Original article

Nutrients and carbon budgets for the Gulf of Lion during the Moogli cruises

Bilans de sels nutritifs et de carbone dans le golfe du Lion pendant les campagnes Moogli

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Abstract

Shelf-slope exchanges and budgets of organic and inorganic nutrients are calculated for the Gulf of Lion continental margin in the northwestern Mediterranean. Computations are based on data from three seasonal marine surveys performed in March 1998, June 1998 and January 1999 in the framework of the French Programme National d'Environnement Côtier. A Land-Ocean Interactions in the Coastal Zone type box model is used to calculate the advective exchanges between the shelf and the adjacent open sea and to estimate the budgets of non-conservative elements (DIP, DIN, DOP, DON, DOC, POC, PON, POP). These budgets consider river discharges, urban sewage supply, atmospheric deposition, and fluxes at the water-sediment and shelf-slope interfaces. Uncertainties on the fluxes and budgets are estimated to assess the robustness of the results with respect to the spatial variability of the system. Results indicate that shelf-slope exchanges by mixing predominate with respect to the major input terms (river discharge and sediment release). Budgets for inorganic nutrients, that show a strong concentration gradient between the shelf and the slope waters, are significantly different from zero and indicate an excess of these elements in the shelf water. For all surveys, these surpluses suggest (i) that the whole shelf system is autotrophic ($1.6–4.3 \times 10^3$ mol C s^{-1}) and acts as a sink of CO_2, and (ii) that it is a site of net denitrification (119 mol N s^{-1}) and acts as a sink of N_2. Average shelf-slope fluxes of dissolved and particulate organic elements generally indicate an export to the open sea. However, the large uncertainty on these fluxes yields budgets for the shelf not significantly different from zero.

Résumé

Les échanges entre le plateau et l'océan ouvert et les bilans de nutriments organiques et inorganiques ont été estimés pour la marge continentale du golfe du Lion en Méditerranée nord occidentale. Les calculs sont fondés sur les données de trois campagnes de mesure saisonnières réalisées en mars 1998, juin 1998 et janvier 1999 dans le cadre du Programme National d'Environnement Côtier. Un modèle en boîte de type LOICZ a été utilisé pour calculer les échanges advectifs entre le plateau et l'océan ouvert adjacent et pour estimer les bilans d'éléments non-conservatifs (PID, NID, POD, NOD, COD, COP, NOP, POP). Ces bilans prennent en compte les apports des rivières, les effluents urbains, les dépôts atmosphériques, et les flux aux interfaces eau-sédiment et plateau-pente. Les incertitudes sur les flux et les bilans, liée à la variabilité spatiale du système, ont été estimées pour tester la robustesse des résultats. Les résultats indiquent que les échanges plateau-pente par mélange dominent les principales sources (rivière et sédiment). Les bilans pour les nutriments inorganiques, qui présentent

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un important gradient de concentration entre les eaux du plateau et celles de la pente, sont significativement différents de zéro et indiquent un excès de ces éléments sur le plateau. Pour toutes les campagnes, ces excès suggèrent que l'ensemble du système (i) est autotrophique $(1.6–4.3 \times 10^3 \ mol \ C \ s^{-1})$ et agit comme un puits CO_2, et (ii) présente un taux de dénitrification nette de 119 mol N s^{-1} et agit comme une source de N_2. Les flux moyens des éléments organiques dissous et particulaires entre le plateau et la pente indiquent généralement une exportation vers l'océan ouvert. Cependant, les grandes incertitudes associées à ces estimations ne permettent pas de conclure sur la réalité de cette exportation.

1. Introduction

1.1. Rationales of biogeochemical budgets in coastal areas

Continental margins, despite their small surface with respect to that of the world ocean, play a significant role in the global biogeochemical cycles of carbon, nitrogen and phosphorus (Liu et al., 2000; Mantoura et al., 1991; Wollast, 1991). Land-derived carbon, particularly the organic forms, may either be respired on the shelf, and thus form a potential source for the atmospheric carbon (Smith and Mackenzie, 1987), or be exported on the shelf and slope sediments supporting the notion of carbon-rich "depocenters" for the continental margins (Walsh et al., 1981; Peng and Broecker, 1984). Besides, the increase input of anthropogenic nutrients (particularly nitrate and phosphate) to the continental shelves may result in an increase in the biological pump—increased primary productivity—and therefore constitute an additional sink for atmospheric carbon dioxide (Walsh et al., 1985; Smith and Mackenzie, 1991). Thus, continental margins form a buffer zone, between the continent and the open sea, where the material of continental origin including that from the anthropogenic activities is caught, transformed and eventually stored or exported to the open sea. International research programs, such as Land-Ocean Interactions in the Coastal Zone (LOICZ) and Joint Global Ocean Flux Study (JGOFS), are devoted among other things to understanding and quantifying the contribution of continental margins to the budget of carbon and associated elements. The main objective is to determine whether continental margins export or import nutrients with the open sea and what is their effect on the carbon cycle in terms of a source or sink of CO_2. However, the actual role of ocean margins in the global biogeochemical cycles remains difficult to achieve and it has been still a matter of controversy to state definitively whether coastal zones export or import nutrients with the open sea and they are sources or sinks for carbon dioxide (Kempe, 1995). The knowledge and understanding as well as quantification of the processes occurring at the ocean margins have still to be increased (Wollast and Chou, 2001b). For that purpose, LOICZ and JGOFS planned to quantify vertical and horizontal carbon and nutrients fluxes in different types of continental margins (boundary current, polar, sub-polar, tropical and marginal systems) where nutrients are used as proxies. A box-model budgeting approach was developed by Gordon et al. (1996) in the framework of LOICZ that allows a straightforward approximation of the nutrients fluxes between the coastal zone and the adjacent open ocean and, consequently, to estimate their budgets.

The Gulf of Lion shelf is a major continental margin of the Mediterranean Sea that receives the input from the Rhone, one of the largest Mediterranean rivers (Unesco, 1993). It has been the subject of intensive physical and biogeochemical oceanographic studies over the last 15 years within the framework of the European Eros (European River Ocean Systems) and the French Ecomarge (ECOSystèmes de Marge continentale) and Programme National d'Environnement Côtier (Pnec) programs (Monaco et al., 1990; Martin and Milliman, 1997). During the 1996–2000 phase, three surveys of the Gulf were made in March, June and January 1998–1999 to provide seasonal snapshots of the physical and biogeochemical structures over the whole margin. Extensive data sets of dissolved and particulate, inorganic and organic nutrients were collected in combination with CTD data and studies of primary and new production (Diaz, 2000; Raimbault, 2000).

This paper assesses the carbon, nitrogen and phosphorus fluxes on the Gulf of Lion' continental shelf based on these three surveys. First, it provides a robust quantification of the flow of nutrients across the system boundaries, using an adapted form of the LOICZ box-model approach, so as to quantify the nutrients budgets on the shelf and hence to characterize its role as a net source or sink for carbon, nitrogen and phosphorus. Second, it interprets these budgets to gain evidence on ecosystem functioning and its seasonal variability. This work complement a preliminary study, based solely on dissolved nitrogen and phosphorus, performed within the framework of LOICZ (Durrieu de Madron et al., 2001), as well as carbon budgets (Durrieu de Madron et al., 2000; Sempéré et al., 2000) and biogeochemical models (Pinazo et al., 1996; Tusseau-Vuillemin et al., 1998; Diaz, 2000) for this area.

