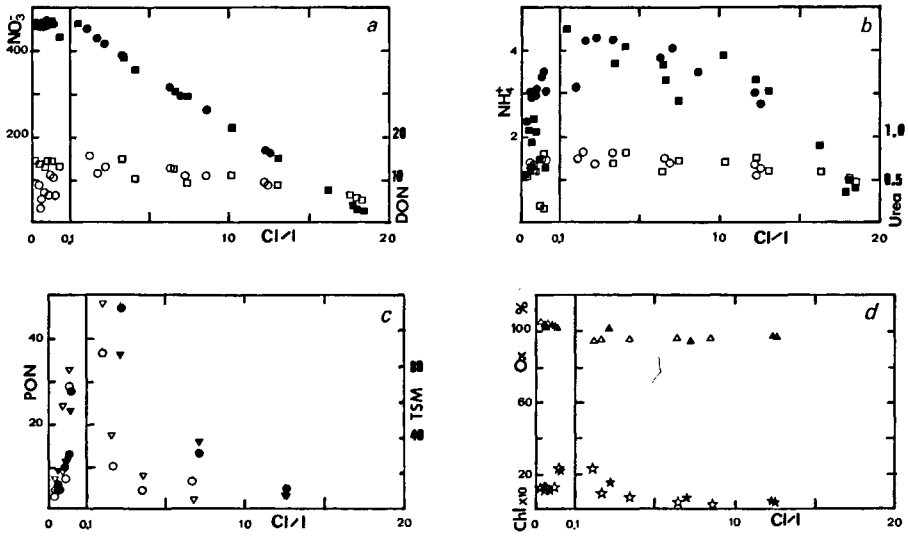

Figure 2

Aulne estuary, winter situation: 6 and 10 April 1984. Mixing diagrams (concentrations of the parameters versus chlorosity, in Cl/l).
a) nitrate (+nitrite) in µM−N (● 4 6 84) (■ 4 10 84) and DON (○ 4 6 84) (□ 4 10 84);
b) ammonium in µM−N (● 4 6 84) (■ 4 10 84) and urea in µM−N (○ 4 6 84) (□ 4 10 84);
c) PON in µmol/l (4 6 84: ▽ surface; ▼ bottom) TSM in mg/l (4 6 84: ○ surface; ● bottom);
d) chlorophyll-a in mg/m³ (4 6 84: ☆ surface; ★ bottom) oxygen sat.% (4 6 84: △ surface; ▲ bottom).

Estuaire de l'Aulne en hiver. Diagrammes de mélange.

Table 1
The turbidity maximum in Aulne River: characteristics of estuarine water.
Caractéristiques de l'eau estuarienne au niveau du bouchon vaseux (fleuve Aulne).

Season	Date	Flow ($m^3 s^{-1}$)	t. c.	TSM ($mg l^{-1}$)	PON ($\mu mol l^{-1}$)	Chl. *a* ($mg m^{-3}$)	Pheo. ($mg m^{-3}$)	Ox. Sat. (%)
Winter	04/06/84	56.0	69	114	37.0	1.64	6.65	102
	04/10/84	34.6	43	15.9	16.0	0.37	1.44	95
Spring	04/11/83	63.5	56	59.3	26.8	2.80	6.40	85
	04/18/84	28.6	98	4,456	1,430	22.6	90.2	17
Summer	07/09/84	2.0	63	97.0	67.0	39.2	31.3	64
Autumn	05/09/83	2.7	80	87.0	–	–	–	77
	10/26/83	5.9	79	242	121	8.79	35.6	61

vative distribution along the estuary. Freshwater nitrate concentrations are 16 times higher in comparison with seawater, which is in agreement with previous observations (Delmas and Tréguer, 1983). Although noticeable variations in freshwater DON and urea concentrations are evidenced in Figures 2*a* and 2*b*, the dilution plots of these parameters appear almost linear. DON concentrations, never exceeding 20 µM-N, account for only 2-3% of total (inorganic and organic) dissolved nitrogen in freshwater when they represent 8-16% in seawater. The urea/DON molar ratio ranges between 0.05-0.22. In both transects, ammonium distribution is nonconservative, showing a large maximum at the middle estuary level. The ammonium maximum (Fig. 2*b*) begins at the turbidity maximum area (Fig. 2*c*) and might be initiated by oxic degradation of PON and DON in the water column. However, according to Knox *et al.* (1981; 1983) the downstream extent of this ammonium maximum can be interpreted as resulting mainly from fluxes at the water-sediment interface.

