

Phosphorus in rainwater: Partitioning inputs and impact on the surface coastal ocean

Abstract—Phosphate concentrations in rainwater were measured at a Ligurian coastal sampling site (Cap Ferrat, France) from February 1997 to February 1998 to study the impact of wet atmospheric phosphorus (P) input on the surface ocean. Soluble and particulate fractions were differentiated to evaluate the atmospheric supply of bioavailable P. Complexed and reactive phases within the dissolved fraction were also separated. Preliminary results showed a high temporal variability in total concentration (0.05–4.3 $\mu\text{mol liter}^{-1}$). The factors controlling the partitioning between reactive and complexed components are not clear. However, the partitioning between dissolved and particulate fractions is linked to emission sources. Soil-derived dust from the Sahara was identified as an important source of atmospheric P, mainly insoluble. Conversely, anthropogenic emissions are sources of soluble P (i.e., basically bioavailable). A significant part of these emissions could originate from incinerators and/or biomass burning. The different wet fluxes are calculated to total 165 $\mu\text{mol m}^{-2} \text{yr}^{-1}$, and the dissolved and particulate inputs are 95 and 70 $\mu\text{mol m}^{-2} \text{yr}^{-1}$, respectively. Taking into account the respective solubility of such inputs, anthropogenic emissions appear to be responsible for relatively high amounts of bioavailable P. Even if the atmosphere is globally a minor source of nutrients (compared with riverine inputs and marine vertical mixing), it might be the only source of P in oligotrophic conditions. For example, assuming that P is a limiting factor in the Mediterranean Sea, the rain event of 19 June 1997 (17 $\mu\text{mol m}^{-2}$ of bioavailable P) potentially induced a new production of 0.02 g C m^{-2} , which is a significant value in such conditions. Converted into biomass and integrated over a 5-m-thick water layer, such an atmospheric input represents 0.35–0.45 mg chlorophyll *a* m^{-2} , an appreciable portion of the total biomass during this period. This observation underlines the major role of the atmosphere during oligotrophic periods in the western Mediterranean.

Phosphorus (P) is an essential element for biological growth. In seawater, a variety of inorganic and organic P compounds can be assimilated by living organisms, with orthophosphate as the preferred form. A controversy exists over which nutrient regulates phytoplankton dynamics in marine environments, nitrogen (N) (Howarth and Cole 1985; Ammerman and Azam 1991), P (Bonin et al. 1989; Krom et al. 1991; Béthoux et al. 1992; Thingstad et al. 1998), or a combination of both, with a phosphate stimulation of nitrate consumption (Raimbault and Pujol-Pay 1993). This discussion, which depends greatly on the effectiveness of atmospheric N_2 fixation by certain marine organisms such as cyanobacteria and *Synechococcus* (Béthoux and Copin-Montégut 1986; Mitsui et al. 1986; Béthoux et al. 1998), still rages.

The western Mediterranean is subject to significant seasonal variations of its trophic state. Winter conditions are characterized by the formation of deep water, which leads to intense vertical mixing and brings nutrients to the surface

waters. With these conditions, hydrological and riverine sources are preponderant (Béthoux et al. 1992, 1998). In contrast, Mediterranean summer is characterized by the stratification of offshore waters that may favor atmospheric input (Migon et al. 1989). However, few studies have directly assessed the contribution of the atmospheric input of nutrients (Béthoux et al. 1998). The extent to which atmospheric input of nutrients contributes to global budgets or induces biological production still needs to be assessed. We attempt here to evaluate the magnitude of wet atmospheric input of P, emphasizing the possible role in promoting biological activity under defined conditions.

Water samples were obtained from Cap Ferrat (43°41'N, 7°19'30"E; altitude 130 m), on the southeastern coast of France. The characteristics of this site (e.g., meteorology, anthropogenic influences) have been discussed elsewhere (Migon and Caccia 1990). Rainwater was collected using an automatic rain collector (KFA Jülich), which opens only when it rains and not under the influence of fog or dew. Rainwater samples were filtered immediately after collection to avoid possible exchange between particulate and dissolved phases. Sartorius SM 11106 (cellulose acetate; porosity 0.45 μm ; diameter 47 mm) filtration membranes were used.

Rainfall <1 mm was not taken into account, for analytical convenience. Even when the P concentration is high, such events do not produce significant phosphate loads.