1.2. Description of the study area

The Gulf of Lion (42–44°N, 3–6°E) has a large crescent-shaped continental shelf (Fig. 1). More than 10 rivers with a total watershed area of about 125 000 km^2 deliver significant water discharges into the gulf. The Rhone river on the north-western part of the gulf delivers about 90% of the total
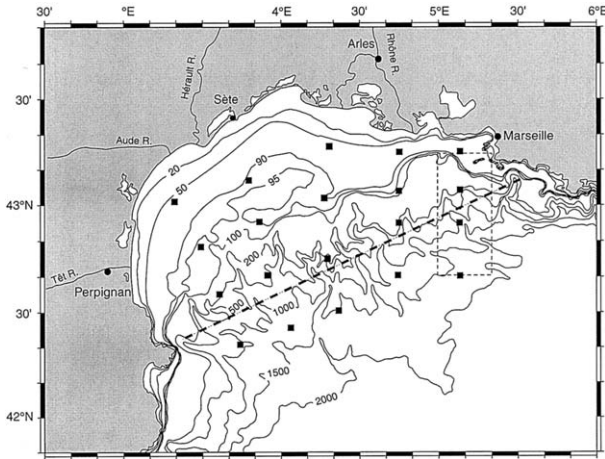
Fig. 1. Map of the Gulf of Lion with the stations network used to build the budgets. The shelf region is delimited by the 150 m isobath. The thick dashed line delineates the shelf stations from the open sea stations. The thin dotted line offshore of Marseille is the region of ADCP measurements compiled during 1997–2000.

riverine water inputs. The shoreline is heavily urbanized (ca. 1.5 million inhabitants), with one of the largest French city, Marseilles (800 000 residents), at the northeastern tip of the shelf. Terrestrial sources of nutrients from sewage treatment waters, runoff and rivers, bring significant supply of nutrients in the form of nitrate and phosphate to the Gulf. Minas and Minas (1989) showed that the Rhone river inputs enhance significantly the primary productivity on the shelf. Aerosols transported to the Gulf of Lion consist of anthropogenic-rich "background" materials supplied continuously from the nearby land, upon which sporadic pulses of Saharan terrigenous dust are superimposed (Chester et al., 1989). Inorganic nitrogen is almost entirely anthropogenic (industrial combustion and vehicle traffic) and contributes to new production (Loÿe-Pilot et al., 1990). Lithogenic inorganic phosphorus may represent half of total atmospheric deposition but the question of its solubility and bioavailability is still open (Ridame and Guieu, 2002).

The system has a large open boundary between the shelf waters and the slope waters offshore. Strong gradients of salinity and nutrients are usually located near the shelfbreak, delineated by the 150 m isobath. A strong cyclonic boundary current, that comprises the northern branch of the general circulation in the western Mediterranean, transports large amount of nutrients (Conan et al., 1998). Whereas the main outer branch permanently flows southwestward along the slope (water flux about $1–2 \times 10^6$ m^3 s^{-1}), shallow flows occasionally penetrate over the shelf under the effect of wind (Millot, 1990; Estournel et al., 2003) and current instabilities (Flexas et al., 2002; Petrenko, 2003). The mesoscale variability of the currents induces an exchange of inorganic and organic elements between the ocean and the shelf, that is rather well represented by a mixing (turbulent diffusion) term (e.g. Durrieu de Madron et al., 1999).

A well-marked seasonality results from surface heat fluxes. In summer, the solar heating of the surface layer causes the formation of a seasonal thermocline around 20–40 m depth. In winter, cold and continental winds as well as air-sea temperature differences induce an important evaporation and heat loss from the sea. The sustained cooling and mixing of the surface layer lead to a relative homogenization of the water column and the formation of dense waters on the shelf that cascade down the slope. This latter process was not observed during the winter/spring surveys, but is considered as a major export mechanism (Tusseau-Vuillemin et al., 1998; Béthoux et al., 2003). The upward transport of nutrient by vertical mixing in winter explains the relative importance of primary productivity rates in the Gulf of Lion compared to those generally measured in the Mediterranean Sea (Diaz et al., 2000).

2. Models and observations

2.1. Modeling approach

Biogeochemical modeling according to the LOICZ approach (Gordon et al., 1996) was applied to estimate the exchange patterns at the boundaries of the coastal system. This box-modeling approach considers that the system over the period of interest is at steady state. Given that the inputs of water and dissolved material to the system are known, the model uses the water volume and salt conservation within the system to infer the exchanges with the adjacent open ocean. For the conservative water budget, we consider river discharge, sewage discharge, precipitation, evaporation, and mixing flow and residual flow at the boundary with the open ocean. For the conservative salt budget, only the cross-shelf exchanges are taken into account. The budget of the non-conservative dissolved elements (nutrients, dissolved and particulate organic matter) on the shelf results from inputs by river, sewage and atmospheric deposition as well as exchanges with the open ocean, and the sediment. Additional output terms are considered for particulate organic matter: fish landing for POC, PON and POP, and sediment burial for POC.

We chose the classical LOICZ single box system to describe the unstratified water column and the dynamics observed during wintertime, from November to early May. As the system later changes to a stratified water column, we developed a modified version of the LOICZ two-layer system to improve the description of the mixing flow between the shelf and the open ocean during summertime, from June to October. Both models are described in Appendix A. The shelf system has a surface area of 12 000 km^2, and a total volume of 9.1×10^{11} m^3. While the shelf has a sloping bottom down to 200 m, the average depth for the one-layer model is about 76 m. For the two-layer models the surface layer thickness is 30 m, and the deep layer average depth is 46 m.

Table 1
Mean values and 95% confidence interval of freshwater discharges, precipitation, evaporation, residual and mixing fluxes for three surveys in the Gulf of Lion. Confidence intervals are statistically estimated confidence interval of each parameters derived from the series of observations. Italic type confidence intervals are an approximation to the corresponding standard deviation. Positive and negative numbers represent inflow and outflow, respectively

Parameters	January 1999	March 1998	June 1998	
			Surface layer	Deep layer
River discharge V_Q (m^3 s^{-1})	2330±*470*	1360±*270*	1570±*320*	
Sewage discharge V_O (m^3 s^{-1})	5±*1*	5±*1*	5±*1*	
Precipitation V_P (m^3 s^{-1})	220±*40*	40±*10*	12±*2*	
Evaporation V_E (m^3 s^{-1})	−630±*130*	−510±*100*	−380±*80*	
System salinity S_{syst}	38.08±0.07	37.91±0.08	37.73±0.12	38.01±0.03
Ocean salinity S_{ocn}	38.29±0.10	38.16±0.13	38.02±0.03	38.24±0.05

2.2. Data

2.2.1. Fluxes of freshwater and nutrients from the continent

Extensive water flux data are available for the Gulf of Lion rivers, from the Compagnie Nationale du Rhone and the Hydro data bank of the French Ministry of Environment (Table 1). Dissolved inorganic nitrogen and phosphorus (DIN, DIP) concentrations are available for all rivers for the last 20 years. Organic nitrogen and phosphorus (DON, DOP, PON, POP) concentrations are available during the period of the cruises only for the Rhone river. Organic carbon concentrations (DOC, POC) were not measured during the period of the cruises, but were estimated from the predictive equations of Sempéré et al. (2000). The Rhone river concentrations were used to extrapolate the river fluxes of organic nutrients from all rivers (Tables 2–4).

