



Phosphate in the sediments of the Gulf of Lions (NW Mediterranean Sea), relationship with input by the river Rhone

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Key words: phosphate, sediment, Gulf of Lions, Mediterranean Sea

Abstract

We investigated P-input by the Rhone river into the Mediterranean Sea taking into account P trapped in the surface sediment of the Gulf of Lions. Total phosphate concentration was determined every cm in the upper 10 cm-layer of sediments sampled at 11 stations in the Gulf of Lions during two cruises (March 1998 and January 1999). Two low downward gradients, one East–West and another North–South, with distance to the Rhone river mouth were found. Except at one station, total phosphate concentration in surface sediments was found to be constant with depth down to 10 cm. Values for individual stations ranged between 400 and 700 $\mu\text{g g}^{-1}$ with an average value of 547 $\mu\text{g g}^{-1}$ (st. dev. = 63 $\mu\text{g g}^{-1}$) for the whole gulf. The low variability in total-P concentration in sediments is in contrast to the large variability in suspended matter load of the river Rhone and suggests the dominance of authigenic P removal mechanisms in P burial. The total P-pool in the upper 10 cm-layer of the sediments in the gulf was estimated at 562 kt, with about 80% trapped into the shelf and 20% into the slope. Annual P-deposition was estimated as 7.2–12.4 kt y^{-1} , from the P-pool in the sediment and the sedimentation rates. This is equivalent to a previous estimation of the river Rhone input, estimated to be about 6.5–12.2 kt y^{-1} . As the Rhone is the major river flowing into the Mediterranean Sea, total P in surface sediments of the Gulf of Lions should be taken into account in P-budgets at the scale of the Mediterranean Sea.

Introduction

Phosphate is an essential nutrient which occurs in low concentration in the aquatic environment. Primary productivity is considered to be essentially controlled by phosphate in lakes (Vollenweider, 1976) but by nitrate in the sea (Thomas, 1966, 1969; Eppley et al., 1973). Nevertheless recent works indicate strong phosphate limitation in several oceanic provinces, particularly the Mediterranean Sea where a low concentration (<20 nM during the summer period) controls planctonic production (Krom et al., 1991; Thingstad et al., 1998; Diaz et al., 2001; Moutin & Raimbault, 2002).

The P-concentration in the Mediterranean Sea depends on its river input and on Atlantic and Mediterranean water exchange across the Strait of Gibraltar. The terrestrial input is estimated at 14% of the P-

exchange at the Strait by Coste et al. (1988) but at 81% by Bethoux (1989). These two authors took into account rivers input in their budget, but phosphate buried in the sediment was not considered. Since the construction of the Aswan dam on the river Nile, the Rhone is the major river flowing into the Mediterranean Sea. It is the major source of sediments into the Gulf of Lions (Leveau & Coste, 1987) which is an interface between freshwater input from the Rhone and the open Mediterranean Sea water. Coastal sediments are able to trap large amount of phosphate (Lucotte, 1988; Golterman & de Oude, 1991). Using the P-concentration in the surface sediment of the Gulf of Lions, and measurements of the sedimentation rates, we estimate the annual flux of phosphate buried in these sediments. This first assessment is compared to the annual P-flux by the Rhone into the Gulf of Lions.

