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Atmospheric phosphorus deposition in a near-coastal rural site in the NE Iberian Peninsula and its role in marine productivity

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ABSTRACT

In this study, African red-rains were collected at Montseny (NE Spain) on a weekly basis and analyzed for total particulate phosphorus (TPP), total dissolved P (TDP) and soluble reactive P (SRP) for the period 1996–2008. Wet and dry weekly deposition of TPP was analyzed for all provenances in 2002–2003. In this period, African sources were found to contribute 66% of the 576 μmol m^{-2} y^{-1} of total particulate phosphorus (TPP) deposited in Montseny, split almost evenly between dry and wet deposition. Measurement of this dry deposition further allowed a direct determination of deposition velocity (V_d), which suggested significant depositional differences between African (V_d = 3.1 ± 0.80 cm s^{-1}) and non-African events (V_d = 1.07 ± 0.13 cm s^{-1}). Measurement of TDP concentrations during the African rains suggests a solubility of 11.2% TPP. SRP solubility was lower (2.2%), highlighting the importance of understanding the composition of the atmospherically derived P component. Samples were collected 25 km from the Mediterranean coast and were assumed to represent the atmospheric P input to coastal waters. On an annual basis, atmospheric-derived soluble P contributed <1% of annual new primary production in the western Mediterranean. However, one strong African dust event (22–27 May, 2008) accounted for 24–33 % of the atmospheric P-induced annual new production. These results highlight the potential biogeochemical importance of seasonality, source, and composition of aerosols deposited in the Western Mediterranean Sea.

1. Introduction

Phosphorus (P) is a fundamental component of all living organisms and a limiting factor for primary production in both marine and terrestrial ecosystems (Schlesinger, 1997; Chadwick et al., 1999; Wu et al., 2000; Mills et al., 2004). Unlike the cycling of other biologically essential elements such as carbon (C) and nitrogen (N), P does not have a stable gaseous phase in oxygenated environments (Benítez-Nelson, 2000). As such, the only natural sources of new P to oceanic waters are via atmospheric deposition and riverine discharge (e.g. Benítez-Nelson, 2000; Mahowald et al., 2008).

The Mediterranean Sea is one of the most oligotrophic marine ecosystems in the world (Béthoux et al., 1998). During summer, both phytoplankton and bacterial production are P limited due to N/P ratios much higher than Redfield ratios and the lack of nutrient supply from deep waters due to stratification (Thingstadt and Razzoulzadegan, 1995; Vaulot et al., 1996; Thingstadt et al., 1998). Dissolution of atmospheric particles rich in P-containing minerals may therefore influence biological production, with dissolution rates affected by a range of factors, such as particle composition, grain size, and surrounding solution characteristics (Colin et al., 1990; Guieu et al., 1997; Ridame and Guieu, 2002). Several studies have shown episodic summer phytoplankton blooms in the Mediterranean in response to nutrient inputs (N, P) from the atmosphere (Migon and Sandroni, 1999; Herut et al., 1999, 2002; Ridame and Guieu, 2002).

The Mediterranean is strongly impacted by Saharan events loaded with mineral dust. This dust deposition averages around ~5–12 tons km^{-2} y^{-1} to the western Mediterranean Sea (Löye-Pilot and Martin, 1996; Àvila et al., 1997, 2007) which represents a P contribution of ~132 to 317 μmol m^{-2} y^{-1}, assuming

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a total P concentration in the Saharan end-member of 0.082% (Guieu et al., 2002). African dust intrusions further have a marked seasonality, with higher frequency between March and October (Guerzoni et al., 1997; Querol et al., 1998; Escudero et al., 2005; Pérez et al., 2008).

The Mediterranean basin is also strongly influenced by anthropogenic sources from vehicle traffic, and industrial and domestic activities (Migon and Sandroni, 1999), including biomass burning (Guieu et al., 2005). In the Western Mediterranean high atmospheric pressures in summer prevent air renewal and allow a regional accumulation of pollutants (Querol et al., 1998). Precipitation is also lower in summer leading to a higher buildup of locally or regionally resuspended particulate matter (PM) resulting from the dryness of soils.

Several studies have provided contrasting estimates on the relative role of dry *vs*. wet deposition in the Mediterranean region (Markaki et al., 2003; Morales-Baquero et al., 2006; Guieu et al., 2010). For P, wet deposition has been reported as the main source of dissolved P to the western Mediterranean (Ridame and Guieu, 2002; Ternon et al., 2010), though other studies have shown that phosphate is readily leached from dry fallout (Migon et al., 2001; Herut et al., 2002, 2005; Carbo et al., 2005). Differences in the contribution wet/dry are likely due to the type of pollutant (anthropogenic *vs.* mineral dust) and to the local weather regime (annual rainfall and the frequency and magnitude of African outbreaks), but more research is needed for a deeper understanding of such depositional processes in this system.

Bioavailable forms of P (dissolved phosphate inputs) dominate in rainwater (Ridame and Guieu, 2002); therefore the wet deposition mode is often assumed to provide most of the readily available nutrients. This rainwater, however, includes both dissolved and particulate forms. Experimental dissolution of loess in seawater produced P dissolution rates of 8–11% of the total P in the sample (Lepple, 1975; quoted in Graham and Duce, 1979; Herut et al., 1999). In seawater-leached aerosol samples collected in Israel, P solubility was between 22–25 and 45–73% (Herut et al., 2002, 2005; Carbo et al., 2005). Ridame and Guieu (2002) found that the %P dissolved from Saharan dust was inversely related to particle concentration for equal water contact time. Rain pH may also influence the dissolution rate, with enhanced dissolution at low pH, generally occurring with polluted rains (Ridame and Guieu, 2002; Markaki et al., 2003). African rains are alkaline and particle-loaded, thus less soluble, but they may dominate as a source of bioavailable P due to their high dust loads.

In order to better understand the effects of P deposition on the western Mediterranean Sea, it is important to determine its deposition pathways (wet *vs*. dry). Direct measurements of the dry deposition flux are needed, since P dry fallout has often been obtained from the product of aerosol concentrations and a deposition velocity value from the literature instead of measuring the flux directly. Another point of interest in the western Mediterranean is to determine the relative contribution of African P deposition relative to non-African, background episodes. Previous studies have found that African wet episodes occurred only 3% of the time annually, while African dry episodes amounted to 15% (Escudero et al., 2005). For wet events, acidity was higher in non-African events (Àvila and Alarcón, 1999), so differential P dissolution depending on air mass trajectory is expected.

The goal of this study is to add to existing knowledge on P deposition to the western Mediterranean Sea by better constraining the sources, magnitude and modes of atmospheric inputs. This has been accomplished by analysing aerosol concentrations and wet and dry deposition fluxes from 2002 to 2003 in a site in NE Spain close to the coast. Because of the important contribution of African sources and the well known interannual variability of African outbreaks, a long-term record (1996–2008) of Saharan bulk weekly samples was also analyzed to determine the potential impact of high P deposition events on the biogeochemistry of the western Mediterranean.