Significant discharges of treated sewage effluent occur at Marseilles. Although the water volume of sewage is small relative to other freshwater inputs, total N and P are highly concentrated in the effluent (data from the Service d'Assainissement of city of Marseilles, personal communication). We used the following stoichiometric ratios between the dissolved inorganic and total fractions: DIN/TN = 0.38 and DIP/TP = 0.5 (San Diego-McGlone et al., 2000) to

estimates discharges coefficients (water: 0.3 m^3 d^{-1} pm^{-1}; DIP: 19 mmol d^{-1} pm^{-1}; DIN: 419 mmol d^{-1} pm^{-1}). Sewage discharges to the sea by the total population living along the coast (1.5 million, 1999 data from the French National Institute for Statistics and Economic Studies) were estimated using the latter discharge coefficients (Tables 2–4).

In the LOICZ approach, nutrients and organic matter from rivers and treated sewage are assumed to have a conservative behavior during the mixing process between unsalted and salted waters. However, this assumption is not confirmed especially for the DIP inputs in the Rhone river; Moutin et al. (1998) suggested that the quantity of the bio-available phosphorus may be significantly lower in the salt water than in the Rhone waters due to the precipitation of the incoming ortho-phosphate iron and calcium oxides. Accordingly, the nutrient fluxes from rivers to the shelf computed in this paper may be overestimated, particularly that of DIP.

2.2.2. Freshwater and nutrients fluxes at the air-sea interface

Evaporation and precipitation are estimated from a high-resolution re-analysis of the ECMWF model outputs made by the Cerfacs in Toulouse (data from Siefridt et al., personal communication). The net balance of precipitation and evaporation is negative throughout the year, with rainfall decreas-

Table 2
Mean values and 95% confidence interval of non-conservative nutrient inputs and concentrations for January 1999 (Moogli 3 cruise in the Gulf of Lion). Confidence intervals are statistically estimated standard deviations of the parameters derived from the series of observations. Italic type confidence intervals are an approximation to the corresponding confidence interval (NA, data not available)

Parameters	DIP	DIN	DOP	DON	DOC	POC	PON	POP
River fluxes $V_Q Y_Q$ (mmol s^{-1})	5400±*1080*	330 840±*66 170*	2650±*530*	98 850±*19 770*	381 620±*76 320*	273 480±*54 700*	6960±*1370*	980±*200*
Sewage fluxes $V_O Y_O$ (mmol s^{-1})	350±*70*	7300±*1460*	NA	NA	NA	NA	NA	NA
Atmospheric deposition $V_{atm} Y_{atm}$ (mmol s^{-1})	60±*60*	17 360±*17 360*	NA	NA	22 000±*4000*	10 000±*10 000*	NA	NA
Benthic fluxes $V_{sed} Y_{sed}$ (mmol s^{-1})	300±2060	4830±14 150	NA	NA	NA	NA	NA	NA
Sediment burial $V_{bur} Y_{bur}$ (mmol s^{-1})	NA	NA	NA	NA	NA	492 000±*156 000*	NA	NA
Fish landing $V_{fl} Y_{fl}$ (mmol s^{-1})	NA	NA	NA	NA	NA	2060±*410*	410±*82*	30±*6*
System concentration Y_{syst} (mmol m^{-3})	0.02±0.01	2.03±0.21	0.07±0.01	4.96±0.27	66.84±6.07	4.42±1.07	0.53±0.13	0.028±0.007
Ocean concentration Y_{syst} (mmol m^{-3})	0.12±0.08	4.19±1.87	0.09±0.02	4.23± 0.74	65.91±15.81	2.58±0.34	0.33±0.11	0.015±0.005

Table 3
Mean values and 95% confidence interval of non-conservative nutrient inputs and concentrations for March 1998 (Moogli 1 cruise in the Gulf of Lion). Confidence intervals are statistically estimated standard deviations of the parameters derived from the series of observations. Italic type confidence intervals are an approximation to the corresponding confidence interval (NA, data not available)

Parameters	DIP	DIN	DOP	DON	DOC	POC	PON	POP
River fluxes $V_Q Y_Q$ (mmol s^{-1})	2350±*470*	183 660±*36 730*	850±*170*	43 380±*8680*	167 760±*33 550*	42 260±*8450*	5970±*1190*	810±*160*
Sewage fluxes $V_O Y_O$ (mmol s^{-1})	350±*70*	7300±*1460*	NA	NA	NA	NA	NA	NA
Atmospheric deposition $V_{atm} Y_{atm}$ (mmol s^{-1})	60±*60*	17 360±*17 360*	NA	NA	4000±*1000*	10 000±*10 000*	NA	NA
Benthic fluxes $V_{sed} Y_{sed}$ (mmol s^{-1})	1620±3400	30 100±49 970	NA	NA	NA	NA	NA	NA
Sediment burial $V_{bur} Y_{bur}$ (mmol s^{-1})	NA	NA	NA	NA	NA	492 000±*156 000*	NA	NA
Fish landing $V_{fl} Y_{fl}$ (mmol s^{-1})	NA	NA	NA	NA	NA	2060±*410*	410±*82*	30±*6*
System concentration Y_{syst} (mmol m^{-3})	0.03±0.01	1.33±0.24	0.08±0.01	4.40±0.21	85.44±8.43	6.42±1.06	0.73±0.13	0.039±0.006
Ocean concentration Y_{syst} (mmol m^{-3})	0.11±0.09	2.25±0.44	0.09±0.02	4.28±0.30	85.43±9.37	4.57±1.43	0.58±0.08	0.030±0.010

ing during summer and evaporation decreasing during spring. The evaporation and precipitation water fluxes for the three surveys are presented in Table 1.

Dry and wet atmospheric deposition of inorganic nitrogen for the Gulf of Lion region were measured in 1988–1989 within the Eros program (Alarcon and Cruzado, 1990; Loÿe-Pilot et al., 1991, 1993; Guieu, 1991). Atmospheric deposition of total phosphorus without local influence has been measured at the atmospheric sampling station of Ostriconi in Corsica in 1999–2000. The DIP flux was estimated to represent 20% of the total atmospheric deposition (Ridame, 2001;

Ridame and Guieu, 2002). This percentage is probably underestimated because a fraction of the dry deposition of anthropogenic origin will dissolve in seawater; to date, no data are available to quantify this dissolution. Atmospheric deposition of nutrients is summarized in Tables 2–4.