Dissolved P was measured by manual spectroscopy (Murphy and Riley 1962). After measurement of reactive P by this technique, the dissolved fraction was acidified with HCl (pH 2) to discriminate between reactive and stable phosphates. Stable phosphates were irradiated with ultraviolet (UV) light (UV digester 705 Metrohm with high-pressure Hg lamp, 200–280 nm, 500 W, temperature 80°C) for approximately 1.5 h. Because the pool of stable phosphates includes UV-resistant compounds (Karl and Yanagi 1997), the irradiation was followed by H_2O_2 oxidation. A spectroscopic procedure was used to measure the total dissolved P.

The particulate fraction was mineralized according to the following procedure. Filters were folded twice and introduced into a Teflon flask (15 ml) to which 900 μl of 65% HNO_3 was added. The flask was closed and put into a larger Teflon bottle (60 ml) that acted as an expansion cell, preventing acidic evaporation and contamination. This apparatus was left for 2–3 h in an oven at 60°C and then for 3–4 h at 150°C until only a black, dry residue remained. The bottle was cooled in a laminar airflow hood and left open until the red smoke dissipated. The residue was dissolved again in 200 μl of 65% HNO_3 and 200 μl of 40% hydrofluoric acid. The samples were oven dried for 2–3 hours at 60°C and then 3–4 h at 150°C until a white dry residue was obtained. This residue was ultrasonically dissolved in 0.5 ml

Table 1. Atmospheric input of dissolved (reactive + complexed) and particulate P.

Sample No.	Rain event	pH	Rainfall (mm)	Phosphorus ($\mu\text{mol m}^{-2}$)			
				Dissolved		Particulate	Total
				Reactive	Complexed		
1	24 Feb 97	4.2	1.8	1.1	0.4	3	4.6
2	20 Apr 97	4.8	8.8	1.9	1.4	1.2	4.4
3	27 Apr 97	4	5.5	1.1	0.5	3.8	5.4
4	5–6 May 97	4	4.2	3.4	1.4	1.7	6.5
5	11–13 May 97	6.6	6.4	1.7	0.3	3.3	5.3
6	1–2 Jun 97	4.6	12.5	1	0.8	1.5	3.3
7	4–5 Jun 97	4.9	30.6	0.7	1.9	1.4	4
8	19 Jun 97	5.1	17.2	16.9	1.6	4.3	22.8
9	26–29 Jun 97	4.8	37.8	0.4	2.5	7	9.9
10	2–3 Jul 97	6.1	4.4	2.9	0.2	0.7	3.8
11	11 Aug 97	6.1	17.2	3.3	1.2	12.8	17.3
12	17–18 Aug 97	4.2	10.8	0.3	0.6	2.3	3.3
13	28 Aug 97	4.9	12.6	0.9	0.0	1.4	2.3
14	2–3 Sep 97	4.5	2.8	0.2	0.0	0.8	1
15	29 Sep 97	3.7	3.1	1.1	0.0	2.4	3.4
16	20–21 Oct 97	4.8	23	8.8	0.0	2.2	11
17	22–24 Oct 97	3.7	2.4	9	1	0.7	10.7
18	5–6 Nov 97	4.7	67.8	5.3	4.4	7.3	16.9
19	9 Nov 97	4.7	41.8	2.2	12.2	1	15.4
20	11–12 Nov 97	4.3	69.6	0.1	0.0	1.7	1.8
21	26–29 Nov 97	4.4	5.3	0.1	0.0	0.7	0.8
22	17–20 Dec 97	5.3	70.5	0.7	0.4	7.9	9
23	31 Dec 97–1 Jan 98	4.9	1.8	0.2	0.2	0.7	1.1
24	14 Jan 98	4.4	14.6	0.2	0.4	0.5	1.1
25	16 Jan 98	4.4	2.3	0.2	0.0	0.1	0.3

of 1 N HNO_3 . The samples were ultimately made up to 5 ml with Milli-Q water.

After mineralization, samples were analyzed according to the spectroscopic protocol described above. The detection limit was $0.05 \mu\text{mol liter}^{-1}$. Blank values (i.e., filter + reagents) were $4 \mu\text{mol liter}^{-1}$. Whether they are polyphosphates or P complexed with organic matter, stable P compounds are hereinafter referred to as complexed P.