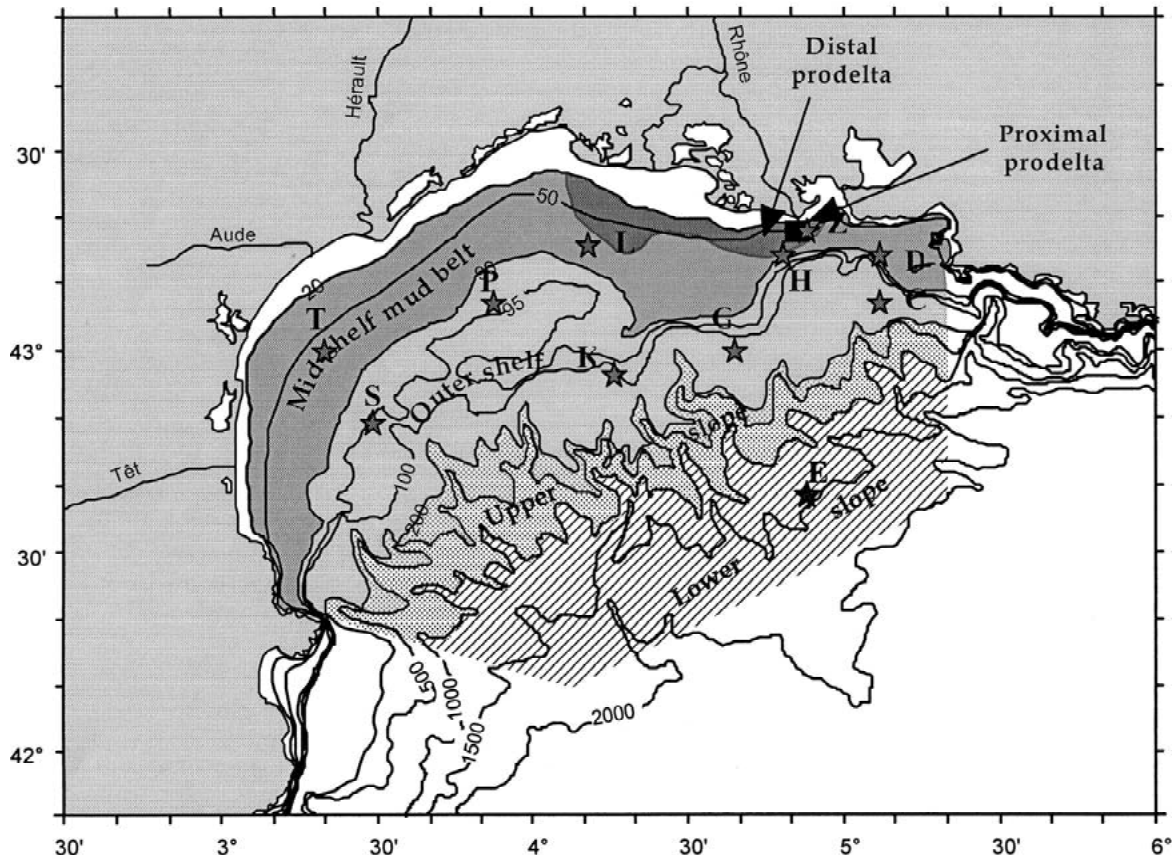


Figure 1. Study site and location of sediment sampled stations in the Gulf of Lions, during MOOGLI (March 1998 and January 1999), redrawn from Durrieu de Madron et al. (2000).

Material and methods

Study site

The Rhone, with a total length of 812 km and a catchment area of almost 97 800 km², is the main river flowing into the Mediterranean Sea. The Rhone transports large quantities of suspended matter towards its estuary, and it represents the dominant (80%) source of sediment for the continental shelf of the Gulf of Lions (Pont, 1997). The mean flow rate was estimated over a 30 years period (1961–1994) to be 1690 m³s⁻¹ with a minimum of 1064 m³s⁻¹ and a maximum of 2388 m³s⁻¹ (Moutin et al., 1998). Total water and solid flow rates were precisely estimated during a one year period (June 1994–May 1995) at 70 × 10⁹ m³ y⁻¹ and at 14 × 10⁶ t y⁻¹ (Pont, 1997). The mean daily concentration of suspended matter was 200 mg l⁻¹. During flow rates >3000 m³s⁻¹, the solid flow rate has reached 11 × 10⁶ t which represented 81% of total

solid flow rate (Pont, 1997). Inter annual variability of solid flow rates was high and a retro-calculation obtained from daily flow rates since 1961 gave a mean annual value of 6.2 × 10⁶ t y⁻¹ with a range of 1.4–16.4 t y⁻¹ (Pont, 1997).

The Gulf of Lions is a continental margin of 21 610 km² (Durrieu de Madron et al., 2000). It represents a wide, progressive margin with a crescent-shaped continental shelf (up to 70 km wide) and a slope which is deeply incised by a large number of submarine canyons which constitute about 50% of the slope surface (Monaco et al., 1990). Four major sedimentary units (Fig. 1) on the shelf (proximal Rhone prodelta, distal Rhone prodelta, mid shelf mud belt and outer shelf), and two on the slope (upper and lower slope) are distinguished by Durrieu de Madron et al. (2000). The sediment supply coming from the Rhone and other lesser rivers and the supply of desert dust from the Sahara make it an important area of deposition (Millot, 1990). Water circulation is controlled by the

Liguro-Provençal current (NE–SW), which forms the principal transfer mechanism (Millot, 1990) on which the outflow plume of the Rhone river is superimposed (Zuo et al., 1991). The Gulf of Lions is a complex hydrological area receiving freshwater from the Rhone river, surface North Atlantic water from the Liguro-Provençal Current and is subject to intense vertical mixing (Lefevre et al., 1997).