As the inputs of atmospheric POC and DOC are undocumented near the Gulf of Lion, we estimated the total POC deposition (wet + dry) from measurements during 2 years in Corsica (Loÿe-Pilot et al., 1992) where the mean annual POC fallout was about 25 mmol C m^{-2} per year, the concentration of DOC in rain water being about 0.1 mmol l^{-1}. For the Gulf

Table 4
Mean values and 95% confidence interval of non-conservative nutrient inputs and concentrations for June 1998 (Moogli 2 cruise in the Gulf of Lion). Confidence intervals are statistically estimated standard deviations of the parameters derived from the series of observations. Italic type confidence intervals are an approximation to the corresponding confidence interval (NA, data not available)

Parameters	DIP	DIN	DOP	DON	DOC	POC	PON	POP
River fluxes $V_Q Y_Q$ (mmol s^{-1})	2190±*440*	133 370±*26 670*	2800±*560*	44 100±*8820*	237 640±*47 530*	99 120±*19 820*	10 050±*2010*	1990±*400*
Sewage fluxes $V_O Y_O$ (mmol s^{-1})	350±*70*	7300±*1460*	NA	NA	NA	NA	NA	NA
Atmospheric deposition $V_{atm} Y_{atm}$ (mmol s^{-1})	60±*60*	17 360±*17 360*	NA	NA	1200±*200*	10 000±*10 000*	NA	NA
Benthic fluxes $V_{sed} Y_{sed}$ (mmol s^{-1})	2280±3430	18 580±29 690	NA	NA	NA	NA	NA	NA
Sediment burial $V_{bur} Y_{bur}$ (mmol s^{-1})	NA	NA	NA	NA	NA	492 000±*156 000*	NA	NA
Fish landing $V_{fl} Y_{fl}$ (mmol s^{-1})	NA	NA	NA	NA	NA	2060±*410*	410±*82*	30±*6*
System concentration surface layer Y_{syst-s} (mmol m^{-3})	0.003±0.003	0.01±0.01	0.07±0.01	4.52±0.24	116.68±9.19	6.30±0.82	0.80±0.08	0.031±0.004
Ocean concentration surface layer Y_{ocn-s} (mmol m^{-3})	0.002±0.002	0.02±0.03	0.09±0.02	4.34±0.27	111.08±19.52	7.61±1.93	0.71±0.09	0.026±0.009
System concentration deep layer Y_{syst-d} (mmol m^{-3})	0.020±0.013	0.92±0.32	0.07±0.01	4.21±0.32	97.94±8.67	3.16±0.90	0.53±0.12	0.028±0.006
Ocean concentration deep layer Y_{ocn-d} (mmol m^{-3})	0.160±0.050	3.83±1.14	0.06±0.02	3.99±0.68	85.47±9.47	3.37±1.91	0.39±0.19	0.022±0.009

of Lion, this leads to a POC input of about 1.0×10^4 mmol s^{-1}. Atmospheric DOC input for the three field surveys ranged between 0.12×10^4 and 20.0×10^4 mmol s^{-1} (Tables 2–4). Input of POC and DOC are low in comparison to the riverine inputs.

2.2.3. Salinity and nutrients observations in the water column

Three field surveys of the Gulf (March, June 1998 and January 1999) yielded extensive data sets of dissolved inorganic and organic nitrogen and phosphorus concentrations, and particulate organic matter (POC, PON and POP) values in combination with CTD data and estimates of primary and new production (Diaz, 2000; Raimbault, 2000). Salinity and nutrient data were depth-averaged at each station for the different layers considered. Only data shallower than 150 m depth are used since exchanges between the shelf and the slope occur mainly within this layer. The data were then horizontally averaged separately for the shelf region and the slope region. Salinity values are summarized in Table 1 and nutrient concentrations for each survey are summarized in Tables 2–4.

2.2.4. Nutrients fluxes at the sediment-water interface

Flux of nutrients at the sediment-water interface was measured at the shelf stations for the three surveys using the whole core incubation technique based on the rate of concentration change in the overlying water versus time (Denis, 1999; Denis et al., 2001). Each core with non-significant correlation ($P < 0.05$) was considered as zero flux. Triplicated or quadrupled measurements for each station took into account the patchy distribution of benthic organisms and organic matter. Release of inorganic nitrogen and phosphorus from the sediment was observed over the whole shelf area. The shelf-integrated values for benthic release of DIP and DIN are summarized in Tables 2–4.

2.2.5. Burial of particulate organic matter in the shelf sediments

Secular mass accumulation rates of sediment on the continental shelf, compiled and mapped by Durrieu de Madron et al. (2001), outline the major sedimentary units of the system (i.e. Rhone prodelta, mid-shelf mud belt, outer shelf). From the average organic carbon content in the surficial sediments of the different units, these authors estimated a burial rate of POC of $49.2 \pm 15.6 \times 10^4$ mmol s^{-1} for the whole shelf.

2.2.6. Export of particulate organic matter by fish landing

Yearly statistics for the French Mediterranean fishery production are compiled by Ofimer (Office national interprofessionnel des produits de la mer et de l'aquaculture). Harbors of the Gulf of Lion received 90% of the fish landing, which remains stable over the last 5 years. Sardines, anchovies and hake are the most common species and their catches represent about two third of the total weight, that is about 2.4×10^4 tons per year (2001 statistics). The corresponding output of the principal organic constituents, i.e. POC, PON and POP, is estimated using proximate water content (75%) and stoichiometric composition of fish organic matter (POC: 13%, PON: 3% and POP: 0.5%; percentages given are for dry weight) (Huss, 1995; Lyle and Elliott, 1998).

2.2.7. Vertical shear of the cross-slope current variance at the shelfbreak

The intensity of the cross-slope current variance at the shelfbreak within the two layers of the stratified two-layer model (0–30 and 30–150 m, see Appendix A) is estimated from the compilation of 4400 current profiles measured offshore of Marseilles with the Acoustic Doppler Current Profiler (ADCP) of the R/V *Tethys II*. The profiles (between 8 and 244 m depth) were obtained from November 1997 to May 2000 within a sector (10' longitude and 2.5' latitude) centered at 42°N and 5°E around the shelfbreak (Fig. 1). The variance of the cross-slope (N–S) current component decreases exponentially with depth. The average variance was 5.4×10^4 cm^2 s^{-2} for the surface layer (0–30 m) and 2.2×10^4 cm^2 s^{-2} for the deep layer (30–150 m).

2.3. Evaluation of uncertainties

The calculation of exchange flows and the imbalance of non-conservative elements contains uncertainties about the fluxes and concentrations. The uncertainty of any function, f, of N independent variables, x_i, is calculated from the relation:

$$\delta f = \left(\sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 (\delta x_i)^2 \right)^{1/2}$$

where δx_i is the uncertainty of the variable x_i. The uncertainty is defined as the 95% confidence interval, which defines an interval about the calculated results within which the value of the measurement can be confidently asserted to lie.

For salinity and non-conservative element concentration in the water column, the uncertainty of the measure at each station is small compare to that of the spatial variability. Consequently, we considered only the uncertainty due to the spatial variability over the shelf and ocean regions. In contrast, the benthic fluxes at each station were highly variable. The uncertainty on the benthic fluxes integrated over the shelf region is estimated from measured variances at each sampling point. In absence of direct estimates for the remaining variables, we consider a fixed relative uncertainty. The uncertainty for the freshwater fluxes (river and sewage inputs, precipitation and evaporation) and fish landing is assumed to be ±20% of the mean flux. Given the high variability of the monthly-averaged atmospheric deposition, this uncertainty is assumed to be ±100% of the mean annual flux.