Unlike dissolved nitrogen compound distributions, particulate matter (TSM, PON, chlorophyll *a*, Fig. 2*c* and *d*) longitudinal profiles are strongly influenced by tide conditions. Concentrations in estuarine water appeared fairly higher during the first transect which corresponded to a higher tidal coefficient and hence stronger tidal currents, as compared to the second transect: recorded values at the turbidity maximum respectively reached 114 and 16 mg TSM l^{-1}, 37 and 16 µmol PON-P l^{-1} (Tab. 1, Fig. 2*c*), 1.64 and 0.37 mg chlorophyll *a* m^{-3}, during the first and second winter cruises. Figure 2*c* shows that the turbid area, although characterized by maximum TSM values at the transition between brackish- and freshwater, largely extends downstream, which is a noteworthy feature of macrotidal estuaries (Bassoulet, 1969; Uncles *et al.*, 1985).

In both winter transects, despite high nutrient loading, phytoplankton biomasses reach low levels, reflecting growth limitation by low temperature and available light (Quéguiner and Tréguer, 1984). Pheophytin concentrations are thus higher than chlorophyll *a* concentrations (*e. g.* chlorophyll *a*/pheophytin = 0.25 at the turbidity maximum, *see* Tab. 1). As displayed in Figure 2*d*, estuarine water however remains almost oxygen-saturated.

Spring situation

Transects conducted on 11 April 1983 and 18 April 1984 were characterized by spring conditions, *i. e.* initial warming of estuarine water with a temperature of nearly 12°C, while mean daily river flows maintain relatively high values: respectively 63.5 and 28.6 $m^3 s^{-1}$ in 1983 and 1984, corresponding to flushing times of 4 and 8 days.

For the first transect (April 1983), conducted under nearly mid-tide conditions (t. c.: 56), nitrate removal by means of algal assimilation is clearly indicated in Figure 3*a*. On the one hand, freshwater nitrate concentrations, not exceeding 370 µM-N, appear much lower than the winter maximum value previously measured

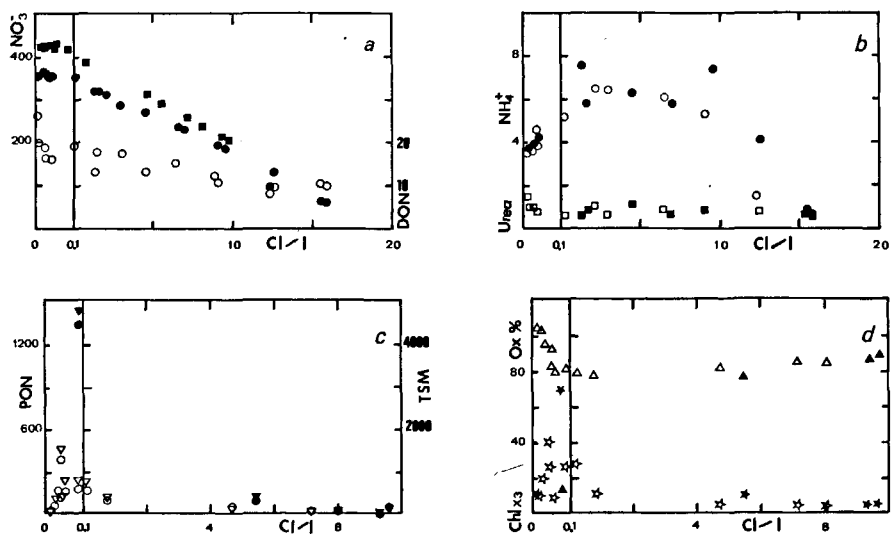

Figure 3
Aulne estuary, spring situation: 11 *April* 1983 *and* 18 *April* 1984. *Mixing diagram* (*concentrations of the parameters* versus *chlorosity in Cl/l*).
a) nitrate (+*nitrite*) *in* µ*M*−*N* (● 4 11 83) (■ 4 18 84) *and DON in* µ*M*−*N* (○ 4 11 83);
b) ammonium in µ*M*−*N* (4 11 83: ○ *surface;* ● *bottom*) *urea in* µ*M*−*N* (4 11 83: □ *surface;* ■ *bottom*);
c) PON in µ*mol/l* (4 18 84: ▽ *surface;* ▼ *bottom*) *TSM in mg/l* (4 18 84: ○ *surface;* ● *bottom*);
*d) Chlorophyll-a in mg/m*³ (4 18 84: ☆ *surface;* ★ *bottom*) *oxygen sat.%* (4 18 84: △ *surface;* ▲ *bottom*).
Estuaire de l'Aulne au printemps. Diagramme de mélange.