Partitioned input—P concentrations in rainwater ranged between 0.05 and $4.5 \mu\text{mol liter}^{-1}$. These concentrations, multiplied by the rainfall amount, produced calculated P input. Table 1 records the atmospheric P input (from February 1997 to February 1998), which was highly variable (0.3 – $22.8 \mu\text{mol P m}^{-2}$).

With total wet P of $165 \mu\text{mol m}^{-2} \text{y}^{-1}$, this input is slightly lower than that of the southeastern Mediterranean ($216 \mu\text{mol P m}^{-2} \text{y}^{-1}$; Herut and Krom 1996). A previous study in the northwestern Mediterranean (Bergametti et al. 1992) estimated the annual total P deposition (wet + dry) as $1,295 \mu\text{mol m}^{-2} \text{y}^{-1}$. Comparison of the present results with this last number suggests a relatively small contribution from wet deposition, i.e., 15% of the total atmospheric deposition, versus 33% for the southeastern Mediterranean (Herut and Krom 1996). However, during the sampling year, only 25 rain events occurred, which should make the impact of the rain deposition greater on a daily time scale. On a yearly time scale, the particulate contribution represents $70 \mu\text{mol P m}^{-2} \text{y}^{-1}$, whereas the dissolved fraction is slightly higher

($95 \mu\text{mol P m}^{-2} \text{y}^{-1}$). Within the dissolved phase, the reactive and the complexed contributions represent 63 and $32 \mu\text{mol P m}^{-2} \text{y}^{-1}$, respectively.

The seasonal variability of the different types of P input is illustrated in Fig. 1. Within the dissolved phase, complexed P concentrations were generally very low, except for two samples (5–6 November and 9 November 1997). The present database does not enable us to establish which parameters control the effectiveness of P complexation in rainwater. Moreover, it is not possible to show any relationship between the partitioning of reactive and complexed P and the emission sources. We hypothesize here that significant complexed P input has a relatively random character.

Partitioning between dissolved and particulate P, however, is directly linked to the origin of the associated air masses. In Fig. 2, particulate P input has been reported in parallel with aluminum (Al) loadings in rainwater; in agreement with previous work (Bergametti et al. 1992; Herut and Krom 1996), particulate P inputs are clearly associated with soil-derived and/or Saharan emissions, themselves characterized by high Al content. The same correlation is observed with iron (Fe), titanium, or calcium (Ca). Two factors presumably control the seasonal pattern of wet atmospheric P input: (1) incoming Saharan air masses affect the northwestern Mediterranean mostly in spring and summer (Loje-Pilot et al. 1986; Moulin et al. 1997), and (2) whatever the origin of the element in the western Mediterranean regions, the seasonal pattern of atmospheric P concentration is inversely related to the precipitation rate, i.e., high concentrations in

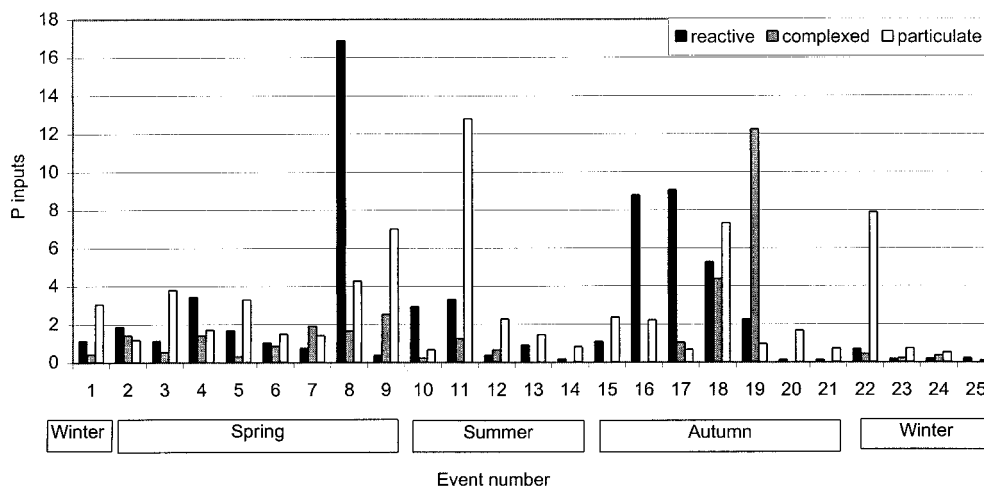


Fig. 1. Seasonal variability of reactive, complexed, and particulate P input ($\mu\text{mol m}^{-2}$).

summer and low concentrations in winter (Bergametti et al. 1992). As a result, wet particulate P input generally affects the Ligurian Sea from spring to the end of summer, which is in agreement with the greater input observed during the present sampling period (see Fig. 1).