2. Materials and methods

2.1. Study site

Atmospheric aerosol concentrations and wet and dry deposition were sampled weekly from March 2002 to December 2003. Sampling was conducted at La Castanya (LC, 41°46′N, 2°21′E, 700 m above sea level), a long-term biogeochemical study site located in the Montseny mountains of the Pre-litoral Catalan Range (Rodà et al., 1999). The site is amidst an extensive holm-oak (*Quercus ilex* L.) forest in Montseny Natural Park, 40 km to the N–NE of Barcelona and 25 km from the Mediterranean coast. Since 2002, this site has been instrumented as a background regional air quality site (EUSAAR network-European Supersites for Atmospheric Aerosol Research, http://www.eusaar.net) (Fig. 1).

The record from LC is taken to be broadly representative of deposition fluxes over the NW Mediterranean due to the large-scale of dust transport (scale of hundreds to thousands of km, Lawrance and Neff, 2009). This presumption is confirmed by the very close correspondence between the African dust events recorded at Montseny and Mallorca (Balearic Islands) from 1984 to 2003, with records of simultaneous African red-rains (rains containing a reddish silty residue from desert dust) in 71% of the cases (Fiol et al., 2005; Àvila et al., 2007). Moreover, it is generally accepted

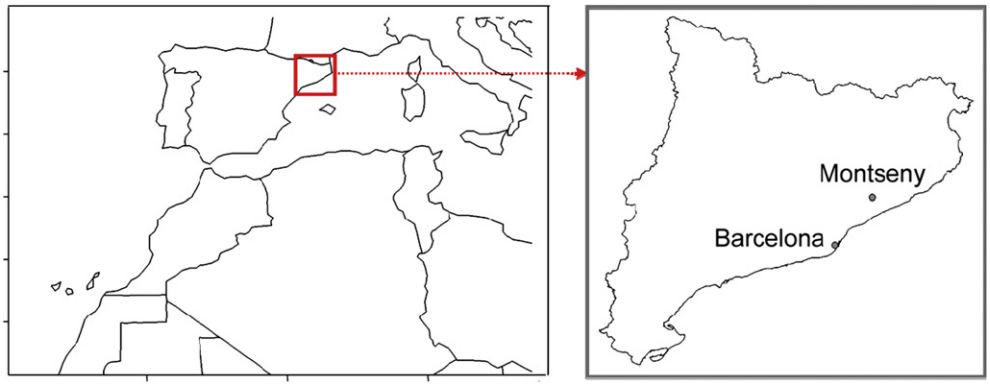

Fig. 1. Map of Montseny study site, NE Spain.

that elemental fluxes measured at a coastal site can be extended to regional open waters (Migon et al., 2001; Herut et al., 2002; Guieu et al., 2010; Koçak et al., 2010).

2.2. Sampling and definitions

Total suspended particles (TSP) were collected with a high volume sampler (DIGITEL DHA-80) at an air flow rate of 30 m^3 h^{-1}. Two consecutive daily filters (quartz fiber, QF20 Schleicher and Schuell) were obtained each week, resulting in a total of 151 filters collected between March 2002 and December 2003. From July 2002 to December 2003, weekly wet and dry deposition samples were collected at LC using a dry/wet deposition collector (ESM Andersen instruments, G78-1001), consisting of two buckets (28 cm-diameter; 30 cm-depth) and a shifting lid which covers the wet collector during dry periods and the dry bucket as rain starts. A data logger keeps a record of the number and timing of the rain events. It should be noted that there is no well-established technique for dry deposition determination. Previous studies have shown that in some cases, dry dust deposition may in fact be the result of deposition conveyed by a few water droplets that are later evaporated, thus confounding the distinction between dry and the wet deposition modes (Löye-Pilot and Martin, 1996). In our study, we consider this effect to be small, as dry deposition weeks were cross checked with the rain record of a co-located rain gauge. However, a more careful study is needed to ascertain the importance of these very small rain events that may even remain unregistered in current rain gauges. In spite of these limitations, the instrumentation and procedures used herein has been widely used around the Mediterranean (Özsoy and Saydam, 2001; Ballestrini et al., 2002; Morales-Baquero et al., 2006).

From January 1996 to December 2008 (except 2002–2003), bulk deposition samples were also collected weekly at LC. From this record, only the weeks containing red-rains (rains that left a reddish dusty residue on rainwater collectors) are considered. Rainfall was collected in 4 (1996–1997) or 2 (1998–2008) bulk deposition collectors placed 1.5 m above the ground, each consisting of a 19-cm diameter-polyethylene funnel with a nylon stopper in the neck connected by a Tygon looping tube to a 10-L polyethylene bottle. At each sampling date, bulk deposition collectors were replaced by a clean sampling kit. Cleaning procedures for funnels, tubes and buckets for bulk, wet and dry deposition included repeated washes of all the material with deionized distilled water until electrical conductivity of the rinse was $\sim$1 μS cm^{-1}.

Dry deposition samples were recovered by washing the dry bucket with 250 ml of distilled deionized water and gently brushing the bucket walls with a clean plastic brush to free adhered particles. Prior to recovery, the sample bucket was carefully scrutinized for the presence of small vegetative debris or insects, and if present, they were removed with clean tweezers. All liquid samples (bulk deposition, wet and dry deposition) were taken to the CREAF laboratory and were subject of previously described protocols (Àvila, 1996; Àvila and Rodà, 2002). Within the lapse of 48 h, samples were filtered through 0.45-μm pore size cellulose acetate Millipore filters to separate insoluble and soluble material. Prior to filtration, samples were stored at 4 °C in the dark; after filtration soluble samples were frozen (−20 °C) and filters were dried at 100 °C for 1 h and later stored in a desiccator. Samples were agitated for 0.5–1 min before filtration such that soluble and insoluble (half filter) aliquots are considered to be representative of the entire sample. Particulate P retained on the 0.45-μm filters is here defined as TPP (total particulate P). The dissolved fraction has been analyzed for total dissolved P (TDP) and for soluble reactive P (SRP). For the period 1996 to 2008 TPP, TDP and SRP were analyzed for the main African rains (29 samples). For 2002–2003 only TPP was analyzed, for all wet (47) and dry (65) samples. Table 1 summarizes the variables and periods reported in this study.

Table 1
Measurements, sample provenances and variables studied at La Castanya (LC), Montseny (NE Spain) for the different sampling periods.