Sediment sampling

Samples were collected during MOOGLI cruises (MOdélisation et Observation du Golfe du Lion) from March 15 to April 2, 1998 and from January 11 to 21, 1999. Sediment cores were taken at 11 stations in the Gulf (Fig. 1) with a Mark VI sediment multicorer (Bowers and Connelly, Scotland), which permitted simultaneous sampling of 4 large-diameter cores (diameter 15 cm, length 30 cm, and 20 cm of water, with an undisturbed sediment water interface), for a total surface of 0.071 m² (Denis et al., 2001). After collection, subsamples of 7 cores of 2.7 cm of diameter were taken from each core. They were cut into 1 cm thick slices, down to 10 cm depth; slices of the same depth were pooled (Denis, 1999). Wet sediment was lyophilized and ground to an homogeneous powder.

Total phosphate analysis

Total phosphate (Tot-P) concentration was measured on replicates (duplicates or triplicates for samples where variability was >1.5%) according to an adaptation of method IBP no 8, 5.7.3, (Golterman et al., 1978). Polyphosphates and org-P were hydrolysed by H₂SO₄ and K₂S₂O₈ to orthophosphate, which are then spectrophotometrically measured according to Murphy & Riley (1962).

Dry sediment (0.2 g) was rehydrated with 10 ml of MilliQ-water and mineralized with 1 ml H₂SO₄ 96% and 2 g K₂S₂O₈, during 1 h at 120 °C and at 1 bar. After centrifugation (10 min, 2550 r min⁻¹), the supernatant was poured in an acid and Milli-Q water-cleaned bottle. The pH of the supernatant was adjusted to 1.5–2 with NaOH 10 M (Merck, 0.0001% PO₄) and brought up to 100 ml with MilliQ-water. Orthophosphate (o-P) was measured at 880 nm on a aliquot of 5 ml after 10-fold dilution. The mean absorbance of blank (same protocole without sediment) was 0.0024 ± 0.0005 (*n* = 26), corresponding to P = 0.75 μg l⁻¹. Tot-P concentrations are expressed in μg g⁻¹ d.w. of sediment. Addition of known amounts of P showed that there were no major interferences of components

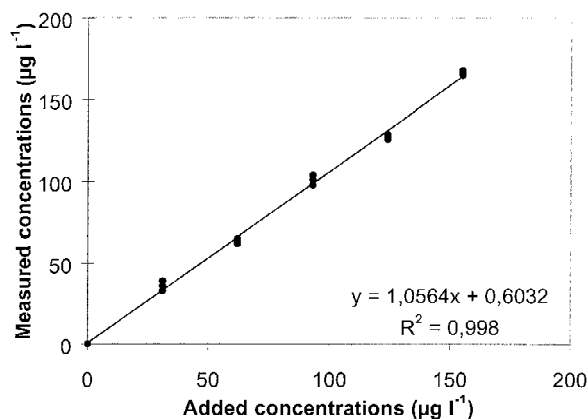


Figure 2. Relationships between theoretical added and measured o-P concentrations.

(Blomqvist et al., 1993) on phosphate measurements (Fig. 2). Recovery of known amounts of P added was 100 ± 5%.

Sedimentation rates

Sedimentation rates (*R*) were calculated from ²¹⁰Pb profiles in surface sediments in the Gulf of Lions (Radakovitch & Heussner, 1999) and from distribution of ¹³⁷Cs and ¹³⁴Cs (Charmasson et al., 1998) in the Rhone prodelta. From these sedimentation rates, accumulation rates (*r*) (g cm⁻² an⁻¹) were determined (Durrieu de Madron, et al., 2000), according to the formula: $r = R(1-\phi)d\rho$ with ϕ (porosity) = 0.5 and ρ (dry density of the sediments) = 1.6 g cm⁻³ (Zuo et al., 1997).

Results

Total-P concentration in surface sediment

Tot-P concentration profiles in the top 10 centimeters of sediment are shown in Figure 3. Results are presented for each station following indication in Table 1, from the river mouth to the open Mediterranean stations. The shallowest station Z (20 m) was located near the mouth on the proximal prodelta. The irregular profile depicted a maximum of 712 μg g⁻¹ between 1 and 2 cm depth. Mean P-concentration of 663 μg g⁻¹ with a st. dev. of 24 μg g⁻¹ (*n* = 10) was the highest measured. Station H, located in the distal prodelta, faced the mouth of the Rhone river at a distance of about 10 km from the coast. P-concentration was constant over depth although a small decrease was observed at 5