Table 5

	January 1999	March 1998	June 1998	
			Surface layer	Deep layer
Water fluxes				
Residual flux V_R (m³ s⁻¹)	$(-1.93 \pm 0.49) \times 10^3$	$(-0.90 \pm 0.29) \times 10^3$	$(-1.21 \pm 0.33) \times 10^3$	
Horizontal mixing flux V_X (m³ s⁻¹)	$(0.35 \pm 0.22) \times 10^6$	$(0.14 \pm 0.09) \times 10^6$	$(0.07 \pm 0.02) \times 10^6$	$(0.11 \pm 0.04) \times 10^6$
Vertical mixing flux V_Z (m³ s⁻¹)			$(0.09 \pm 0.06) \times 10^6$	
Non-conservative nutrient fluxes				
DIP (10⁴ mmol s⁻¹)	3.5 ± 3.6	1.1 ± 1.4	-0.01 ± 0.02	1.6 ± 0.8
DIN (10⁴ mmol s⁻¹)	75 ± 81	12 ± 11	0.07 ± 0.2	33 ± 18
DOP (10⁴ mmol s⁻¹)	0.7 ± 0.9	0.1 ± 0.3	0.1 ± 0.2	-0.1 ± 0.3
DON (10⁴ mmol s⁻¹)	-26 ± 32	-2 ± 5	-2 ± 2	-2 ± 9
DOC (10⁴ mmol s⁻¹)	-45 ± 590	-8 ± 172	-50 ± 147	-141 ± 154
POC (10⁴ mmol s⁻¹)	-65 ± 57	-26 ± 30	8 ± 15	2 ± 24
PON (10⁴ mmol s⁻¹)	-7 ± 7	-2 ± 3	-0.7 ± 0.8	-1.6 ± 2.6
POP (10⁴ mmol s⁻¹)	-0.5 ± 0.4	-0.1 ± 0.2	-0.04 ± 0.07	-0.07 ± 0.1

3. Results and discussion

The estimated shelf-slope exchanges of water and elements are reported in Table 5 and the budgetary analysis is presented in Table 6.

3.1. Shelf-slope exchanges

The Gulf of Lion' shelf has a low residual export volume compared to the large mixing exchanges between the shelf and the slope regions. A sensitivity analysis indicated that most of the uncertainty on the residual flow reflected uncertainty about river input. The large uncertainty about the mixing transport was due essentially to the salinity gradient between the shelf and the slope regions.

Shelf-slope exchanges predominate in winter and were about 10% of the along-slope water transport (ca. 2×10^6 m³ s⁻¹). Mixing exchanges decreased by three to sixfold for the spring and summer surveys. This seasonal trend with maximum exchanges during winter agrees with the measured variability of along-slope current. Durrieu de Madron et al. (1999) and Lapouyade and Durrieu de Madron (2001) showed from annual to multi-annual current records that the mesoscale variability of the surface and deep currents on the slope has a clear seasonal signal with maximum fluctuations during winter, which favors the cross-slope exchanges of matter.

The exchange time of water in the shelf system can be calculated simply as

$$\tau = \frac{VS}{(\,|V_r| + V_x)}$$

Where VS ($= 9.1 \times 10^{11}$ m³) is the volume of the shelf water and $|V_r| + V_x$ is the total flow across the shelf-ocean boundary. Thus, the residence time of the shelf water is between 1 and 2 months.

The exchange fluxes predicted by the box model (despite large uncertainty values) generally indicate that the shelf area acts as a sink for dissolved inorganic nutrients, and as a source to the offshore waters for most of the organic matter (Table 5).

During the winter surveys, the DOP flux showed an opposite trend to those of other organic matter. This suggests that the Gulf of Lion acts during the winter period as a net sink for both DOP and DIP, and, it is worthwhile to note that the model reproduces the peculiar status of the phosphorus elsewhere observed over the whole shelf, where a severe phosphorus depletion was systematically detected in the shelf waters relative to those of the slope during the winter-early spring (Diaz, 2000; Diaz et al., 2001). The riverine inputs, mainly from the Rhone river have very low phosphorus content with a N to P ratio of about 78 (Table 4) which is far greater than the classical Redfield ratio (Redfield et al., 1963); this latter feature probably increases the phosphorus depletion in the Gulf of Lion. In this sense, the special status of phosphorus in this Mediterranean area is very similar to that observed in several major marginal seas such as the

Table 6

Estimates (and 95% confidence interval) of non-conservative nutrient budgets for three surveys in the Gulf of Lion. Positive and negative numbers represent an excess and a deficit in the system, respectively

Nutrient budgets	January 1999	March 1998	June 1998	
			Surface layer	Deep layer
ΔDIP (10⁴ mmol s⁻¹)	4.1 ± 3.6	1.5 ± 1.5	0.4 ± 0.2	1.7 ± 0.9
ΔDIN (10⁴ mmol s⁻¹)	111 ± 82	36 ± 13	24 ± 7	26 ± 19
ΔDOP (10⁴ mmol s⁻¹)	1.0 ± 0.9	0.2 ± 0.3	0.4 ± 0.2	-0.1 ± 0.3
ΔDON (10⁴ mmol s⁻¹)	-16.6 ± 32.0	2.3 ± 5.2	-0.2 ± 4.9	0.4 ± 9.5
ΔDOC (10⁴ mmol s⁻¹)	-5 ± 593	9 ± 171	-200 ± 217	33 ± 222
ΔPOC (10⁴ mmol s⁻¹)	-86 ± 59	-70 ± 34	-10 ± 26	-18 ± 36
ΔPON (10⁴ mmol s⁻¹)	-6.4 ± 7.4	-1.5 ± 2.5	-2.2 ± 2.2	0.8 ± 3.3
ΔPOP (10⁴ mmol s⁻¹)	-0.4 ± 0.4	-0.05 ± 0.2	0.1 ± 0.1	-0.04 ± 0.1

South China sea basin (Chen et al., 2001), in the Northern Baltic sea (Lignell et al., 1992) and in the Bay of Biscay, Northeastern Atlantic (Herbland et al., 1998).

During the early-summer survey, the surface layer of the shelf becomes a net source for DIP to the slope waters and a net sink for POC. These features are in line with field measurements showing the shelf area as a preferential site for the regenerative processes particularly during summer (Diaz, 2000). In the deep layer, the model predicts nutrient exchanges between the slope and shelf waters different from those of the surface layer: for example, more DIN and DIP are imported than exported from the slope to the shelf in the deep layer. This import is in a ratio of 20:1 (DIN:DIP), typical of that found for deep Mediterranean water (McGill, 1969). The model result is in accordance with the observations of LIW upwelling on the shelf in early summer (Minas and Minas, 1989; Conan and Pujo-Pay, 1995). The estimated net export of DOP to the slope water suggests that the deep layer may be a preferential zone for POP remineralization.