Sampling	Measurements	Provenances	Variable	*n* (weeks)
March 2002–Dec. 2003	Aerosol (TSP)	All	TPP	151
July 2002–Dec. 2003	Wet deposition			45
July 2002–Dec. 2003	Dry deposition			65
1996–2008	Bulk deposition	African	SRP, TDP, TPP	29

2.3. Analytical methodology

2.3.1. TSP filters and bulk, wet and dry deposition filters

TSP mass concentrations were determined by standard gravimetric procedures (Querol et al., 2001). For deposition, a known volume of bulk, wet or dry solutions was filtered on pre-weighed filters and re-weighed after drying at 100 °C for 1 h (plus 30 min rest in a desiccator). All filters received the same treatment, with half of each filter digested in closed PFA reactors with HNO_3:$HClO_4$:HF at 90 °C. The acidic solution was allowed to cool and was then dried on a hot plate at 200 °C. The dry residue was redissolved in 2 mL of HNO_3 and subsequently diluted to a volume of 25 mL. The contents of major elements and some trace, including P, were determined by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectometry; IRIS Advantage TJA Solutions, THERMO) at the IDAEA-CSIC laboratory. During all analytical runs, blank values corresponding to blank Millipore filters (mean TPP concentration of blanks = 0.0004 μmol L^{-1}; min = 0.0002 μmol L^{-1} and max = 0.0009 μmol L^{-1}; $n = 8$) were subtracted from measured concentrations. Certified reference materials (1633b, and reference samples SO-1-dust, MAG-1-marine mud) were run throughout the different analytical runs. Accuracy was 8–10% of certified values which ranged between 0.23 and 1.0% P concentration. Repeated replicate analysis demonstrated precision within 10%.

2.3.2. Wet and dry soluble P

At the Radiobiogeochemistry Laboratory of the University of South Carolina, TDP and SRP were analyzed in 40 African rain samples representing 29 weeks of deposition, and including replicate field samples (from 2 to 4 replicated collectors) of 9 weekly rain samples. Rain samples from Montseny were introduced in 10 ml vials, packed in Styrofoam boxes with ice packs and sent frozen by express air-mail. SRP and TDP concentrations in filtered samples were determined using the methods described by Koroleff (1983) and Monaghan and Ruttenberg (1999), respectively. The latter method includes combustion at 500 °C to convert all the organic P into inorganic P prior to spectrophotometric analysis. Dissolved organic P (DOP) is subsequently determined by difference (TDP − SRP = DOP). SRP and DOP are operationally defined terms, presumed to be dominated by inorganic (PO_4^{3-}) and organic P, respectively. Detection limits were 0.04 μmol L^{-1}, defined as three times the standard deviation of the blanks. Field replicate analyses agreed to within 5% of each other. When replicated samples differed by more than 0.2 μmol L^{-1}, only the lowest value was retained in the data set. For 9 events, replicate samples were analysed for TDP, with very good reproducibility (mean of s.d = 0.083 μmol L^{-1}). Through linear regression analysis of TDP with K^+ and NH_4^+ (used as indicators of biogenic contamination; Tsukuda et al., 2004) two samples were identified as contaminated and excluded.

2.4. Classification of provenances

Synoptic maps and HYSPLIT back trajectories from the Air Resources Laboratory (available at http://www.arl.noaa.gov/ready/hysplit4.html, Draxler and Rolph, 2003) were used to classify African *vs.* non-African provenances. Back trajectories were computed in the vertical velocity model (starting point at 12 UTC from LC coordinates run backwards for 144 h) at 750, 1500 and 2500 m.a.s.l. Identification of African dust outbreaks was complemented by satellite images (SeaWifs) and dust forecast models (DREAM, http://www.bsc.es/projects/earthscience/DREAM; SKIRON, http://forecast.uoa.gr/) and satellite information (MODIS, http://rapidfire.sci.gsfc.nasa.gov/; TOMS AI Index, http://toms.gsfc.nasa.gov/). To classify a weekly sample as being from an African provenance, the day (or days) of precipitation within the weekly bulk or wet deposition sample were identified and back trajectories, satellite images, dust models and atmospheric synoptic patterns were screened for the rain days. The week was considered "African" when all of the combined evidence suggested an African outbreak. For dry deposition, different air mass provenances may contribute to the particulates deposited within a week, and here it is more probable that some mixing occurred. These weeks were classified as African if at least one African intrusion lasting for 2–4 days determined by back trajectories, satellite images, dust models and synoptic patterns occurred within the week long period. Synoptic patterns associated with African intrusions were identified as described in Escudero et al. (2005).

2.5. Statistical analyses

Linear regression and correlation analysis, and ANOVA (pair-wise post-hoc comparisons with the Tukey test) were computed with Statistica™. ANOVA analysis is used to show the effect of an independent variable or factor (here, season) on a continuous dependent variable (here, deposition fluxes) when independent variables are nominal. Post-hoc testing is specifically designed to make many comparisons among the groups of means determined by the factor of interest.

To give an indication of the uncertainty of the mean, arithmetic means are accompanied by ±standard error.

Temporal aerosol concentrations and deposition values revealed a seasonal trend which was modelled as:

$$Y_i = a_0 + a\,B\cos(2 + \pi/365t + \Phi) \quad (1)$$

where Y_i is the TPP concentration, a_0 is a constant, a is the coefficient of the periodic term, ϕ stands for its phase in radians and t is the number of days lapsed. This model has two components: one is a constant coefficient (a_0) that gives the mean aerosol concentration for the whole studied period, and the other is a cosine term with a period of 365 days which accounts for the seasonal variation observed in the data. The presence of the cosine term required the use of nonlinear regression techniques (Levenberg–Marquardt algorithm built-in STATISTICA™) to adjust the model to the observations.

3. Results

3.1. Aerosol composition and concentrations

Aerosol TPP concentrations were correlated with the mass of suspended particles (TPP = 4.64 + 0.74 TSP, $r = 0.67$; $p < 0.001$, with TPP in nmol m^{-3} and TSP in mg m^{-3}). African events contained the highest TSP and TPP concentrations (Fig. 2). TSP in Montseny is mainly crustal-derived (27% of total mass) as shown by apportionment analysis (Pey et al., 2009).

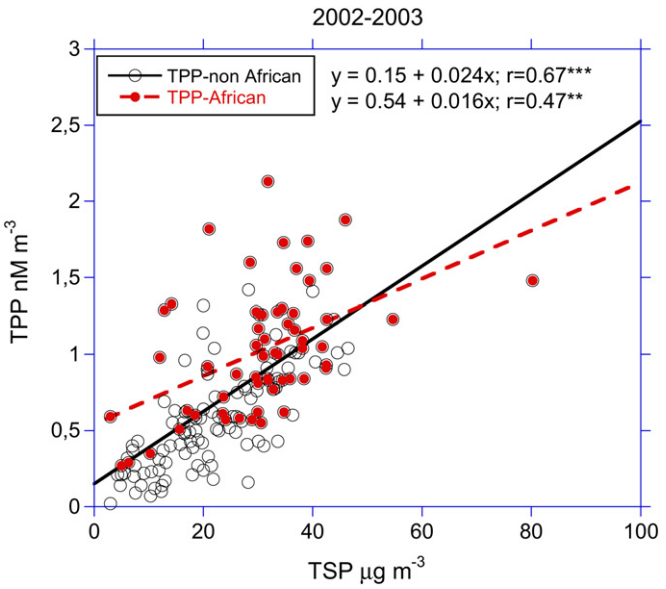

Fig. 2. Aerosol total particulate phosphorus (TPP) plotted against Total Suspended Particles (TSP). Regression lines for African (filled dots) and non-African (white dots) are also shown. ***indicates significance of regression $p < 0.001$ and **indicates $p < 0.01$.