Wet Saharan events can bring very large amounts of dust (up to 3 g m^{-2} ; Lojze-Pilot and Martin 1996), which contains on average 0.35% P (Guieu and Thomas 1996) or approximately $340 \mu\text{mol P m}^{-2}$, principally in particulate form. This theoretical value seems very high, but the maximum solubility of P in Saharan material was estimated to be 8% (Lepple 1971), which would reduce the input to a maximum value of $27 \mu\text{mol P m}^{-2}$. The present data do not include crust-derived or Saharan input $>17 \mu\text{mol P m}^{-2}$ (11 August 1997), with only $3 \mu\text{mol}$ reactive P m^{-2} .

Phosphates transported with mineral material are principally bound to iron oxides or associated with Ca, magnesium (Mg), Al, and Fe, which are known to be weakly soluble (Losno 1989; Bergametti et al. 1992). Even if inorganic P concentrations are sometimes high in Saharan rainwaters, the very low solubility of apatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) is known to control the solubility of phosphate in water, and P is easily adsorbed onto iron hydroxides at pH values encountered in alkaline rainwater, i.e., pH 5–8 (Golterman 1995a). Krom et

al. (1991) suggested that PO_4^{3-} might be partly removed from the water column by adsorption onto Fe-rich dust particles. The efficiency of phosphate adsorption onto iron hydroxides should be significantly increased by the high Ca^{2+} and Mg^{2+} concentrations in seawater (Golterman 1995b). According to Herut et al. (1999), when Saharan dust reaches surface seawater, it immediately releases phosphate and then removes phosphate from solution by adsorption (20–40%). By comparison, these authors found that the uptake of phosphate due to microbial activity was approximately 30–40%. For a constant pH value in seawater and low phosphate concentrations, the adsorption process should dominate, whereas at higher P concentrations, apatite precipitation should become more important (Golterman 1995a), although it may be kinetically hindered (Yeoman et al. 1988). The combination of precipitation and adsorption processes should decrease the possible fertilizing role of atmospheric P in crust-derived and/or Saharan rainwater in the surface marine layer.

The enrichment with P with respect to the concentration ratio P:Al in Saharan dust (fine fraction $< 50 \mu\text{m}$; Guieu and Thomas 1996) and the Earth's upper crust (Wedepohl 1995) is given in Fig. 3. Even if some samples are typically dust derived, many others exhibit significant enrichments. Taking into account that recycled P from marine sources is negligible ($<2\%$; Bergametti et al. 1992), it is assumed this excess P is of anthropogenic origin. This point is important because, basically, urban-derived material is soluble and thus presumably bioavailable. It is assumed anthropogenic P is included in small particles or on their surface, whereas crustal P is associated with larger particles of very low solubility (Losno 1989). On a yearly time scale, anthropogenic P emission sources, e.g., incinerators, fertilizers, chemicals, detergents, and pesticides (Dojlido and Best 1993), should be responsible for more P than should the detrital source, and almost all soluble P should be provided by anthropogenic activities.

Nevertheless, some samples (at least two) exhibit a surprisingly high P enrichment, and the anthropogenic source must be better defined, taking into account that agricultural and industrial activities are not very important in this Med-

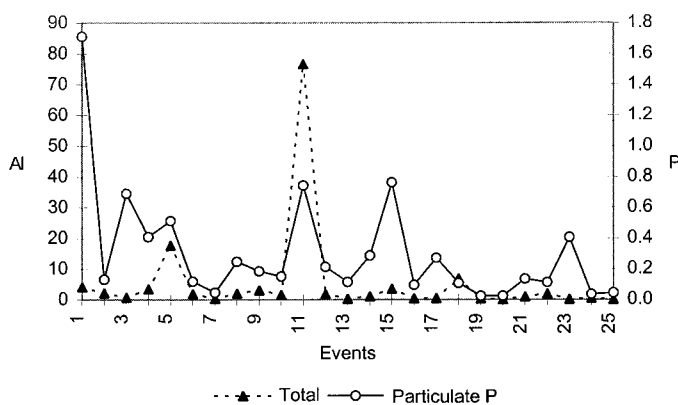


Fig. 2. Particulate P input versus total Al input ($\mu\text{mol m}^{-2}$).