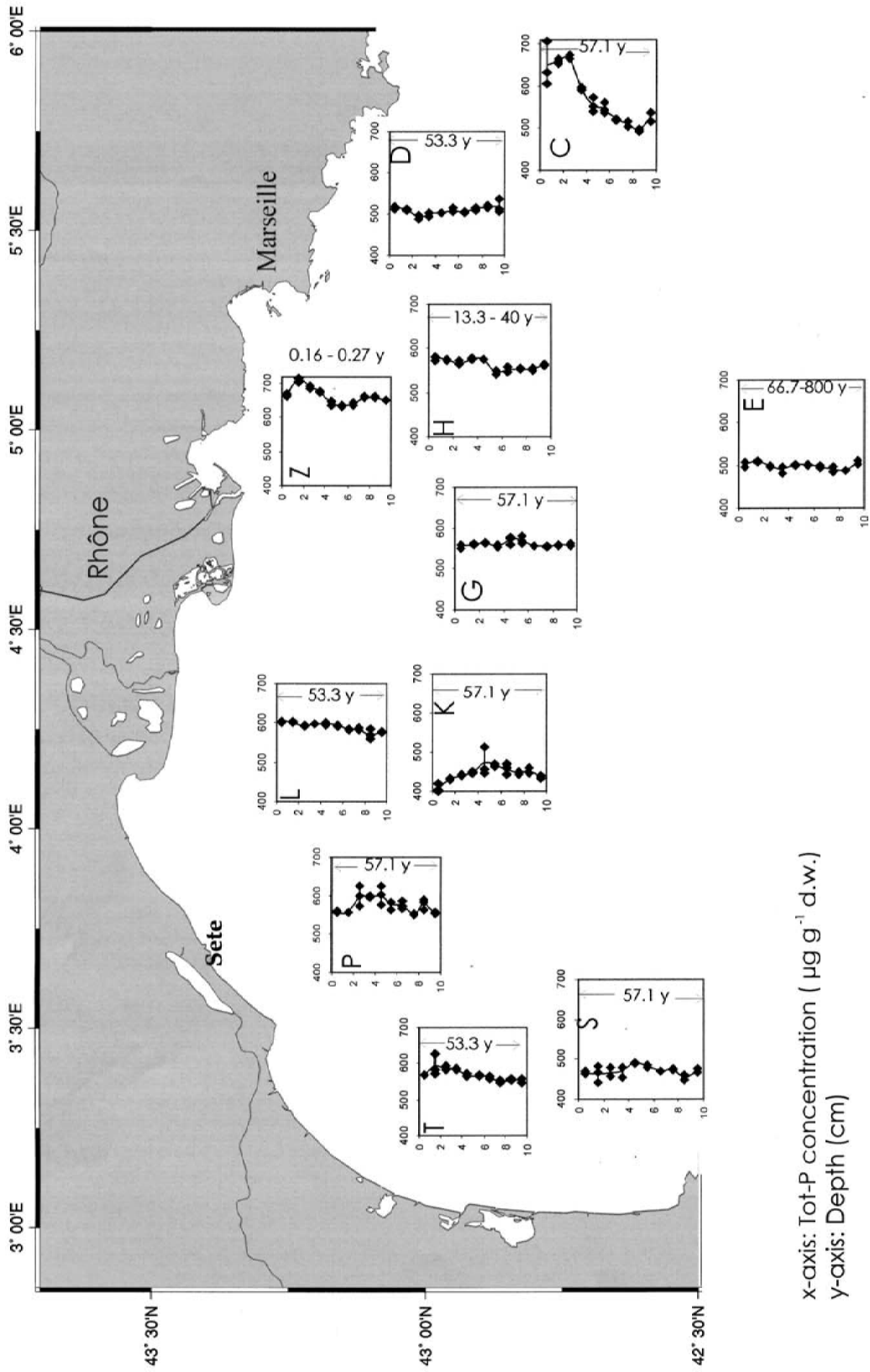


Figure 3. Tot P-concentrations in surface sediment of the Gulf of Lions.

Table 1. Station location, depth, porosity and Tot P-concentration in sedimentary units of the Gulf of Lions

Sedimentary units	Stations	Latitude N	Longitude E	Depth (m)	Cores sampled n	Mean porosity ^a Mean \pm S.D (n = 10)	Total phosphate concentration Mean \pm S.D (n = 10) ($\mu\text{g g}^{-1}$)
Proximal Rhone prodelta	Z	42° 19.70	04° 53.25	20	4	- ^b	663 \pm 24
Distal Rhone prodelta	H	43° 14.53	04° 53.10	98	3	0.58 \pm 0.07	564 \pm 12
Mid shelf mud belt (20–90 m)	D	43° 14.98	05° 08.03	94	4	0.52 \pm 0.06	509 \pm 8
	L	43° 11.95	04° 12.91	91	3	0.63 \pm 0.06	590 \pm 11
	T	43° 00.94	03° 19.83	64	4	0.63 \pm 0.06	569 \pm 15
Outer shelf (90–200 m)	C	43° 04.00	05° 07.60	162	3	0.33 \pm 0.06	573 \pm 65
	g	43° 03.99	04° 44.95	102	4	0.55 \pm 0.06	561 \pm 6
	K	42° 58.98	04° 14.93	98	4	0.41 \pm 0.03	446 \pm 18
	S	42° 49.09	03° 27.56	99	3	0.49 \pm 0.07	471 \pm 10
	P	43° 07.28	03° 47.93	96	4	0.56 \pm 0.05	575 \pm 19
Slope (200–2000 m)	E	42° 39.87	04° 45.04	1370	4	- ^b	498 \pm 7

^aRecalculated from Denis (1999).