High correlations were found in TSP between P and Al, Ca, Mg and Fe (correlation coefficient between 0.71 and 0.74), consistent with the crustal P origin. High correlation was also found between P and organic carbon (OC, $r = 0.74$) indicating also a biogenic/biomass burning source. Potassium, which represents a mixture of crustal and biogenic sources presented the highest correlation with P ($r = 0.83$). This again suggests that atmospheric P is derived from a mixture of sources (crustal, biogenic and biomass burning).

Aluminium is often used as indicator of the crustal origin of aerosols, and for Saharan aerosols a P/Al ratio of 0.013 has been reported (Guieu et al., 2002). Excess P concentration relative to P/Al in the Saharan dust end-member is assumed to represent the

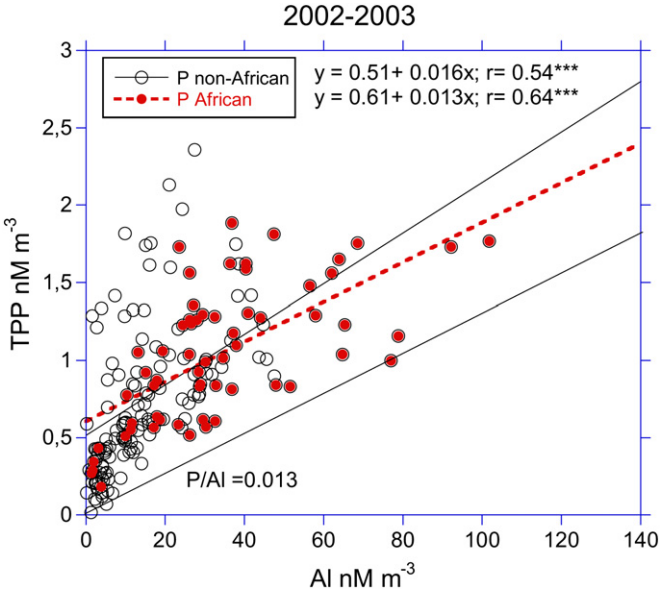

Fig. 3. Aerosol total particulate phosphorus (TPP) concentrations plotted against Al concentrations (in nM m^{-3}).

Table 2
Statistics for total particulate phosphorus (TPP) concentrations in aerosols (total suspended particles, TSP) at La Castanya, Montseny (NE Spain) from March 2002 to December 2003.

	TSP μg m^{-3}	TPP in TSP (all samples) nmol m^{-3}	TPP in TSP (non-African) nmol m^{-3}	TPP in TSP (African) nmol m^{-3}
Arithmetic mean	24.7	0.74	0.58	0.99
Standard error	0.985	0.035	0.031	0.032
Median	24.0	0.63	0.50	0.95
Min.	3	0.016	0.016	0.27
Max	80	2.13	2.13	1.88
n	151	151	95	56

fraction of P derived from anthropogenic activities. At Montseny, P was significantly correlated with Al. A considerable overlap was found between African and non-African sources so that the respective regressions were not significantly different (Fig. 3). This may indicate that African dust interacts with anthropogenic derived pollutants, producing a mixing of mineral dust with industrial emissions and biomass burning. However, the mean P/Al ratio for non-African events was higher than for African (0.11 ± 0.021 *vs.* 0.04 ± 0.030) and the % anthropogenic contribution for non-African events (73.4 ± 1.7) was significantly higher than for African (58.5 ± 2.45; $p < 0.05$). The anthropogenic contribution for all samples was inversely related to TSP levels ($r = -0.40$; $p < 0.01$).

Mean TSP levels at Montseny in the period March 2002–December 2003 were 24.7 ± 0.99 μg m^{-3}, ranging from 3 to 80 μg m^{-3} (Table 2). Mean TPP concentration in TSP-aerosols was 0.74 ± 0.035 nmol m^{-3} (range: 0.016–2.13 nmol m^{-3}, Table 2). There was a marked seasonal pattern for the particulates and their TPP content, with minimum concentrations in winter and higher values in summer (Fig. 4). Spring and early summer of year 2003 were highly affected by African intrusions; this seasonality is usual, but year 2003 was specially affected. The summer of 2003 was affected by high pressures over Europe, which induced a heat wave in Western Europe from June to August. This may have influenced the aerosol load (with a local and regional contribution besides African transport) over Montseny. Back trajectory analysis shows that most of the African intrusions occurred during 2003 summer. Since TPP concentrations in aerosols were higher in the African episodes compared to non-African ones (0.99 nmol m^{-3} *vs.* 0.58 nmol m^{-3}, $p < 0.05$), this suggests that African influence determined the cycle. However, the seasonal model (Equation (1)) showed the highest TPP correlation ($r = 0.74$; 55% variance explained) with the seasonal trend of non-African episodes, while the inclusion of African events decreased the correlation ($r = 0.68$;

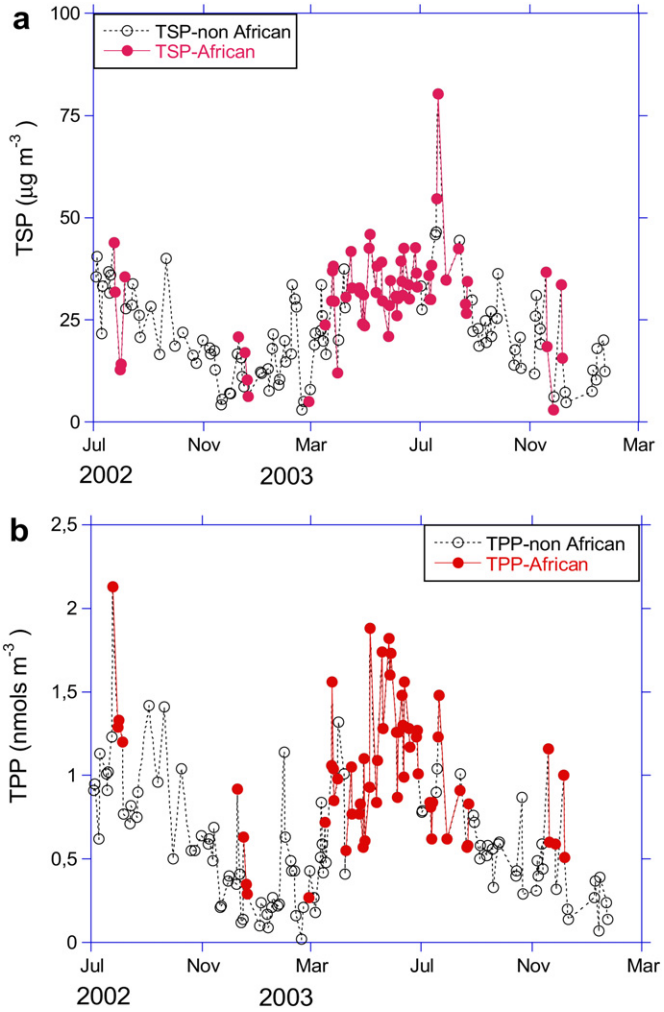

Fig. 4. Temporal variation of: a) TSP (μg m^{-3}) and b) TPP concentrations (nmol m^{-3}) in aerosols at La Castanya (Montseny). Full dots indicate African events.