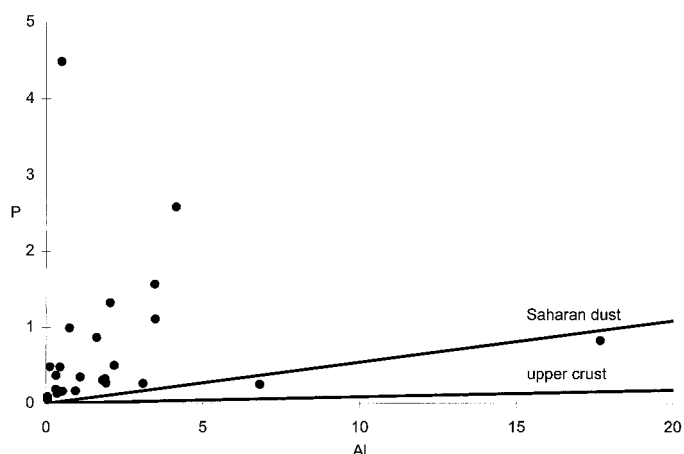


Fig. 3. P enrichment calculated from P:Al ratios in Saharan dust (fraction $< 50 \mu\text{m}$; Guieu and Thomas 1996) and in the Earth's upper crust (Wedepohl 1995). P and Al concentrations expressed as $\mu\text{mol liter}^{-1}$.

iterranean region. Figure 4 plots the dissolved P input (supposedly of anthropogenic origin) and urban-derived trace metal input. The plots suggest a very poor link between dissolved P and cadmium (the same result occurs with copper and even more so with lead, which is known to form insoluble phosphates; Dojlido and Best 1993). This lack of association might be partly due to the fact that most of anthropogenic phosphates are associated with organic species. However, a close relationship is observed with zinc (Zn) (Fig. 5a) and potassium (K) (Fig. 5b). These elements are known to be reliable indicators of waste incineration (Zn; Nriagu and Pacyna 1988; Pacyna 1989) and natural biomass burning (K; Andrae 1983; and, to a lesser extent, Zn; Artaxo et al. 1990). Such emission sources can potentially load the atmosphere with high amounts of soluble P (Artaxo et al. 1990) and are probably responsible for significant anthropogenic P spreading over coastal and marine areas. The city of Nice is equipped with a waste plant whose residual muds (typically $110 \text{ tonnes d}^{-1}$) are dried. This dry mud contains $10,000\text{--}20,000 \text{ mg P kg}^{-1}$ (Barraya 1997). After drying, the mud is incinerated at l'Ariane, approximately 10 km away from the shoreline. Another urban incinerator is located at Antibes, 38 km from the sampling site. Both may act as significant P emission sources.

The two most enriched samples (22–24 October 1997 and 31 December 1997–1 January 1998) probably result from regional and specific contamination (small domestic fires were observed 1–2 km from the sampling site); forest and bush fires might constitute an important source of soluble P.

Impact—Overall, the atmosphere contributes little to nutrient cycling in the Mediterranean (Migon et al. 1989; Béthoux et al. 1992, 1998; Krom et al. 1992). In continental seas such as the Mediterranean, Atlantic nutrient input is limited because of the depleted incoming surface water. The supply of N and P is thus primarily dependent on riverine and atmospheric input. The main source of P is the leaching of soils, whereas the dissolution of atmospheric N_2 constitutes a huge stock of N. Assuming that certain marine or-