(Delmas and Tréguer, 1983), this corresponding to low oxygen supersaturation (100-103%). On the other hand, nitrate is removed from estuarine water where negative anomalies (deviations from straight-lined dilution plots) ranging from 10 to 20 µM-N are evidenced. However, it must be pointed out that the water renewal is faster than the phytoplankton development: this permits nitrate anomalies to be, quite rapidly, evenly distributed along the whole estuary, and thus results in an almost straight dilution plot.

During the second transect (April 1984), the nitrate distribution, shown in Figure 3 *a*, exhibits the same trend as in the winter situation: freshwater concentration near the winter maximum and the linear dilution plot are indicative of conservative behaviour. Although this may be explained by a lag in spring condition emergence (due to lower incident light as compared to 1983), this may also result from the tidally-induced sediment resuspension (Fig. 3 *c*, Tab. 2) that limits light penetration, since this transect was performed under spring-tide conditions (t. c.: 98).

For both transects, Figure 3 *b* indicates that ammonium distributions resemble those encountered during winter, with a maximum positive anomaly of 2-3 µM-N in the middle portion of the estuary. The spring DON distributions (Fig. 3 *a*) are quite similar to those measured during winter (Fig. 2 *a*) with concentrations ranging between 16-26 µM-N in freshwater to 8-10 µM-N in seawater. As in winter, urea levels vary only slightly, not reaching 2 µM-N (Fig. 3 *b*), and account for only a low part of the DON stock.

Comparison between both spring transects reveals the prevailing importance of tide conditions upon suspended matter concentrations in estuarine waters (Tab. 2). On mid-tide (April 1983), despite a relatively high river flow (63.5 $m^3 s^{-1}$), TSM concentrations do not exceed 60 mg l^{-1} at the turbidity maximum whereas values as high as 4,450 mg l^{-1} (Fig. 3 *c*) are recorded during the spring-tide transect with a comparatively slower river flow (28.6 $m^3 s^{-1}$). Furthermore, during this latter cruise, high values characterize every suspended matter parameter (1,430 µmol PON-P l^{-1} and respectively 22.6 and 90.0 mg m^{-3} for chlorophyll *a* and pheophytin). Such behaviour is directly attributable to the intensity of tidal currents which fortnightly resuspend, in spring-tide conditions, important amounts of sediments from the estuarine bottom. Such a high suspended load also favours heterotrophic activity in the water column, thus leading to a typical oxygen undersaturation, near 80% (Fig. 3 *d*), evenly distributed over the whole estuary, both in surface and bottom waters (with one individual value as low as 17% at the turbidity maximum, Fig. 3 *d*). As shown in Figure 3 *c*, the turbidity maximum extends well downstream, as has been previously mentioned for the winter situation, resulting from resuspension by intense tidal currents (Uncles *et al.*, 1985).

Summer situation

A typical summer situation was observed on one occasion, on 9 July 1984, under mid-tide conditions (t. c.: 63), as water temperature (21°C) was very close to the annual maximum value and river flow had decreased to 2 $m^3 s^{-1}$ corresponding to a flushing time of about 30 days.