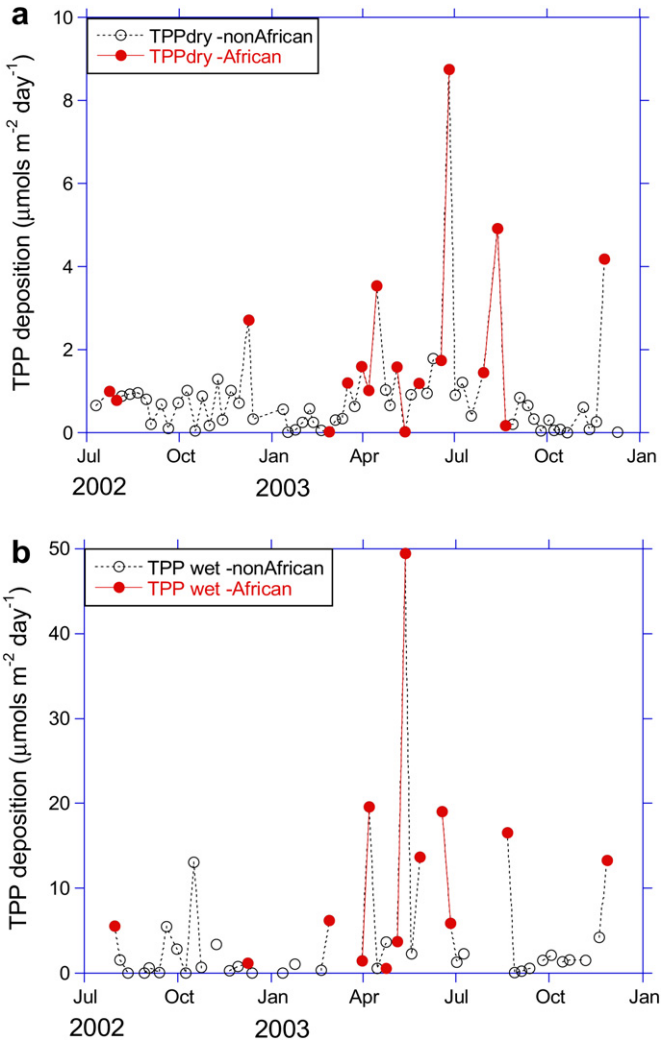

Fig. 5. Temporal variation of TPP daily deposition (μmol m^{-2} d^{-1}) in: a) dry and b) wet deposition modes at La Castanya (Montseny). Full dots indicate African events.

46% variance explained), indicating a seasonal trend irrespective of the occurrence of African episodes.

3.2. Dry/wet TPP deposition and African source partitioning

From July 2002 to December 2003, 65 dry deposition and 45 wet-only deposition samples were collected at LC and analysed for TPP. Dry deposition was collected every week, but since not all weeks had rainfall, fewer wet samples were obtained relative to dry samples.

The temporal evolution of wet and dry daily TPP deposition is shown in Fig. 5. On a daily basis, arithmetic mean wet deposition (4.86 ± 1.28 μmol m^{-2} d^{-1}) was higher than mean dry deposition (0.95 ± 0.17 μmol m^{-2} d^{-1}; $p = 0.0017$). There was also higher variability in wet deposition, with maximum values up to 50 μmol m^{-2} d^{-1} compared to maxima of only 9 μmol m^{-2} d^{-1} for dry deposition. A seasonal pattern was evident in both deposition modes, with higher fluxes during spring-summer. Moreover, the highest deposition values usually corresponded to African events, either in the wet or dry deposition mode. ANOVA analysis of daily TPP deposition grouped by seasons and rain type showed African deposition to be higher, especially in the wet mode (Fig. 6).

The cosine seasonal model showed a remarkable seasonal variation for dry deposition ($r = 0.59$, 34.4% variance explained), which was much lower for wet deposition either considering all events ($r = 0.38$; 15% variance explained) or non-African events alone ($r = 0.39$; 16% variance explained). Thus, dry deposition more closely followed the seasonal patterns observed for P aerosols.

For the period July 2002 to December 2003, annual TPP deposition at LC was 576 μmol P m^{-2} y^{-1} (Table 3), evenly distributed between wet (285 μmol P m^{-2} y^{-1}) and dry deposition (291 μmol P m^{-2} y^{-1}). Despite the abovementioned differences in daily mean deposition rates in dry and wet modes, the higher number of dry deposition days compared to wet deposition days resulted in similar total annual deposition in both modes. African weeks accounted for 380 μmol P m^{-2} y^{-1} (66% of annual total, Table 3), with deposition partitioned into 212 μmol P m^{-2} y^{-1} in the wet and 168 μmol P m^{-2} y^{-1} in the dry modes. Therefore, dry deposition accounted for 44% of total TPP deposition in African events, while for non-African ones dry deposition predominated (63%, Table 3). Overall, the major contribution to TPP deposition was from wet African weeks (37% of total deposition) followed by dry African deposition (29%) and non-African dry deposition (21%). Wet deposition from non-African weeks only amounted to 13% of TPP deposition.

3.3. African rain samples from 1996 to 2008

Given the importance of African TPP deposition, we examined these inputs more closely by analysing TDP and SRP for African red-rains from 1996 to 2008. The mean annual TPP deposition in red-rains in this period (29 samples corresponding to red-rains between 1996 and 2008) was 217 μmol m^{-2} y^{-1}, a value that falls within the range of TPP African deposition that can be calculated from the P content in the African end member (0.08% Guieu et al., 2002) and the African deposition flux in the western Mediterranean (5–12 kg km^2 y^{-1}), which results in 132–317 μmol P m^{-2} y^{-1}. Because these measurements only refer to African wet weekly samples, we need to correct them for total annual deposition. For this correction, the percent wet African to total deposition for year 2002–03 (37%, Table 3) was applied to the 1996–2008 mean TPP red-rain deposition, producing an estimate of 588 μmol m^{-2} y^{-1} TPP for the period 1996–2008, which closely compares with the wet deposition obtained for the period 2002–2003 (576 μmol m^{-2} y^{-1}, Table 3). For African rainfall samples, there was a good correlation between TPP and TDP ($r = 0.65$; $p < 0.0002$) and TPP *vs.* SRP deposition ($r = 0.88$; $p < 0.0001$). On a weekly basis, TDP accounted for 11.2% of TPP, while SRP was only 2.2% of TPP (Table 4).