The model results on the organic carbon fluxes (i.e. the shelf acts as a source of DOC) are also consistent with recent field observations (Diaz, 2000) that reveal a large DOC accumulation over the shelf in spring and summer followed by a winter decline. While the results are based on short term surveys, the calculated nitrate fluxes accord with those obtained across an annual cycle (Tusseau-Vuillemin et al., 1998) using a biogeochemical model coupled with a general circulation model. The daily estimates of the net advective flux across the margin boundary, which includes the continental slope, indicate that for most of the time the Gulf of Lion acts as a sink of oceanic nitrate. Furthermore, Tusseau-Vuillemin et al. (1998) calculated net nitrate fluxes across the oceanic boundaries of the Gulf of Lion for two different periods of about 330 mol s^{-1} (0.4 thousands of tons of N–NO$_3$ per day), which are of the same order of magnitude as those estimated by the box model. Similarly, the export of POC estimated for the winter survey (650 mol s^{-1}) is comparable to the export estimated by Lapouyade and Durrieu de Madron (2001) from comparison of the inflow and outflow of the Northern Current across a hydrological section encompassing the Gulf of Lion (1040 mol C s^{-1}). Moreover, the two earlier studies showed that the margin acts as a source of nitrate and particulate matter to the open sea mainly in winter, during events of dense shelf water cascading that washes out in the shelf water towards the intermediate or deep slope waters. These latter features, and especially those concerning the net export of particulate matter to the shelf-slope, have been recently found in the general functioning of several major continental margins such as the northern Gulf of Biscay (Wollast and Chou, 2001a, b), the East China Sea continental shelf (Chen and Wang, 1999) and the Middle Atlantic Bight (Biscaye et al., 1994). It is worth noting that the winter (January 1999) survey took place a few weeks before a huge event of dense shelf water cascading down the slope and across the whole western Mediterranean deep basin (Béthoux et al., 2003) that entrained about 1.8×10^5 m^3 s^{-1} of water during 1 month.

3.2. Balance of non-conservative materials and air-sea exchanges implications

Non-conservative DIP and DIN fluxes, as well as dissolved and particulate organic phosphorus (DOP, POP), nitrogen (DON, PON) and carbon (DOC, POC) fluxes, were calculated using the estimated volume transports. Fluxes of non-conservative elements are dominated by river inputs, sediment release and shelf-ocean mixing fluxes. Only budgets for DIP, DIN, and occasionally for DOP are significantly different from zero. A sensitivity analysis indicated that most of the uncertainty arose from term for the shelf-slope mixing transport, which in turn relates to the shelf-slope gradient and the uncertainty of the elemental mean concentration in these regions. This clearly shows that this box-model approach gives better results where strong gradients exist, and that error estimates are essential to avoid misinterpretation of the budgets.

The imbalance of the DIN in the system (Table 6) suggests that either the exchange terms may be missing in the computation of the budget or, more likely, that several biological processes affect the stock of DIN on the shelf. The removal of DIN by the denitrifying bacteria is generally considered as an anaerobic process, i.e. with a low occurrence in oxygenated water column. However, the denitrification process can occur in the shelf sediments (Codispoti, 1995) but also over the water column in some anaerobic microenvironments such as in sinking particulate organic matter (Bianchi et al., 1992) and may account for a relatively high rate (Alldredge and Cohen, 1987). In the Mediterranean Sea and especially in the Gulf of Lion, the plume of the Rhone river with very turbid waters and high DIN concentrations has been shown as a preferential environment for denitrification (Omnes et al., 1996). Also, in the water column of the Gulf of Lion, Michotey and Bonin (1997) measured low denitrification (ca. 100 µmol m^{-3} d^{-1}) associated with particles, with a peak activity (up to 250 µmol m^{-3} d^{-1}) in autumn and barely detectable rates (~2 µmol m^{-3} d^{-1}) during the summer oligotrophic conditions. Following to the LOICZ procedure (Gordon et al., 1996; Smith and Hollibaugh, 1993), an estimate can be made of net nitrogen metabolism (Nfixation-denitrification) of the system, based on system mass imbalance of dissolved nitrogen (ΔDIN, ΔDON) and phosphorus (ΔDIP, ΔDOP), and C:N:P stoichiometric assumptions. With the assumption that the dominant primary producer is phytoplankton, a classical Redfield N:P ratio of 16:1 has been used to compute the net nitrogen metabolism (Nfixation-denitrification) of the system, that is negative and around –119 mol s^{-1} (–0.86 mmol N m^{-2} d^{-1}) across the three surveys (Fig. 2). Considering an annual base and neglecting the seasonal variations, this result implies a maximum value of 0.31 mol N m^{-2} per year for the denitrification rate; this latter value is close to the value of 0.137 mol N m^{-2} per year found by Wollast (1998) for a global shelf average. The fact
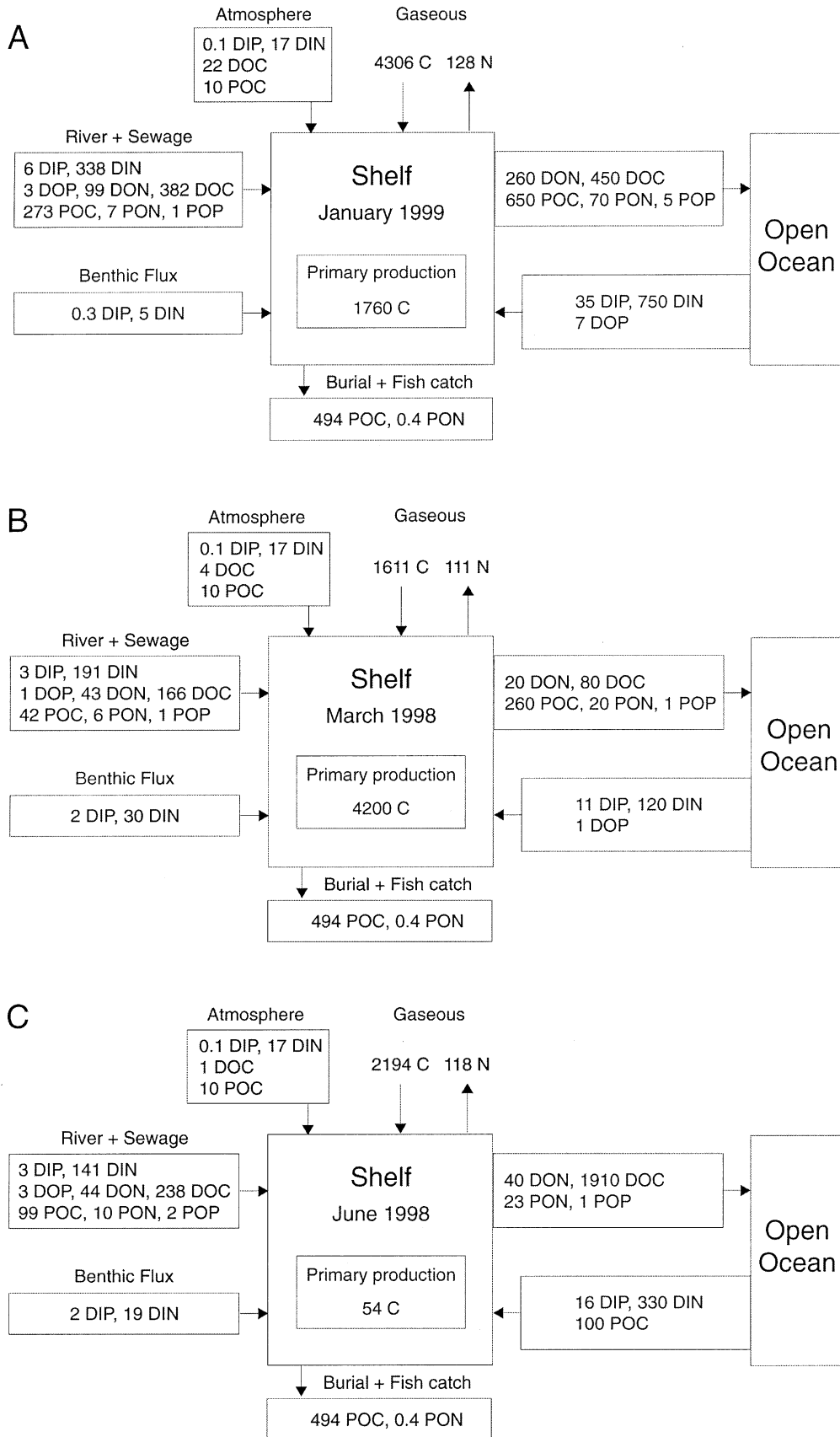
A