In such a situation, nitrate, ammonium and urea distributions are nonconservative, as evidenced in Fig. 4 *a* and 4 *b*, and mixing diagrams reveal severe anomalies between freshwater and seawater (19.29 Cl l^{-1}) with respective concentrations of 94.4-1.52 µM (NO_3+NO_2)-N, 4.11-0.40 µM NH_4-N and 1.76-0.45 µM urea-N. The summer situation originates mainly from intense concomitant activities of autotrophic and heterotrophic microorganisms as inferred from Figures 4 *b* to *d*. High primary production can in all likelihood be expected from high photosynthetic pigment concentrations encountered in surface water: values as high as 49.3 and 37.1 mg m^{-3}, respectively for chlorophyll *a* and pheophytin are observed in surface waters of the turbidity maximum (TSM concentration: 97 mg l^{-1}). However, at the same time, prevailing heterotrophic activity is evidenced by oxygen undersaturation, reaching down to 60% as shown in Figure 4 *d*, and by ammonium distribution (Fig. 4 *b*). Downstream, simultaneous increases of oxygen undersaturation and ammonium levels in bottom water (which characteristics largely differ from those in surface water) might originate from the intense heterotrophic activity occurring at the water-sediment interface during summer, as has been demonstrated by Knox *et al.* (1981; 1983), Souchu (1986), and Douchement (1987).

Table 2
Bay of Brest: characteristics of freshwater (Aulne River) and reference sea water (station I1, fig. 1).
Caractéristiques de l'eau du fleuve Aulne et de l'eau de mer de la station de référence (station I1, fig. 1).

Season	Date		Chlorosity (Cl l^{-1})	Nitrate +Nitrite (µM−N)	Ammonium (µM−N)
Winter	04/10/84	river water	0.01	463	1.3 (2)
		seawater	19.35	5.1	1.1 (1)
Spring	04/11/83	river water	0.01	354	3.4 (2)
		seawater	18.98	13.0	0.5 (2)
Summer	07/09/84	river water	0.01	96	4.1 (2)
		seawater	19.90	2.5	0.6 (2)
Autumn	10/26/83	river water	0.01	202	3.4 (2)
		seawater	19.75	5.1	1.8 (1)

(1) Data from National Survey (J. Dussauze, pers. comm.).
(2) This work.

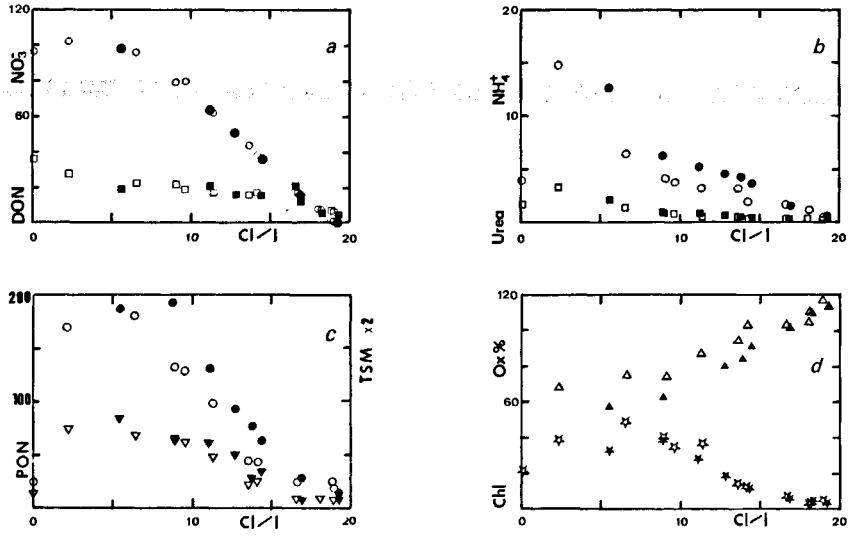

Figure 4

Aulne estuary, summer situation: 9 July 1984. Mixing diagrams (concentrations of parameters versus *chlorosity in Cl/l).*
a) Nitrate (+nitrite) in µM−N (○ surface; ● bottom) and DON in µM−N (□ surface; ■ bottom);
b) Ammonium in µM−N (○ surface; ● bottom) and urea in µM−N (□ surface; ■ bottom);
c) PON in µmol/l (▽ surface; ▼ bottom) TSM in mg/l (○ surface; ● bottom);
d) Chlorophyll-a in mg/m³ (☆ surface; ★ bottom) oxygen sat.% (△ surface; ▲ bottom).

Estuaire de l'Aulne en été. Diagrammes de mélange.

Unlike the other nitrogen compounds of the dissolved phase, the distribution of DON does not go through a maximum, as shown in Figure 4*a*, where concentrations gradually decrease from 36.0 µM-N in freshwater to 5.7 µM-N in seawater. Moreover, DON summer concentrations increase in comparison with winter and spring, in relation to *in situ* recycling (Le Jehan and Tréguer, 1984). Urea contributes to DON stock in the range 2-12% and its distribution along the estuary, depicted in Figure 4*b*, follows the same pattern as ammonium.