^bNot available.

cm depth. The mean P-concentration at H was 564 $\mu\text{g g}^{-1}$ (st. dev. = 12; n = 10). Stations D, L and T were located in the mid shelf mud belt. A slight decrease with depth was observed, from 604 to 571 $\mu\text{g g}^{-1}$ and from 594 $\mu\text{g g}^{-1}$ to 522 $\mu\text{g g}^{-1}$, at stations L and T, respectively. A minimum of 492 $\mu\text{g g}^{-1}$ was observed at a depth of 3 cm at station D, but concentration was constant with depth as shown by its concentration of 516 and 518 $\mu\text{g g}^{-1}$ measured at 1 and 10 cm depth. At station D, located in the eastern part of the Gulf of Lions, the mean Tot-P concentration was 509 $\mu\text{g g}^{-1}$ (st. dev. = 9) lower than the mean Tot-P concentration of 590 $\mu\text{g g}^{-1}$ (st. dev. = 11) and 569 $\mu\text{g g}^{-1}$ (st. dev. = 15) at stations L and T, respectively.

Stations C, G, K, S and P are located on the outer shelf. The position of station C corresponds to the SOFI site (Site d'Observation Fixe, a laboratory site regularly sampled from 1997 to 2000). It is located near the shelf break. Tot-P concentration profile depicted large variations with depth which are only observed at this station. The concentration measured in the top 0–5 cm were high, ranging from 649 to 668 $\mu\text{g g}^{-1}$, similar to that observed at station Z near the river mouth. Under 5 cm depth, the concentration was around 500 $\mu\text{g g}^{-1}$.

Tot-P concentrations measured at stations G, S and P were constant over depth. A minimum average concentration of 471 \pm 10 $\mu\text{g g}^{-1}$ was measured at station S, the most distant from the Rhone mouth. At the stations G and P the mean Tot-P concentration was respectively 561 $\mu\text{g g}^{-1}$ (st. dev. = 6) and 575 $\mu\text{g g}^{-1}$ (st. dev. = 19). Tot-P concentration at station K increased regularly up to 5 cm, from 408 to 473 $\mu\text{g g}^{-1}$, and then decreased down to 10 cm reaching 435 $\mu\text{g g}^{-1}$. The mean concentration was 446 $\mu\text{g g}^{-1}$ (st. dev. = 19) which was the lowest mean concentration measured during this study.

Station E was the station sampled on the slope, at a depth of 1370 m. The Tot-P profile was constant over the top 10 cm of sediment with a mean concentration of 498 $\mu\text{g g}^{-1}$ (st. dev. = 7). For the whole Gulf, we calculated an overall mean Tot-P concentration of 547 $\mu\text{g g}^{-1}$ (st. dev. = 63; n = 110).

Sedimentation rates and average age of the top 10 cm of sediment

Mass accumulation rates measured in each sedimentary unit of the Gulf of Lions (Table 2) decreased rapidly seaward and gradually along-shore, from 30 to 50 $\text{g cm}^{-2} \text{y}^{-1}$ on the proximal Rhone prodelta

Table 2. Tot-P_{sed} per sedimentary units in the Gulf of Lions, mass accumulation and sedimentation rates, mean age of surface sediment. Estimation of P-pool in the top 10 cm of sediment (kt) and phosphate deposition during one year of each sedimentary unit and the whole Gulf of Lions.

Sedimentary units	Area (km ²)	Phosphate concentration Mean ± S.D (μgP g ⁻¹)	Mass accumulation rates ^a (g cm ⁻² y ⁻¹)	Sedimentation rates (cm y ⁻¹)	Age of the top 10 centimeters of sediment (y)	P-pool (kt)	Phosphate deposition (kt y ⁻¹)
Proximal Rhone prodelta	10	663 ± 24 (n=10)	30–50	37.5–62.5	0.16–0.27	0.33	1.2–2.1
Distal Rhone prodelta	600	564 ± 12 (n=20)	0.2–0.6	0.25–0.75	13.3–40	17	0.4–1.3
Mid shelf mud belt	4500	556 ± 42 (n=30)	0.15	0.188	53.3	125	2.3
Outer shelf	6500	525 ± 61 (n=50)	0.14	0.175	57.1	171	3.0
Slope	10 000	498 ± 7 (n=10)	0.01–0.12	0.0125–0.15	66.7–800	249	0.3–3.7
Total	21 610					562	7.2–12.4