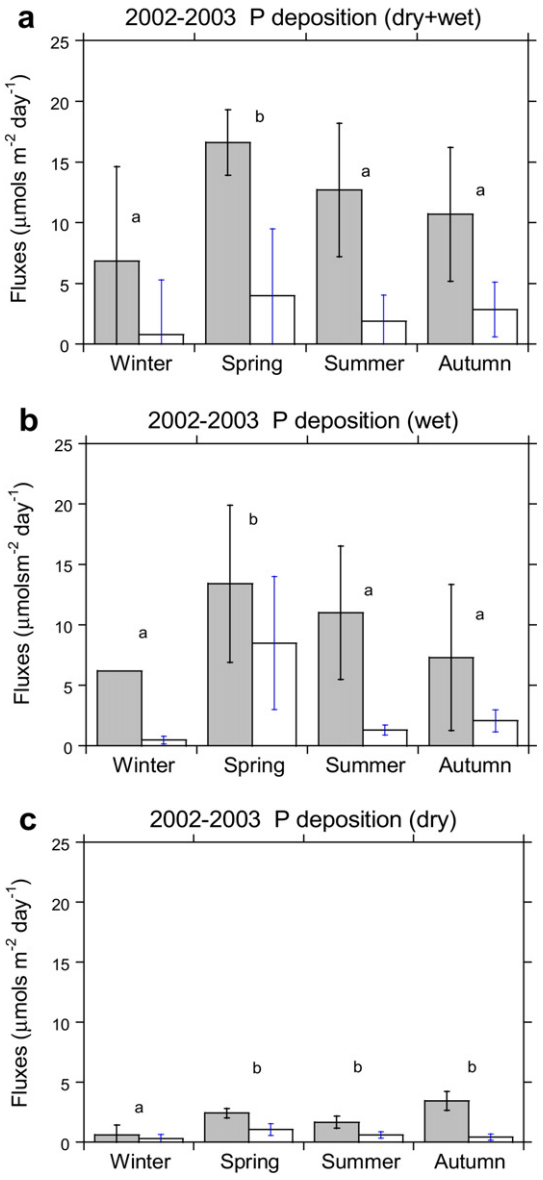

Fig. 6. ANOVA analysis of TPP deposition with season and rain type by provenance for the period July 2002–December 2003. a) Total deposition (dry + wet), b) Wet deposition and c) Dry deposition. Shaded bars = African events; white bars = non-African events. Different letters indicate significant statistical differences with post-hoc Tukey tests ($p < 0.05$) for season. Winter = January, February, March; Spring = April, May, June; Summer = July, August, September; Winter = October, November, December. Differences between rain types (African *vs.* non-African) were always significant for wet and total deposition, but for dry deposition only significant differences were found in autumn.

Table 3
African, non-African, and annual total particulate phosphorus (TPP) deposition (in μmol m^{-2} y^{-1}) and their dry percentage contribution to total wet plus dry deposition at La Castanya, Montseny (NE Spain) from July 2002 to December 2003.

	Wet	Dry	Total (Wet + Dry)	% Dry to Total
African	212.5	167.8	380.3	44.1
Non-African	72.9	123.2	196.1	62.8
Total Annual	285.4	291.0	576.4	50.5
% African to Annual	74.5	57.7	66.0	

Table 4
Statistics for weekly deposition (μmol m^{-2} $week^{-1}$) for TPP, TDP, SRP and DOP at La Castanya (Montseny, NE Spain) for red-rain weekly samples from 1996 to 2008. DOP estimated from TDP minus SRP.

	TPP	TDP	SRP[a]	DOP
Arithmetic mean	78.2	8.82	1.70	4.82
Standard error	23.8	1.83	0.59	1.66
Min.	2.6	0.35	0.05	0.3
Max	661	33.9	8.03	22.1
n	29	27	13	13

[a] Calculated without values below detection limit (Total weeks = 27; above detection limit = 13).

4. Discussion

4.1. Seasonality and provenances

TPP in aerosols and dry deposition during 2002–2003 was well correlated with a seasonal model ($r = 0.68$ and 0.59, respectively), but wet deposition showed a more irregular seasonal pattern ($r = 0.38$). TPP wet deposition was not correlated with precipitation ($r = -0.021$; $p = 0.89$); rather, it was much more influenced by the sporadic occurrence of African events (Fig. 5), similarly to findings of Morales-Baquero et al. (2006) in Sierra Nevada, southern Spain, and Bergametti et al. (1992) in Corsica. Bergametti et al. (1992) found higher P concentrations in aerosols from North-Africa than from European trajectories (0.57 nmol m^{-3} *vs.* 0.33 nmol m^{-3}). At Crete and Turkey, TPP aerosol concentrations from the S and SW (corresponding to North-Africa) were higher than from N–NE, NW and W (1.2–1.3 nmol m^{-3} and 0.6–0.7 nmol m^{-3} for Crete and Turkey, respectively; Markaki et al., 2003). In our study, aerosol TPP concentrations closely matched the findings for the Eastern Mediterranean: 0.99 nmol m^{-3} for African and 0.58 nmol m^{-3} for non-African provenances (Table 2).

4.2. Calculation of the P deposition velocity (V_d)

Many studies obtain dry deposition fluxes from the relationship between the deposition flux (F_d) and atmospheric concentrations (C_a) through the deposition velocity parameter (V_d):

$$F_d = C_a \cdot V_d \quad (2)$$

Estimates of V_d for P deposition are limited. One of the most widely used estimate is that obtained by Duce et al. (1991) for compounds in the coarse fraction (including P), which was established at 2 cm s^{-1} Bergametti et al. (1992) in Corsica calculated a P V_d of 2.7 cm s^{-1} from P aerosol measurements and P total deposition during the dry period. At Crete, using inorganic P measured in aerosols and dry inorganic P deposition, a mean V_d of 2.3 cm s^{-1} was estimated (Markaki et al., 2003).

Our data at Montseny provide another data set to add to these V_d estimations for particulate P. Aerosol concentrations and dry deposition showed similar seasonal trends, indicating strong linkages between them. Because dry deposition rates are size dependent and P is usually found within the coarse fraction of particles (diameters>1 μm; Duce et al., 1991; Prospero et al., 1996; Markaki et al., 2003), our measurements of dry deposition onto a dry bucket will contain most of the gravitational flux, the main deposition pathway for coarse particles. Using Equation (2), an average V_d of 1.6 ± 0.3 cm s^{-1} was obtained for all samples in 2002–2003. When accounting for air mass provenance, a significantly lower V_d of 1.07 ± 0.13 cm s^{-1} was found for non-African events ($n = 45$), compared to 3.1 ± 0.80 cm s^{-1} for African weeks ($n = 16$; $p = 0.00025$), indicating higher settling velocities for coarser desert dust particles. Indeed, a particle size mass distribution study for dust at Crete found that 85% of dissolved P was associated with particle diameters between 1 and 10 μm and showed a similar distribution to Ca, a tracer of crustal material (Markaki et al., 2003). Measurements of the grain size distribution (particle diameter measured with a Coulter LS100 counter) of 4 African rain samples collected at Montseny indicated a median particle diameter of 9.8 μm, which is similar to that obtained for the particulate phase of 7 Saharan rains collected at Corsica (median of 8 μm; Guieu et al., 2002), thus confirming large particle diameters for African aerosols.