PON summer concentrations are 24.0 µmol N l^{-1} in freshwater and 8.4 µmol N l^{-1} in seawater. However, maximum PON values are observed at the 5.5 Cl l^{-1} chlorosity level near the turbidity maximum area which was not located at the freshwater-estuarine interface (Fig. 3*c*) but rather displaced downstream by tidal current action.

Autumn situation

The two cruises conducted during this season were characterized by low water with respective mean daily flows of 2.7 and 5.9 m^3 s^{-1} (related flushing times: 30 and 25 days) on 9 September and 26 October 1983, under mid-tide conditions (t.c. near 80). During the second transect, temperatures sharply decrease, with values close to 13°C. Figures 5*a* and 5*b*, referring to the first transect, indicate that dissolved nitrogen compound distributions appear to be intermediate between summer and winter situations, showing the non-conservativity of nitrate, ammonium, and urea in the transition from freshwater to seawater (17.92 Cl l^{-1}) with respective concentrations of 202.0-23.1 µM (NO_3+NO_2)-N, 3.40-2.67 µM NH_4-N and 2.57-1.02 µM urea-N. For the first transect (Fig. 5*b*), a large ammonium maximum is also evidenced in the middle part of the estuary.

As in the case of summer, the main characteristic of the autumn situation is long flushing time, of about one month, *i.e.* sufficiently long to permit, as a consequence of biological phenomena, the establishment of nonconservative nutrient distributions. However, in autumn, recycling processes prevail over photosynthetic activity, as can be inferred from higher values of pheophytin concentrations (35.6 mg m^{-3}) compared with chlorophyll *a* (8.79 mg m^{-3}) and oxygen undersaturation (minimum value: 60% upstream in the estuary). Distributions of ammonium, indistinguishable between subsurface and bottom waters, evidenced in Figure 5*b*,

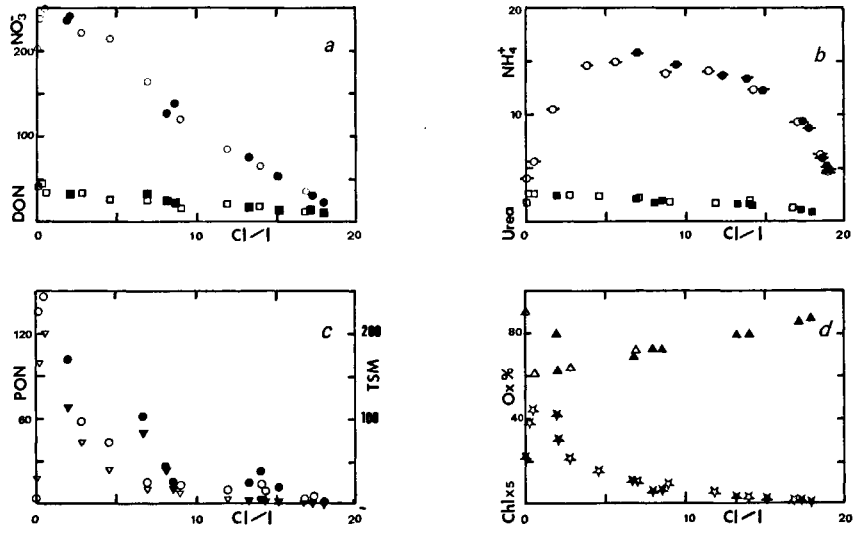

Figure 5

Aulne estuary, autumn situation: September and October 1983. Mixing diagrams (concentrations of parameters versus *chlorosity in Cl/l).*
a) nitrate (+nitrite) in µM−N (10 26 83: ○ surface; ● bottom), and DON in µM−N (10 26 83: □ surface; ■ bottom);
b) ammonium in µM−N (9 5 83: -○- surface; -●- bottom) and urea in µM−N (10 26 83: ○ surface; ● bottom);
c) PON in µmol/l (10 26 83: ▽ surface; ▼ bottom) TSM in mg/l (10 26 83: ○ surface; ● bottom);
d) Chlorophyll-a in mg/m³ (10 26 83: ☆ surface; ★ bottom) and oxygen sat.% (10 28 83: △ surface; ▲ bottom).