^aFrom Durrieu de Madron et al. (2000).

to 0.01–0.12 g cm⁻² y⁻¹ on the slope (Durrieu de Madron et al., 2000). Corresponding sedimentation rates varied from 37.5–62.5 cm y⁻¹ near the mouth to 0.0125–0.15 cm y⁻¹ on the slope which in turn, gives an average age for the top 10 cm of sediment of 0.16–0.27 y (1.9–3.2 months) and 66.7–800 y, respectively. Each sedimentary unit is well defined by different sedimentation rates (Table 2).

P-pool in surface sediments

P-pool was assessed according to the P-concentration and calculation of dry sediment mass represented by the top 10 cm of sedimentary units (Table 2). There was about 562 kt of Tot-P in the top 10 cm of sediment in the whole Gulf of Lions, with more than 310 kt in the shelf and about 250 kt in the slope (Table 2).

Annual accumulation of phosphate in surface sediments

Knowing the P-pool and the average age of the surface sediments, we estimated the average quantity of phosphate deposited during one year for each sedimentary unit (Table 2). About 7.2–12.4 kt of phosphate were deposited each year in the Gulf of Lions, with 80% on the shelf and 20% on the slope (Table 2).

Discussion

Spatial and vertical distributions of Tot-P concentration in surface sediments, relationships with temporal trend

The Tot-P concentrations from different coastal margins are presented in Table 3. Our data agree with the range of 403–701 μg g⁻¹ measured by Fernex et al. (2001) for the continental shelf in the Rhone delta area (1986–1987), although their method for Tot-P was different (extraction with HCl after ignition to 600 °C). In comparison with other Gulfs or estuaries, the Tot-P concentration in the sediment of the Gulf of Lions is relatively low (Table 3).

Two major axes of spatial variation are the distance from the Rhone mouth and secondly the East–West dominant oceanic current. A slight, but general decrease from the river mouth to the open-sea stations was observed: the proximal station showed the highest concentration (663 μg g⁻¹ with a st. dev. of 24) while the Tot-P concentration decreased slightly towards the open sea stations, except for station C located near the shelf break. Tot-P concentrations in sediments of the stations distant from the mouth were generally lower than at the stations nearby. This trend could be simply related to the P-input by the Rhone. Sedimentation rates in the proximal Rhone prodelta were high and variable (38–63 cm y⁻¹). These highest values in the Gulf of Lions suggest that the sediment supplied to the

Table 3. Comparison of Tot P-concentration ranges in sediments of different coastal areas found in literature and present results.

Coastal areas	Depth	Depth of sediment	Tot-P ($\mu\text{g g}^{-1}$ of P)	Date	Reference
Gulf of Lions	20–1370 m	10 cm	400–700	1998	This study
Continental shelf in the Rhone delta area (Gulf of Lions, France)		0–3 cm	403–701	1986–1987	Fernex et al. (2001)
Northern Taiwan's Tanshui Estuary			328–1240		Fang (2000)
Mouth of the estuary in Charleston Harbor (South Carolina, U.S.A.)		20 cm	572–703	1996	Sundareshwar et al. (1999)
Bay of Seine (France)	< 30 m	2 cm	155–651	1992–1994	Andrieux & Aminot (1997)
Coastal marine sediment, in Aarhus Bay, (Denmark)	16 m	10 cm	620–1178	1990–1991	Jensen et al. (1995)
Coastal lagoons (Palavas, France)	2 m	0–5 cm	561–617	1990	Moutin et al. (1993)
Lower St Lawrence estuary portion of the Laurentian Trough (Québec)	> 300 m	35cm	930–1705	1984, 1985, 1987	Sundby et al. (1992)

northwestern Mediterranean Sea is largely dominated by the Rhone, and that most of the sediment supplied by the Rhone is deposited near the mouth. The remaining quantity is deposited on the shelf and the upper slope, while only a small amount is transported to the deep-sea basin (Zuo et al., 1991).

A small decrease in Tot-P concentration from the eastern to the western part of the Gulf of Lions was noted. At stations located near the coast, the Tot-P concentration was $663 \mu\text{g g}^{-1}$ (st. dev. = 24) in station Z, $590 \mu\text{g g}^{-1}$ (st. dev. = 11) in station L, $575 \mu\text{g g}^{-1}$ (st. dev. = 19) in station P and $569 \mu\text{g g}^{-1}$ (st. dev. = 15) in the western station T. The Tot-P concentration at station T, one of the shallowest, but most distant mouth stations, was relatively high. This could be due to deviation of Rhone river plume southwestward by the general circulation (Millot, 1990), preventing an extension southward. Other, small rivers, like Herault, Orb, Aude, might be potential sources of material. These are not quantified.