4.3. Mean aerosol and deposition values

TPP mean concentration in aerosols (0.74 ± 0.035 nmol m^{-3}) was similar to values in Corsica (0.33–0.63 nmol m^{-3}, Bergametti et al.,

Table 5
Annual deposition (μmol m^{-2} y^{-1}) for TPP, and TDP or DIP from references around the Mediterranean and from this study.

	Wet	Dry	Total (Wet + Dry)	Period	Reference
TPP					
Sierra Nevada (Spain)	144.4	368.5	512.9	2001–02	Morales-Baquero et al. (2006)
Corsica (France)			1295	1985–88	Bergametti et al. (1992)
Corsica (France)			1184	1985–87	Guieu et al. (2002)
Cap Ferrat (S. France)	70			1997–98	Migon and Sandroni (1999)
Cap Ferrat (S. France)		60–250		June–July 1998	Migon et al. (2001)
Crete (Greece)	178			1999–00	Markaki et al. (2003)
Erdemli (Turkey)	250.2			1999–00	Markaki et al. (2003)
Israel	290.3		1000	1996–98	Herut et al. (1999)
Israel		800		2001–03	Carbo et al. (2005)
All Mediterranean (mean of 9 sites)			1064.5	2001–02	Guieu et al. (2010)
Montseny (NE Spain)	285.4	291.0	576.4	2002–03	This study
Montseny (NE Spain)	289[a]		588[a]	1996–08	This study
DIP or TDP					
Cap Ferrat (S. France)	95			1997–98	Migon and Sandroni (1999)
Western Med			464–608	2001–02	Markaki et al. (2010)
Central Med			355–371	2001–02	Markaki et al. (2010)
Eastern Med			243–480	2001–02	Markaki et al. (2010)
Crete (Greece)	68.4	125	193.4	1999–00	Markaki et al. (2003)
Erdemli (Turkey)	168			1999–00	Markaki et al. (2003)
Israel	280–290	400		1992–98	Herut et al. (1999, 2002)
Israel		500		2001–03	Carbo et al. (2005)
Villefranche s. Mer (S. France)	12–16			1999	Ridame and Guieu (2002)
Montseny (NE Spain)	46–60	56–80	102–140	2002–03	This study

[a] Mean TPP deposition for wet African events corrected from wet Africa percent to total annual, from Table 3.

1992) and the Eastern Mediterranean (0.43–0.77 nmol m^{-3} at Crete and Turkey, respectively; Markaki et al., 2003), but lower than in southern France (1.65 nmol m^{-3}, in Cap Ferrat; Migon et al., 2001), though this later study was only for a one-month period. The mean daily TPP deposition fluxes were 4.64 ± 1.28 μmol m^{-2} d^{-1} and 0.95 ± 0.17 μmol m^{-2} d^{-1}, for the wet and dry modes respectively. Migon et al. (2001) estimated lower dry deposition fluxes in the range of 0.15–0.7 μmol TPP m^{-2} d^{-1}, an estimate that was obtained from the product of aerosol concentrations and V_d values from the literature (0.1–0.5 cm s^{-1}; Duce et al., 1991) for the summer period in Cap Ferrat, southern France.

Ridame and Guieu (2002) reported deposition values in the range from 0.03 to 2.6 μmol m^{-2} d^{-1} of DIP considering only African rain events at Villefranche sur Mer (south France). Taking into account that the partitioning of atmospheric P between soluble and insoluble forms for Saharan rains may vary between 8 and 15% of total P (Lepple, 1975; Herut et al., 1999, 2002; Ridame and Guieu, 2002), and using 10–15% as an indicative value for the percent dissolution, the above DIP figures would translate into 0.2–23 μmol TPP m^{-2} d^{-1}. Thus, our results are towards the lower range of previous estimates.

The annual TPP deposition flux at LC was 576–588 μmol m^{-2} y^{-1} by the two estimation methods used. Deposition was similarly distributed between wet and dry deposition. The annual P fluxes at Montseny are towards the lower end of the TPP fluxes measured at various locations throughout the Mediterranean region (Table 5), but similar to those obtained in southern Spain (Sierra Nevada). Our results suggest that, in NE Spain, the major TPP deposition pathway is through African rains (37%), followed by African dry dust deposition (29%). However, dust input from African rains at Montseny (5 g m^{-2} y^{-1}) is lower than that measured in Corsica (12–14 g m^{-2} y^{-1}; Löye-Pilot et al., 1986; Bergametti et al., 1989) and much lower than in the eastern Mediterranean (20–40 g m^{-2} y^{-1}; Ganor and Mamane, 1982). This is consistent with an increasing trend in mean annual PM10 levels from the western to the eastern Mediterranean Sea (Querol et al., 2009), which would account for the higher dry deposition in the eastern basin. These differences between geographic regions are most likely related to dissimilar wind and rain patterns and to the distance to the dust source, and may account for the variability in nutrient deposition amounts and the differences in preferential depositional pathways between basins (Guieu et al., 2010).

At Montseny, dry deposition represented 50% for all events and 44% of the African TPP deposition. This contrasts markedly with other studies in the western Mediterranean which have reported dry deposition of Saharan dust to be negligible (Löye-Pilot and Martin, 1996; Ridame and Guieu, 2002). On the other hand, in a study of P deposition in the eastern Mediterranean (Crete), DIP from dry deposition accounted for 65% of total deposition (Markaki et al., 2003), a result that is probably related to the previously mentioned higher impact of dust intrusions in the eastern basin. Our data provide a first estimate of the dry/wet partitioning for the western Mediterranean. The paucity of data regarding dry and wet fluxes and the fact that P solubility is different in wet and dry deposition modes (Herut et al., 1999, 2005), attests to the need of more studies for a better knowledge of the effect of P deposition on marine productivity in the western Mediterranean Sea.