Estuaire de l'Aulne en automne. Diagrammes de mélange.

can be interpreted as resulting from increased tidally-induced mixing during the autumn cruises. For these reasons, the turbidity maximum (121-139 µmol PON l^{-1}, 170-242 mg TSM l^{-1}) is confined within moderately saline waters (chlorosity 0.5-1.0 Cl l^{-1}), as displayed in Figure 5*c*.

DISCUSSION

The seasonal regimes of the Aulne River estuary

In estuarine systems, dissolved nitrogen distributions result from interactive physical processes (advection, diffusion), biological phenomena (uptake, recycling) and reactions with the solid phase (adsorption-desorption, fluxes at the sediment-water interface over the whole estuary). Delmas and Tréguer (1983) devised new mixing diagrams which can be used in parallel with classical mixing diagrams (Liss, 1976) to permit proper identification of the phenomena responsible for nonconservative behaviour of dissolved elements. To overcome rapid variations in freshwater end-member characteristics, these authors recommend consideration of seawater as the reference end-member in macrotidal ecosystems, since this well-mixed component can be considered as a constant parameter for a period of at least one month (Delmas and Tréguer, 1983). Consequently, in the present study, seawater characteristics have been measured (Tab. 2) on each estuarine cruise, at a reference station located at the mouth of the Bay of Brest (station I1, Fig. 1), out of the direct influence of anthropogenic inputs (Delmas and Tréguer, 1983).

The nutrient estuarine water concentration SN measured in each sample follows the formula:

$$SN = SN_R X + SN_M(1-X) + A \qquad (1)$$

where $X = (Cl_M - Cl)/Cl_M$ is the fraction of freshwater in the sample, Cl and Cl_M being respectively the chlorosity of sample and seawater end-member whose nutrient concentration is SN_M; SN_R is the nutrient concentration of the freshwater end-member; A is the anomaly of nonconservativity, variable upon the location of the station along the estuary.

In their new mixing diagrams, Delmas and Tréguer (1983) introduced the parameter SN_0, the nutrient freshwater theoretical concentration, calculated from equation (2):

$$SN = SN_0 X + SN_M(1-X). \qquad (2)$$

In a SN−Cl mixing diagram, SN_0 is given by the intersection of the secant, drawn from the seawater end-member to the point representative of the sample characteristics, with the ordinate axis. Knowledge of the characteristics of the river end-member is not necessary to calculate SN_0. SN_0−Cl diagrams allow a rapid and synthetic identification of the behaviour of nutrient along the estuary (*see* Fig. 10 and p. 351-353 *in* Delmas and Tréguer, 1983, for more details concerning the application of the method).

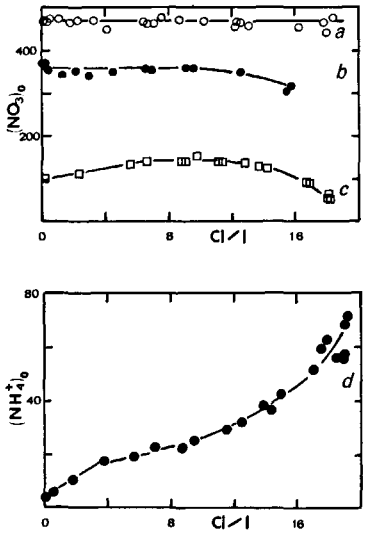

Figure 6

Aulne estuary: modified mixing diagrams according to Delmas and Tréguer (1983). Theoretical nutrient concentrations in freshwater (in µM−N) versus chlorosity in Cl/l.
a) nitrate (winter); b) nitrate (spring); c) nitrate (summer); d) ammonium (summer).

Diagramme de mélange SN_0−Cl selon Delmas et Tréguer (1983) : estuaire de l'Aulne.

In winter, as inferred from Figure 6*a*, $(NO_3)_0$ remains fairly constant along the estuary, indicating a strictly conservative nitrate distribution (horizontal line). Under spring conditions, shown in Figure 6*b*, $(NO_3)_0$ decreased at the downstream end of the estuary, as a result of algal uptake occurring predominantly in less turbid waters. For both seasons, the influence of the small tributary, the Douffine River (Fig. 1), is negligible. This is obviously not the case in summer, as evidenced in Figure 6*c*, when the upstream initial increase in $(NO_3)_0$ can be related to permanent input of nitrate from a gunpowder-factory situated on the Douffine River bank. Summer $(NO_3)_0$ and $(NH_4)_0$ positive anomalies, shown in Figure 6*c* and *d*, are associated respectively with prevailing uptake in non turbid waters and recycling over the whole estuary.