Atmosphere

0.1 DIP, 17 DIN
22 DOC
10 POC

Gaseous

4306 C   128 N

River + Sewage

6 DIP, 338 DIN
3 DOP, 99 DON, 382 DOC
273 POC, 7 PON, 1 POP

Shelf

January 1999

Primary production

1760 C

260 DON, 450 DOC
650 POC, 70 PON, 5 POP

Open Ocean

Benthic Flux

0.3 DIP, 5 DIN

35 DIP, 750 DIN
7 DOP

Burial + Fish catch

494 POC, 0.4 PON

B

Atmosphere

0.1 DIP, 17 DIN
4 DOC
10 POC

Gaseous

1611 C   111 N

River + Sewage

3 DIP, 191 DIN
1 DOP, 43 DON, 166 DOC
42 POC, 6 PON, 1 POP

Shelf

March 1998

Primary production

4200 C

20 DON, 80 DOC
260 POC, 20 PON, 1 POP

Open Ocean

Benthic Flux

2 DIP, 30 DIN

11 DIP, 120 DIN
1 DOP

Burial + Fish catch

494 POC, 0.4 PON

C

Atmosphere

0.1 DIP, 17 DIN
1 DOC
10 POC

Gaseous

2194 C   118 N

River + Sewage

3 DIP, 141 DIN
3 DOP, 44 DON, 238 DOC
99 POC, 10 PON, 2 POP

Shelf

June 1998

Primary production

54 C

40 DON, 1910 DOC
23 PON, 1 POP

Open Ocean

Benthic Flux

2 DIP, 19 DIN

16 DIP, 330 DIN
100 POC

Burial + Fish catch

494 POC, 0.4 PON

Fig. 2. Schematic diagram for the carbon and nutrients budgets (in mol s^{-1}) for three surveys in the Gulf of Lion continental shelf: (A) January 1999, (B) March 1998 and (C) June 1998. Primary production is integrated over the surface of the continental shelf (12 000 km^2).

that the denitrification process in the whole shelf slightly dominates the N_2 fixation process implies on one hand that the Gulf of Lion systematically acts as a sink for nitrate, on the other hand it suggests that the rates of N_2 fixation are of the same order of magnitude as the denitrification rates, i.e. very low in the Gulf of Lion by considering the denitrification measurements performed by Michotey and Bonin (1997).

According to the LOICZ procedure (Gordon et al., 1996; Smith and Hollibaugh, 1993), the calculated mass imbalance of phosphorus (ΔDIP) with stoichiometric C:P ratio for the major primary producer in the system allows an estimate of net ecosystem metabolism (NEM). NEM is more conveniently annotated as ($p - r$), where p is production and r is respiration. Based on a C:P Redfield ratio of 106:1, the Gulf of Lion was interpreted to be autotrophic by a minimum value of 1610 mol C s^{-1} (11.6 mmol C m^{-2} d^{-1}) for the spring survey to a maximum value of 4306 mol C s^{-1} (31.3 mmol C m^{-2} d^{-1}) during the winter survey. An intermediate value of 2194 mol C s^{-1} (15.8 mmol C m^{-2} d^{-1}) was observed during the early summer cruise. This result implies that the study area would be a net producer of organic matter and thus acting as a net sink for CO_2. This feature agrees with the review of Gattuso et al. (1998), that indicates that the majority of coastal ecosystems—except estuaries—works as net autotrophic systems on an annual basis. An independent computation of the net metabolism for the shelf waters of the Gulf of Lion recently provided an analogous result (Sempéré et al., 2000). They directly calculated the bacterial respiration in the water column and at the sediment/water interface ($8.4 \pm 7.7 \times 10^{10}$ mol C per year) and the total carbon fixed by phytoplankton (13.6×10^{10} mol C per year) in the shelf water. Their estimate of the NEM of 5.2×10^{10} mol C per year is in accordance with the present calculations, which yield an average value of 8.5×10^{10} mol C per year. The most recent estimations of the global coastal NEM vary from 12×10^{12} mol C per year (Rabouille, 1997) to about 200×10^{12} mol C per year (Wollast, 1998). According to the review of Gattuso et al. (1998), this great range of variation may be essentially due to differences in the estimate of the global respiration term (r). These latter figures combined with those of the present study indicate that the NEM of the Gulf of Lion may represent from 0.05% to 0.70% of the global coastal NEM which is a rather large contribution regarding the very small surface of the study area with respect to the total surface of coastal zones.

4. Conclusion

Hydrographic and nutrients data collected during three seasonal surveys in the Gulf of Lion indicate that salinity and concentration of most organic and inorganic elements significantly vary between the shelf and the open sea (slope) area. The simple box modeling approach used to calculate the shelf-slope fluxes of water, salt and non-conservative

element yields robust results, which are however, subject to large uncertainties.

Results indicate that advective fluxes between the shelf and the open sea have an important influence with respect to the other major inputs (river discharges and sediment release fluxes). Mixing flow at the shelfbreak mainly supports the shelf-slope exchanges. Consequently, the stronger depletion of inorganic nutrients (DIN, DIP) in the shelf waters than in the slope waters leads to a gain for the shelf box, thus providing nutrients to support the local productivity. In summer, the fluxes are significantly reduced. Balancing the DIP budgets suggests that the biological system on the shelf is autotrophic and thus acts as a sink of CO_2. The intensity of NEM agrees with that calculated for a previous study. In addition, balancing the DIN budgets suggests that denitrification predominates over nitrogen fixation, and that the system is net denitrifying and thus acts as a source of N_2.

Current studies on underground freshwater discharge and the impact of bottom trawling on the shelf will provide an additional input of carbon, nitrogen and phosphorus to the system. This new term will not change the conclusions of the present budgets, because it will a priori reinforce the excess of dissolved inorganic elements (DIN, DIP) on the shelf. Modeling of the dense shelf water formation and cascading over the 1995–2000 period, including the exceptional event of 1999, is underway and will permit assessment of the temporal variability of this export process and its role in the exchanges of water and dissolved elements between the shelf and the open sea. Furthermore, direct measurement of CO_2 flux at the ocean-atmosphere interface are presently being made in the Gulf of Lion and will provide a better estimate of the air-sea fluxes as well as the spatial and temporal (seasonal) variability.