4.4. Estimation of bioavailable P deposition to the NW Mediterranean

TPP and TDP concentrations averaged 3.5 ± 0.96 μmol L^{-1} P and 0.27 ± 0.03 μmol L^{-1} P ($n = 26$) respectively in red-rains collected in the period 1996–2008. The good correlation between TPP and TDP concentrations ($r = 0.65$; $p < 0.0002$), suggests that TPP undergoes dissolution in rainwater. The average percent TDP dissolution respective of TPP in red-rains was 11.2%, close to the 8–11% values reported for P dissolution from dust (Herut et al., 1999; Lepple, 1975). Dissolution percentages were negatively correlated with rainwater pH ($r = -0.52$; $p = 0.02$). For rainwater with pH values between 5.6 and 7.0, P dissolution was 26.9% while for pH > 7.0 it decreased to 7.5%. Our data refer to a population of dust-loaded rains of African provenance, but pure African events in the western Mediterranean are scarce, as the aerosol data in Montseny demonstrate (Fig. 3): some points classified as African lie well above the crustal line (P/Al = 0.013) indicating that they also contain an anthropogenic P contribution. Most of these African rains have likely encountered polluted air masses on their way to the NE Iberian Peninsula and may have incorporated more soluble P species associated with anthropogenic pollution (biomass burning, incineration and other industrial processes). Alternatively, the dust air masses may have come upon aged recirculating air masses (Millán et al., 1997) containing acidic trace gases (HNO_3, SO_2) which can be absorbed onto the water coated dust particle and react to form sulphate and nitrate (Phadnis and Carmichael, 2000; Hanke et al., 2003). The carbonate content in the dust (Àvila et al., 1997, 2007; Löye-Pilot et al., 1986) will neutralize the acidity associated to sulphate and nitrate, but during this process, solubilisation of P-minerals would likely occur.

Several African red-rain samples were also measured for SRP, with much lower mean concentrations than those found in the TDP pool (0.068 ± 0.007 μmol L^{-1} P, $n = 13$). In fact, nearly half of the SRP analysed samples were below the detection limit. When encountering values below detection limits, one can either remove these values or use instead a very low figure representing the below detection value (some authors use the lowest detected value divided by two; others use the 3 × standard deviation of the blanks). However, either procedure induces a bias of the true correlations (Lyles et al., 2001). Because a complete analysis of this issue is beyond the scope of this paper, we have calculated the basic statistics and correlations with the two procedures, and found that differences were of degree but did not appreciably change interpretations: correlations between SRP and TPP changed from $r = 0.65$, $n = 13$ $p < 0.05$ when considering only detected pairs to $r = 0.88$, $n = 27$, $p < 0.001$ when including a value for undetected values (= 0.02 μmol P), and the SRP averages decreased by 15% when including a value for the undetected values.

SRP concentrations measured in this study were ~50% lower than the concentrations measured by Markaki et al. (2010), but within the range obtained by Herut et al. (1999) using similar methods. DOP concentrations were similarly lower, only ~6% as opposed to the 13–19% measured in eastern Mediterranean (Carbo et al., 2005). We hypothesize that our lower %SRP and DOP are due to the strong influence of African dust, and is consistent with the solubility results reported by Ridame and Guieu (2002). These differences between TDP, DOP, and SRP concentrations highlight the importance of determining the P source and speciation in establishing the P pools bioavailable for planktonic uptake following deposition.

TPP deposition values for the period 2002–2003 (for which the wet and dry partitioning in background and African weekly samples were measured) were converted to dissolved P fluxes using average solubility percentages for African (11.2%) and background events (30–50%, from literature references). This produced wet + dry soluble P fluxes of 43 μmol m^{-2} y^{-1} for African rain samples and 59–98 μmol m^{-2} y^{-1} for non-African ones, and thus a total deposition of ~100–140 μmol m^{-2} y^{-1} (Table 6). When splitting data into wet and dry deposition, TDP deposition was estimated as 46–60 μmol m^{-2} y^{-1} in the wet mode and 56–80 μmol m^{-2} y^{-1} in the dry mode (Table 6). Dry deposition

Table 6
Estimation of the dissolved P inputs (μmol m^{-2} y^{-1}) from the measured values of total particulate phosphorus (TPP) for wet, dry and total deposition split into African and non-African weekly samples at La Castanya (Montseny) for the period July 2002–December 2003.

	TPP input	% dissolution	Dissolved	Dissolved input range
Wet				
African	212.5	11.2	23.7	
Non-African	72.9	30	21.9	
		50	36.5	46–60
Dry				
African	167.8	**11.2**	18.8	
Non-African	123.2	30	37.0	
		50	61.6	56–80
Wet + Dry				
African	380.3	11.2	42.6	
Non-African	196.1	30	58.8	
		50	98.1	100–140

from background polluted air masses, with higher solubility, explain the increased P contribution of the dry deposition mode. A compilation of data from the literature on soluble P deposition (measured predominantly as DIP) around the Mediterranean indicates that dissolved fluxes at Montseny are similar to those measured at Crete, but higher than those determined at a closer coastal site in southern France (Villefranche sur Mer; Table 5).

Recent studies have shown that P atmospheric deposition to the Mediterranean may significantly influence annual new production rates, considering Dugdale and Goering (1967) definition of new production as the annual primary production supported by externally supplied nutrients (e.g. nitrogen or phosphorus). Using the Redfield molar ratios C:P 106:1 (Redfield et al., 1963), atmospheric P-induced production in the eastern Mediterranean represents ~4–11% of new production (Herut et al., 2002; Carbo et al., 2005) and as high as 20–38% during the stratified oligotrophic period (Markaki et al., 2003). This is in contrast with a negligible contribution in the western Mediterranean, where it has been evaluated as 0.1–0.2% of the annual new production (Ridame and Guieu, 2002). Considering soluble P inputs estimated at Montseny (100–140 μmol m^{-2} y^{-1}) as representative for inputs in the NW Mediterranean coastal waters and using the C:P Redfield ratio, new production due to atmospheric P is estimated between 0.13 and 0.18 g C m^{-2} y^{-1}. Compared to new production values for the western Mediterranean (35, 42 and 52 g C m^{-2} y^{-1}, from Bethoux (1989), Marty and Chiavérini (2002) and Morel and André (1991) respectively), this atmospheric P-induced production is ~0.3–0.5% of new production, thus confirming the findings by Ridame and Guieu (2002). Nevertheless, as also suggested by other authors in the Mediterranean, large episodic dust events may have a higher impact. For example, a high intensity dust event in 22–27 May 2008 delivering 3.7 g m^{-2} African dust provided a TDP input of 34 μmol P m^{-2} (0.32 μmol L^{-1} TDP; 106 mm precipitation). Using the assumptions above, such a deposition event would trigger a new production of 0.043 g C m^{-2}, which represents 24–33% of annual values of the new production induced by atmospheric P.

5. Conclusions

The results of this study show that dry deposition accounted for ~50% of total annual particulate phosphorus deposition which amounts to 576 μmol P m^{-2} y^{-1}. This indicates that the dry deposition pathway needs to be considered when nutrient budgets for the Mediterranean are calculated. African events were very relevant in the annual budget (66% of TPP); in these African weeks wet deposition dominated over dry deposition. TPP deposition in northeastern Spain lies toward the lower range of reported values for Corsica and the eastern Mediterranean, in agreement with an increasing impact of African dust from west to east in the Mediterranean.

This study corroborates the findings of other researches in the Western Mediterranean suggesting that African events, albeit undergoing lower TPP dissolution rates, may represent an important source of nutrients to surface waters, specially when they occur during the stratification period when nutrients are depleted at the surface.

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