According to Boyle *et al.* (1974), assuming a constant value for freshwater flow (R), mean net DIN $(NO_3 + NO_2 + NH_4)$ flux flowing through any given section of the estuary can be estimated by the following equation:

$$F = SN^* R, \qquad (3)$$

where SN* is given by the intersection of the tangent to SN(Cl) at Cl with the ordinate axis. Table 3 summarizes F values for three sections of the estuary and under different seasonal conditions. At the mouth of the estuary, DIN fluxes range from about 20 metric tons N d^{-1} in winter and spring to approximately or less than 1 metric ton N d^{-1} in summer and fall. Douffine River is responsible for a complementary discharge of 0.1-0.9 metric ton N d^{-1} throughout the year, which makes this tributary contribution not negligible in summer and autumn. Table 3 confirms the conservativity of DIN fluxes during winter, whereas in spring, 15% of the freshwater originating incoming flux is removed during transport along the estuary, by means of moderate (controlled by water turbidity) algal uptake. In summer, nitrate removal at the estuary outlet is only 0.2 metric ton N d^{-1}. In winter and spring the adjacent marine ecosystem receives maximum terrestrial-orig-

Table 3

DIN fluxes through Aulne estuary: daily river flows ($m^3\ s^{-1}$); the theoretical freshwater DIN concentrations for a given section, SN ($\mu M-N$), are calculated at the intersection of the tangent with the ordinate axis; the calculated DIN fluxes, F (metric tons N d^{-1}), are calculated according to Boyle* et al. *(1974); indices I, D and O respectively refer to inlet of the estuary (A_{10}), Aulne-Douffine confluence (A_7): ADC, and outlet (A_1) of the estuary (Fig. 1).*

Débits journaliers, concentrations théoriques d'azote inorganique dans l'eau douce, flux d'azote inorganique.

Season	River flow	Estuary inlet		ADC		Estuary outlet		Inlet-outlet
		SN_I^*	F_I	SN_D^*	F_D	SN_O^*	F_O	F_I-F_O
Winter (04/84)	34.6	464	19.4	471	19.7	471	19.7	+0.3
Spring (04/83)	63.5	357	27.4	369	28.3	304	23.3	−4.1
Summer (07/84)	2.0	100	0.24	117	0.28	3	0.01	−0.2
Autumn (10/83)	5.9	205	1.47	258	1.86	217	1.56	+0.1

inated nitrogen inputs, whereas estuarine recycling prevails during the remainder of the year (Souchu, 1986).

The nutrient discharge of the Aulne River compared with other European rivers

As far as its drainage basin (1,660 km^2) is concerned, Aulne River annual DIN loading (about 5,000 metric tons N y^{-1}) is heavy in comparison with the Loire River, which annually discharges 67,000 tons NO_3-N (Martin *et al.*, 1980) originating from a 122,000 km^2 area. Unlike large Western European estuarine systems catching ammonium-rich urban outfalls (estuarine water levels reaching up to 100 µM NH_4-N; review *in* Martin *et al.*, 1980), the studied system mainly receives DIN as nitrate (averaging 95% of DIN on an annual scale). In comparable rivers running over similar geological ground, highest recorded nitrate concentrations do not exceed 50 µM NO_3-N (B. Soulard, pers. comm.) when agricultural activity is restricted to forestry management only. In the present study, measured DIN concentration excess (reaching about 400 µM NO_3-N at the winter maximum) can be ascribed to intensive agriculture and cattle rearing, this latter activity having sharply increased (60% increase in livestock numbers) during the last decade. However the estuarine system situation now appears to be stabilized, as no perceptible increase in winter nitrate levels has been measured in the Aulne River (station A10) for the last ten years (Delmas and Tréguer, 1983).