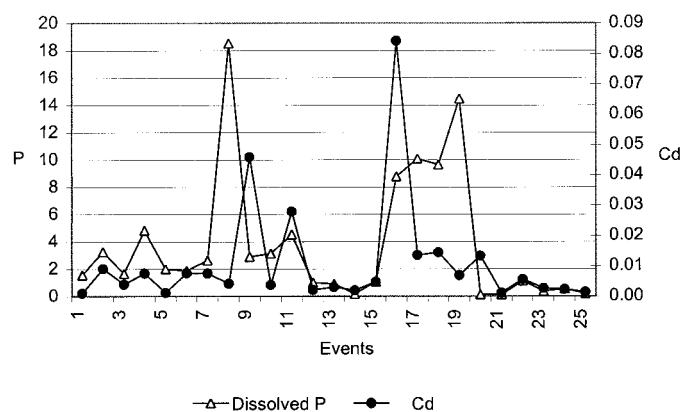


Fig. 4. Dissolved (mainly anthropogenic) P input versus total cadmium input ($\mu\text{mol m}^{-2}$).

ganisms (e.g., cyanobacteria and *Synechococcus*) are capable of metabolizing this dissolved N (Béthoux and Copin-Montégut 1986; Mitsui et al. 1986; Béthoux et al. 1998), they need P for their growth. The alternative hypothesis is that the main sources of dissolved N and P are, respectively, riverine NO_3^- and PO_4^{3-} . The molecular ratio $\text{NO}_3^-:\text{PO}_4^{3-}$ is, on average, 11 in rivers (Meybeck 1982) and 22 in deep Mediterranean water (Béthoux et al. 1998). This discrepancy may be explained by effective assimilation of atmospheric N_2 , which supports the assumption that P is a limiting factor

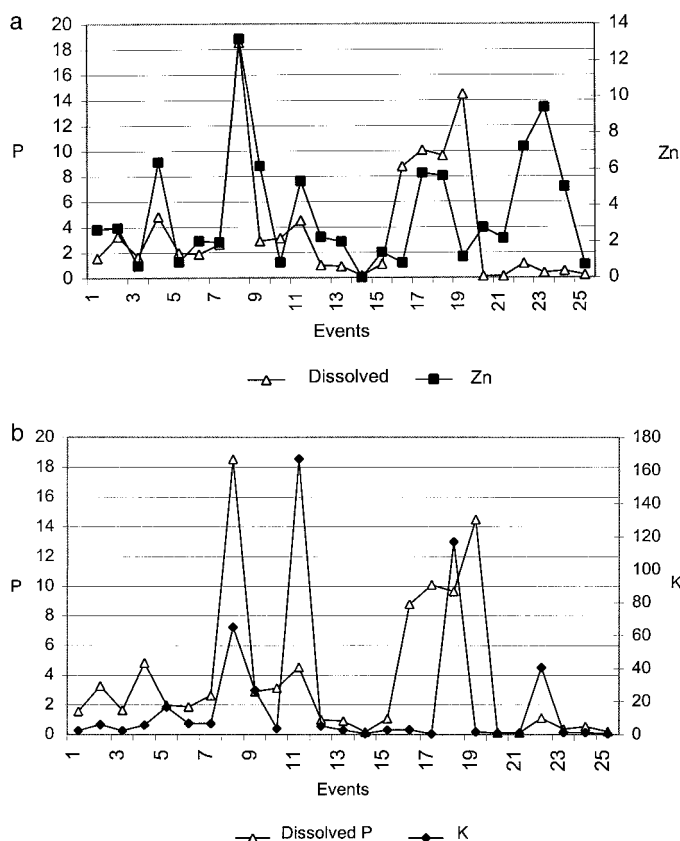


Fig. 5. Dissolved P input versus total Zn input (a) and total K input (b) ($\mu\text{mol m}^{-2}$).

in the Mediterranean (Bonin et al. 1989; Krom et al. 1991; Béthoux et al. 1992; Thingstad et al. 1998).

Therefore, on the basis of the present data, the contribution of atmospheric P in terms of biological production can be calculated with a carbon (C):P Redfield ratio of 106. If only dissolved reactive P is considered as bioavailable, atmospheric P should induce a yearly new production of $0.08 \text{ g C m}^{-2} \text{ y}^{-1}$. By comparison, the annual estimate of new production for the western Mediterranean basin (straits + rivers + vertical mixing + atmosphere) ranges between 13 and $24 \text{ g C m}^{-2} \text{ y}^{-1}$ according to Béthoux et al. (1992) or around $18 \text{ g C m}^{-2} \text{ y}^{-1}$ as advanced by Minas et al. (1988). Rainwater, thus, contributes only 0.3–0.6% of the annual new production.