Acknowledgements

Appendix A

A.1. *One-layer model*

We briefly summarize the one box model already described by Gordon et al. (1996). For the conservative water budget, we consider river discharge (V_Q), sewage discharge (V_O), precipitation (V_P), evaporation (V_E), and mixing flow (V_X) and residual flow (V_R) at the boundary with the open ocean (Fig. 2A). In the following equations, inflows are

considered as positive and outflows are considered as negative. The equilibrium between the water inflows and outflows is:

$$(V_Q + V_O + V_P + V_X) - (V_E + V_X) + V_R = 0$$

For the conservative salt budget, only the cross-shelf exchanges are taken into account. The equilibrium between the salt fluxes entering and escaping the system is written:

$$(V_X S_{ocean}) - (V_X S_{shelf}) + V_R S_R = 0$$

where S_{shelf} is the mean shelf salinity, S_{ocean} the mean open ocean salinity. Because the residual flow can be either out (freshwater inflow exceeding evaporation) or into the system (net evaporation) the appropriate salinity for residual flow is the average salinity between the two systems, $S_R = (S_{shelf} + S_{ocean})/2$.

The budget of the non-conservative dissolved element Y on the shelf results from inputs by river ($V_Q Y_Q$), sewage ($V_O Y_O$) and atmospheric deposition ($V_{atm} Y_{atm}$) as well as exchanges with the open ocean ($V_X Y_{ocean}$, $V_X Y_{shelf}$ and $V_R Y_R$), and the sediment ($V_{sed} Y_{sed}$). The imbalance (ΔY) between the inputs and outputs is:

$$\Delta Y = (V_Q\, Y_Q + V_O\, Y_O + V_{atm}\, Y_{atm} + V_{sed}\, Y_{sed} \\ + V_X\, Y_{ocn}) - (V_X\, Y_{syst}) + V_R\, Y_R$$

Given that the riverine and atmospheric inputs as well as the salinity and dissolved element concentrations are known, the residual and mixing exchanges flows between the shelf and the open ocean are calculated as:

Residual flux:

$$V_R = V_E - (V_Q + V_P + V_O)$$

Mixing flux:

$$V_X = - V_R \frac{S_R}{(S_{ocn} - S_{syst})} \\ = - (V_Q + V_P + V_O - V_E) \frac{S_R}{(S_{ocn} - S_{syst})}$$

Thus the imbalance of non-conservative element is:

$$\Delta Y = V_Q\, Y_Q + V_O\, Y_O + V_{atm}\, Y_{atm} + V_{sed}\, Y_{sed} \\ + V_X(Y_{ocn} - Y_{syst}) + V_R\, Y_R$$

A.2. Two-layers model

For the stratified system, we developed a two-layer model using the same basic scheme as for the one layer model. For the conservative water budgets in the two layers, we consider river discharge (V_Q), sewage discharge (V_O), precipitation (V_P), evaporation (V_E), vertical mixing (V_Z), surface and deep shelf-slope mixing (V_{X-s} V_{X-d}) and residual (V_R) exchanges. The equilibrium between the water inflows and outflows in the surface layer is:

$$(V_Q + V_O + V_P + V_{X-s} + V_Z) - (V_E + V_{X-s} + V_Z) + V_R = 0$$

For the deep layer the water balance is described by:

$$(V_{X-d} + V_Z) - (V_{X-d} + V_Z) = 0$$

For the conservative salt budgets, the surface layer balance is:

$$(V_{X-s} S_{ocn-s} + V_Z S_{syst-d}) \\ - (V_{X-s} S_{syst-s} + V_Z S_{syst-s}) + V_R S_R = 0$$

The deep layer salt balance is:

$$(V_{X-d} S_{ocn-d} + V_Z S_{syst-s}) \\ - (V_{X-d} S_{syst-d} + V_Z S_{syst-d}) = 0$$

The residual and mixing exchanges terms between the shelf and the adjacent open ocean can be calculated if one makes an additional assumption. We hypothesize that the horizontal mixing is proportional to the layer thickness and to the cross-slope current variance. Indeed, Durrieu de Madron et al. (1999) suggested that the turbulent mixing, due to meandering of the Northern Current around the shelfbreak, induces a significant exchange of matter between the shelf and the slope. This mixing can be presented as a function of the current variance in the cross-slope direction. Thus the vertical variation of mixing intensity can be written as:

$$\frac{V_{X-s}}{V_{X-d}} = \alpha \frac{H_s}{H_d}$$

where H_s and H_d are the thickness of the surface and deep layers at the shelfbreak, and α is the ratio of the mean cross-slope current variances between the surface and deep layers.

The imbalance of the non-conservative dissolved element for the surface layer (Fig. 3b) is:

$$\Delta Y_s = (V_Q\, Y_Q + V_O\, Y_O + V_{atm}\, Y_{atm} + V_{X-s}\, Y_{ocn-s} \\ + V_Z\, Y_{syst-d}) - (V_{X-s}\, Y_{syst-s} + V_Z\, Y_{syst-s}) + V_R\, Y_R$$

The imbalance for the deep layer is:

$$\Delta Y_d = (V_{X-d}\, Y_{ocn-d} + V_Z\, Y_{syst-s} + V_{sed}\, Y_{sed}) \\ - (V_{X-d}\, Y_{syst-d} + V_Z\, Y_{syst-d})$$

The solutions for the residual and mixing flows are:

Residual flux (surface layer):

$$V_R = V_E - (V_Q + V_P + V_O)$$

Horizontal mixing flux (surface layer):

$$V_{X-s} = \frac{\alpha H_s}{H_d} V_{X-d} \\ = - \frac{V_R S_R}{(S_{ocn-s} - S_{syst-s}) + \dfrac{H_d}{\alpha H_s}(S_{ocn-d} - S_{syst-d})}$$

Horizontal mixing flux (deep layer):

$$V_{X-d} = -\frac{V_R S_R}{\dfrac{\alpha H_s}{H_d}(S_{ocn-s} - S_{syst-s}) + (S_{ocn-d} - S_{syst-d})}$$

Vertical mixing flux:

$$V_Z = V_{X-d}\frac{(S_{ocn-d} - S_{syst-d})}{(S_{syst-d} - S_{syst-s})} = -\frac{V_R S_R(S_{ocn-d} - S_{syst-d})}{\left(\dfrac{\alpha H_s}{H_d}(S_{ocn-s} - S_{syst-s}) + (S_{ocn-d} - S_{syst-d})\right)(S_{syst-d} - S_{syst-s})}$$

Thus, the imbalance of non-conservative element for the surface layer is:

$$\Delta Y_s = V_Q Y_Q + V_O Y_O + V_{atm} Y_{atm} + V_{X-s}$$
$$(Y_{ocn-s} - Y_{syst-s}) + V_Z(Y_{syst-d} - Y_{syst-s}) + V_R Y_R$$

Imbalance of non-conservative element (deep layer):

$$\Delta Y_d = V_{X-d}(Y_{ocn-d} - Y_{syst-d})$$
$$- V_Z(Y_{syst-d} - Y_{syst-s}) + V_{sed} Y_{sed}$$

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