Two noteworthy features of the studied ecosystem are the relatively small amounts of algal biomass encountered in estuarine water (as compared to the nutrient stock available) and the high oxygen concentration, which rarely falls below 60% saturation (notwithstanding heavy DIN loading). The severe limitation of primary production partly results from reduced availability of light, especially during winter (low incident radiation) and spring (heavy suspended matter load) when freshwater exhibits the highest DIN concentrations. Moreover, surface water oxygenation associated with intense vertical mixing occurring under spring-tide and low-water conditions favours ecological balance duration in the estuary.

The present study also highlights the negligible contribution (<1% of the incoming flux) of DON to total dissolved nitrogen (TDN) inputs. This is unexpected in a system where cattle rearing is well developed. Nevertheless, we must point out that during summer, DON accounts for about 40% of TDN in estuarine waters, mainly because of *in situ* biological regeneration (Banoub and Williams, 1973; Wafar, 1981). DON concentrations measured during both 1984 winter cruises are far lower than previous results (Le Jehan and Tréguer, 1984). This may have been due to the decreased activity of a slaughter-house which constituted an important source of organic matter; but we cannot preclude analytical shortcomings for the previous data set. Our measurements indicate that urea, recognized as a potential source for algal growth (Le Jehan and Tréguer, 1984; Quéguiner *et al.*, 1986), only represents a trifling component of the total DON stock.

The composition of particulate matter

In terms of particulate organic matter (POM) composition (ranges: 0.1-6 mg C l^{-1}, 0.01-1 mg N l^{-1}), Aulne River estuary is comparable with West European large river estuaries (Cauwet and Martin, 1982; Meybeck, 1982; Eisma *et al.*, 1982; Ittekkot *et al.*, 1982; Etcheber, 1983). POM seasonal characteristics (Tab. 4) show variations in the origin of this component, as average POC/TSM mass ratios range between 3.5-4.1% in winter and 7.4% in summer. Moreover, during the latter season, POC/(chlorophyll *a*+pheophytin) ratios reach minimum values comparable with those previously described in the Loire (Billen *et al.*, 1986) and Gironde (Relexans and Etcheber, 1982) estuaries.

Table 4

Mean particulate organic matter characteristics in Aulne estuary: POC/TSM mass ratios and POC/PON molar ratios.

Composition moyenne de la matière particulaire dans l'estuaire de l'Aulne : rapports pondéraux POC/TSM et rapports molaires POC/PON.

Season	POC/TSM	POC/PON
Winter	0.04 (±0.005)	8.6 (±0.4)
Spring (1983)	0.04 (±0.003)	8.4 (±0.5)
Spring (1984)	0.035 (±0.002)	7.3 (±0.2)
Summer	0.07 (±0.006)	6.6 (±0.3)
Autumn	0.06 (±0.005)	8.4 (±0.1)

Assuming an average algal ratio of 35 (Billen *et al.*, 1986), we can therefore estimate that a component of algal origin accounts for 65-80% of Aulne River estuary POM in summer, whereas in the other seasons, terrestrial detritus prevail (only 5% of POM algal-originated). POC/PON molar ratios (6.6 ± 0.3) are close to the Redfield ratio in summer and reach high winter values (8.6 ± 0.1) indicative of prevailing terrestrial organic matter inputs (Flemer and Biggs, 1971; Loder and Hood, 1972; Pocklington and Leonard, 1979). Preferential protein degradation would account for an autumn increase in the latter ratio (Romankevitch, 1984).

CONCLUSION

This type of estuarine ecosystem, characterized by the agricultural activities prevailing on the drainage basin, exhibits heavy nitrogen loads, especially in the form of nitrate. As photosynthetic activity is severely reduced by strong vertical mixing caused by tidal current actions, this system exports the main part of DIN flux towards the adjacent marine ecosystem, leading to high spring primary production in the latter (Quéguiner and Tréguer, 1986; Quéguiner *et al.*, 1986). Terrestrial DON inputs are negligible in winter and spring, whereas in summer and autumn, the relative increase in estuarine DON (up to 40% TDN) must be attributed to *in situ* biological recycling.

Tidally-induced sediment resuspension is the main determinant of particulate matter distribution, which is characterized by a significant downstream extension of the turbidity maximum.

Mechanisms controlling ecosystem biological activity (high nutrient inputs, heavy suspended load under spring tides, water oxygenation from the atmosphere as a result of vertical mixing) are in equilibrium, thus permitting a global ecological balance to be maintained throughout the estuary.

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