This estimate is only a lower limit; some amount of the complexed P may be available to the phytoplankton, and P is assumed to be partly assimilated in the surface water. For example, Graham and Duce (1982) estimated on the basis of 40 aerosol samples that $36\% \pm 15\%$ of particulate P is released upon contact with seawater after 12 h. The amount of particulate P released from rainwater to seawater and, more generally, the bioavailability of P presumably depend on many parameters, such as the chemical origin and size of the particles, meteorological conditions at the sea surface, and physicochemical and biological processes in the surface layer. Therefore, complexed P (which leads to a production of $0.04 \text{ g C m}^{-2} \text{ y}^{-1}$) and part (36%) of the particulate ($0.03 \text{ g C m}^{-2} \text{ y}^{-1}$) suggest a new production of $0.15 \text{ g C m}^{-2} \text{ y}^{-1}$, which is an upper limit. That number is 0.6–1.1% of the yearly total new production.

This level of production may seem like very little. However, in oligotrophic conditions, owing to well-developed stratification, surface waters are isolated from underlying waters. Thus, the atmosphere may constitute a favored pathway for nutrients to the open sea, a pathway not directly affected by riverine input (Migon et al. 1989). When marine concentrations are low, nutrients cannot accumulate and are immediately consumed by primary production. Therefore, high wet atmospheric input of bioavailable P should be taken into account during the oligotrophic period.

The highest input occurred 19 June 1997, with $17 \mu\text{mol reactive P m}^{-2}$ (see Table 1). Theoretically, such an input represents new production ranging between 0.02 and 0.025 g C m^{-2} (the upper value takes into account complexed P and 36% of particulate P). By comparison, in June the daily primary production ranges between 0.4 (Morel and André 1991) and 0.6 (Antoine and Morel 1995) $\text{g C m}^{-2} \text{ d}^{-1}$ in this marine region.

The relationship between the C in phytoplankton and chlorophyll *a* (Chl *a*), the usual biomass indicator, is $C/\text{Chl } a = 55$ (Herbland and Le Bouteiller 1983). This value enables us to compare these numbers with biomass measurements in the same marine area, as characterized by Chl *a* content. For this calculation, primary production values are normalized to an estimated homogeneous surface layer. A homogeneous layer, averaged over 1 yr, is of little significance and it is worth considering only the case of episodic events, such as that of 19 June 1997. For this period, based on the weekly hydrological data provided by the Observatoire Océanologique de Villefranche-sur-mer (France), no

significant wind event disturbed the Ligurian Sea, and the homogeneous surface layer was approximately 5 m thick. In this water column, the range of primary production values for this event is thus 4–5 mg C m^{-3} , which corresponds to 0.07–0.09 $\text{mg Chl } a \text{ m}^{-3}$. Integrated over the 5-m thickness, this gives 0.35–0.45 $\text{mg Chl } a \text{ m}^{-2}$. The integrated Chl *a* content in this water ranged from 0.2 to 0.6 $\text{mg Chl } a \text{ m}^{-2}$ in June 1995 (Vidussi et al. 1999), and there was 20–40 $\text{mg Chl } a \text{ m}^{-2}$ in the whole euphotic layer (0–100 m). Although higher Chl *a* values were found in deeper waters (15–20 m depth), these data are significant with respect to the total biomass. This high Chl *a* content probably induces a secondary biomass peak, which should be observable with remote sensing. This prediction is in agreement with the preferential relationship between the atmosphere and the surface marine layer during oligotrophic periods.

In conclusion, the contribution from the atmosphere to P cycling, even if it is globally low, is not negligible, and budget calculations still require improvements. Atmospherically transported anthropogenic P, particularly from incinerators and biomass burning, may play a major role. In oligotrophic conditions, atmospheric P input may induce new production.

Primary production measurements are regularly carried out at the DYFAMED marine site, located in the central Ligurian Sea ($43^{\circ}25'N$, $7^{\circ}52'E$), 28 miles (45 km) offshore from Cap Ferrat. With the help of a synchronous sampling strategy at Cap Ferrat and the DYFAMED site, the next step of this study is the observation of the marine response to atmospheric P input (e.g., primary production measurements, pigment markers, sediment trap data) using high-frequency data acquisition.

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