Another consequence of the influence of the northern current could be the low concentration measured at station K, which was among the lowest ones. The northern current forms meanders and follows the continental slope in the Gulf of Lions, with speeds ranging from 50 cm s^{-1} near the surface and few cm s^{-1} at a few hundreds of meters depth. Deep waters may rise in different areas on the shelf (Millot, 1990) with the result that particles may be resuspended. Station K in the middle of the Gulf is located in a zone probably strongly influenced by this current, which may be related to the high percentage of sand (44%) measured at this station (Denis, 1999).

The Tot-P concentration increased in the first centimeters of sediment in station C, H, D and L. This P-enrichment of the top layer is assumed to be due to the increased P-load in the Rhone, but there are no direct data available. P-input by the Rhone into the Mediterranean Sea depends largely on particulate phosphate input which were not regularly studied before 1994 (Moutin et al., 1998). However, the mean concentration of nitrate, which represents more than 80% of N-input from the Rhone to the Mediterranean Sea, has been shown to have increased by about 50% during the last two decades (Moutin et al., 1998). A similar P-increase probably occurred at the same period. In the river Rhine, o-P concentration has been measured since the late 1940s (DeJong et al., 1989). Average concentrations were low and stable up to the 1960s but a large increase was noted in the 1980s; the following period was characterized by a fluctuation but generally high level of concentrations (o-P = $0.3\text{--}0.4 \text{ mg l}^{-1}$). Tot-P measured after 1973 showed a decrease from 0.85 to about 0.6 mg l^{-1} in 1985.

To test the hypothesis of P enrichment of surface sediment in relation with increased loading, it is necessary to examine all processes that can cause such profiles. While mixing due to physical or biological processes may lead to uniform profiles (Kemp et al., 1976), variations of sediment characteristics with depth (pH, redox conditions, bacterial activity) may lead to different sediment adsorption capacities and to a strong vertical gradient of the Tot-P concentration with depth (Krom & Berner, 1981; Balzer, 1986; Sundby, 1992; Moutin et al., 1993), which is not automatically linked to the P-loading.

Homogeneity of Tot-P concentration in the sediments is not directly linked with Tot-P concentration in suspended matter of the Rhone river. Indeed, a large variability of this concentration was found (Moutin et al., 1998), particularly when concentration of suspended matter exceeds 150 mg l^{-1} in the Rhone river. From 39 measurements during a one year study period, P_{part} varied from 0.02 to 2.17 mg g^{-1} with an arithmetic mean of 0.76 mg g^{-1} (st. dev. = 0.51) and a median of 0.72 mg g^{-1} . It seems that a new equilibrium between phosphate and solid matter is reached in the sediment of the Gulf of Lions which suggests the dominance of authigenic P removal mechanisms in P burial.

Calculation of P-budget

The relative horizontal and vertical homogeneity of Tot-P concentration in surface sediments gives an opportunity to have a first order P budget for the Gulf of Lions. Although a slight decrease of the Tot-P concentration in the sediments from the river mouth to the slope could be shown, these concentrations varied only between 400 and $700 \mu\text{g g}^{-1}$. Apart from station C, concentrations were constant over the sediment depth: the average is, therefore, representative of the concentration in the surface sediments. The Tot-P concentration variation was less than a factor 2 whatever the location and the depth of the sediment sampled. Thus, an average concentration of $547 \mu\text{g g}^{-1}$ (st. dev. = 63; $n = 110$) may be obtained for the whole Gulf of Lions.

The homogeneity of Tot-P concentration in space and in depth at the different sedimentary units, allows us to calculate a P-pool of about 562 kt in the top 10 cm of sediments (Table 2). In order to emphasize the role of sediment in the biogeochemical P-cycle in the Gulf of Lions, we may compare the pool in surface sediments and in the water column. The latter is maximal when deep Mediterranean waters which have a P-concentration of about 400 nM (Mc Gill, 1969) fill up the Gulf in winter. Then, the P-pool in the whole water column is about 150 kt, that does not represent more than 30% of P-pool in the top 10 cm of the sediment layer. This percentage would be much less when considering only the prodelta areas.

On an annual basis, Tot-P-deposition from the water column to the sediment, was estimated to $7.2\text{--}12.4 \text{ kt y}^{-1}$ (Table 2). Tot-P-input by the Rhone into the Mediterranean Sea was estimated to $6.5\text{--}12.2 \text{ kt y}^{-1}$ (Moutin et al., 1998). Therefore, the annual P-

input by the Rhone seems identical to the quantity trapped in surface sediment of the Gulf of Lions in one year. At present, it is not known whether phosphate in sediment originates from the Rhone or from sedimentation of organic material synthesized in the Gulf. To answer that question, it would be necessary to study vertical deposition and to fractionate the different P-compounds.

This first order budget shows that it is necessary to take into account phosphate in sediments in a P-budget for the Gulf of Lions. As the Rhone is the main river flowing into the Mediterranean Sea, it influences the P-budget at the scale of the whole Mediterranean Sea and concern the central question on the relative influence of anthropogenic P-input against other input. The influence of the exchange at the Strait of Gibraltar relative to that of river input of nutrients has been widely discussed (Coste et al., 1988; Bethoux et al., 1998). The concentrations of N and P of the Atlantic inflow are lower than those in the Mediterranean outflow. The P-concentration of surface inflow was $0.37 \mu\text{M}$, while that of the deep outflow was $0.45 \mu\text{M}$ (Coste et al., 1988). According to Coste et al. (1988), the losses in the Strait should be compensated by the input from rivers. The equilibrium state of nutrient concentration in the Mediterranean Sea required this balance, but input by rivers must be decreased by output through the sediment reservoir. Our results suggest that the Rhone river is probably a lower input than previously thought, as large amount of P seemed to be definitively trapped by surface sediment in the Gulf of Lions. The Gulf, with the Rhone river, could not be considered like a sink or like a source of phosphate for the Mediterranean Sea.

By taking the annual input of suspended matter of the Rhone into the Mediterranean Sea at $14 \times 10^6 \text{ t y}^{-1}$ (Pont, 1997) and our mean average Tot-P concentration of $547 \mu\text{g g}^{-1}$ in the surface sediment of the Gulf of Lions, an annual deposition of 7.7 kt of phosphate, well in the range of $7.2\text{--}12.4 \text{ kt y}^{-1}$ previously estimated, is found. The later estimation depends on total annual solid flow rate estimation which is characterised by a high inter annual variability. With a value of suspended matter of $6.2 \times 10^6 \text{ t y}^{-1}$, reported as an expected average solid flow rate (Pont, 1997), an annual deposition of 3.2 kt of phosphate is found. This value is under the range of $7.2\text{--}12.4 \text{ kt y}^{-1}$ previously estimated from sediment P-pool and sedimentation rates. This difference can be explained by an underestimation of the annual average solid flow rate or by an overestimation of mass accumulation rates. El Habr

& Golterman (1987) estimated in 1984–1985 the water flow rate at $50 \times 10^9 \text{ m}^3$ and the total suspended matter load at $2.6 \times 10^6 \text{ t y}^{-1}$. Recently, Sempéré et al. (2000) calculated suspended matter flow rate from relationships between the daily Rhone river discharge and corresponding loads. They found a range of 2–23 t y^{-1} between 1987 and 1996, with an average of 9.90 t y^{-1} (st. dev. = 6.43). The value of $14 \times 10^6 \text{ t y}^{-1}$ cannot be considered as an inter annual average but indicates that the Rhone river is able to transport large quantities of suspended matter (Pont, 1997). An accurate knowledge of solid flow rates in Rhone input and of sedimentation rates in the Gulf of Lions should permit a more precise evaluation of P-budget in the Mediterranean Sea.

Carpenter et al. (1987) and Smith et al. (1995) have demonstrated the importance of particle mixing, generally due to bioturbation processes, on the ^{210}Pb distribution in sediments of the coastal zones. Most of the maximum accumulation rates determined by ^{210}Pb can thus be overestimated and mass budgets may be subject to important disequilibrium (Radakovitch et al., 1999). Moreover, sedimentation rates can be overestimated in considering a mean porosity of 0.5 for sediments of the whole Gulf.

Whatever the correct explanation for the discrepancy, deposited sediments in the Gulf of Lions are able to trap large amounts of P and should be taken into consideration in a P-budget. The present impact of anthropogenic P, at the scale of the Mediterranean Sea, might be less than previously estimated (Bethoux et al., 1992).

Acknowledgements

This work was part of the framework French PNEC program (Programme National d'Environnement Côtier). The authors would like to acknowledge P. Raimbault, responsible of the Mediterranean part of the program and of MOGLI cruises, L. Denis, P. Harris and C. Grenz for sample collection and helpful cooperation. We would like to thank M. Golterman for his valuable help in critical reading of the manuscript. We are also very grateful to Dr Golterman-Hardenberg for her time and dedication.

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