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 μmols 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.

Keywords: African dust, wet/dry deposition, particulate matter, phosphorus, Mediterranean, marine productivity

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 (Benitez-Nelson, 2000). As such, the only natural sources of new P to oceanic waters are via atmospheric deposition and riverine discharge (e.g. Benitez-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 (Thingstad and Razzoulzadegan, 1995; Vaulot et al., 1996; Thingstad 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 ~132-317 μmols m^{-2} y^{-1}, assuming 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 to 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- 2003 in a site in NE Spain close to the

123 coast. Because of the important contribution of African sources and the well known
124 interannual variability of African outbreaks, a long term record (1996-2008) of Saharan
125 bulk weekly samples was also analyzed to determine the potential impact of high P
126 deposition events on the biogeochemistry of the western Mediterranean.

127 2. Material and methods

128 2.1. Study site

129 Atmospheric aerosol concentrations and wet and dry deposition were sampled
130 weekly from March 2002 to December 2003. Sampling was conducted at La Castanya
131 (LC, 41º46'N, 2º21'E, 700 m above sea level), a long-term biogeochemical study site
132 located in the Montseny mountains of the Pre-litoral Catalan Range (Rodà et al., 1999).
133 The site is amidst an extensive holm-oak (*Quercus ilex* L.) forest in Montseny Natural
134 Park, 40 km to the N-NE of Barcelona and 25 km from the Mediterranean coast. Since
135 2002, this site has been instrumented as a background regional air quality site
136 (EUSAAR network-European Supersites for Atmospheric Aerosol Research,
137 http://www.eusaar.net).

138 The record from LC is taken to be broadly representative of deposition fluxes
139 over the NW Mediterranean due to the large-scale of dust transport (scale of hundreds to
140 thousands of km, Lawrance and Neff, 2009). This presumption is confirmed by the very
141 close correspondence between the African dust events recorded at Montseny and
142 Mallorca (Balearic Islands) from 1984 to 2003, with records of simultaneous African
143 red-rains (rains containing a reddish silty residue from desert dust) in 71% of the cases
144 (Fiol et al., 2005; Àvila et al., 2007). Moreover, it is generally accepted that elemental
145 fluxes measured at a coastal site can be extended to regional open waters (Migon et al.,
146 2001; Herut et al., 2002; Guieu et al., 2010; Koçak et al., 2010).

147 2.2 Sampling and definitions

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

167 From January 1996 to December 2008 (except 2002-2003), bulk deposition
168 samples were also collected weekly at LC. From this record, only the weeks containing
169 red rains (rains that left a reddish dusty residue on rainwater collectors) are considered.
170 Rainfall was collected in 4 (1996-1997) or 2 (1998-2008) bulk deposition collectors

171 placed 1.5 m above the ground, each consisting of a 19-cm diameter-polyethylene
172 funnel with a nylon stopper in the neck connected by a Tygon looping tube to a 10-L
173 polyethylene bottle. At each sampling date, bulk deposition collectors were replaced by
174 a clean sampling kit. Cleaning procedures for funnels, tubes and buckets for bulk, wet
175 and dry deposition included repeated washes of all the material with deionized distilled
176 water until electrical conductivity of the rinse was ~ 1 μS cm^{-1}.

177 Dry deposition samples were recovered by washing the dry bucket with 250 ml
178 of distilled deionized water and gently brushing the bucket walls with a clean plastic
179 brush to free adhered particles. Prior to recovery, the sample bucket was carefully
180 scrutinized for the presence of small vegetative debris or insects, and if present, they
181 were removed with clean tweezers. All liquid samples (bulk deposition, wet and dry
182 deposition) were taken to the CREAF laboratory and were subject of previously
183 described protocols (Àvila, 1996; Àvila and Rodà, 2002). Within the lapse of 48h,
184 samples were filtered through 0.45-μm pore size cellulose acetate Millipore filters to
185 separate insoluble and soluble material. Prior to filtration, samples were stored at 4ºC in
186 the dark; after filtration soluble samples were frozen (-20ºC) and filters were dried at
187 100ºC for one hour and later stored in a dessicator. Samples were agitated for 0.5 - 1
188 min before filtration such that soluble and insoluble (half filter) aliquots are considered
189 to be representative of the entire sample. Particulate P retained on the 0.45-μm filters is
190 here defined as TPP (total particulate P). The dissolved fraction has been analyzed for
191 total dissolved P (TDP) and for soluble reactive P (SRP). For the period 1996 to 2008
192 TPP, TDP and SRP were analyzed for the main African rains (29 samples). For 2002-
193 2003 only TPP was analyzed, for all wet (47) and dry (65) samples. Table 1 summarizes
194 the variables and periods reported in this study.

195 2.3 Analytical methodology

196 2.3.1. TSP filters and bulk, wet and dry deposition filters

197 TSP mass concentrations were determined by standard gravimetric procedures
198 (Querol et al., 2001). For deposition, a known volume of bulk, wet or dry solutions was
199 filtered on pre-weighed filters and re-weighed after drying at 100ºC for 1 hour (plus 30
200 min rest in a desiccator). All filters received the same treatment, with half of each filter
201 digested in closed PFA reactors with HNO_3:$HClO_4$:HF at 90°C. The acidic solution
202 was allowed to cool and was then dried on a hot plate at 200^{o}C. The dry residue was re-
203 dissolved in 2 mL of HNO_3 and subsequently diluted to a volume of 25 mL. The
204 contents of major elements and some trace, including P, were determined by ICP-AES
205 (Inductively Coupled Plasma Atomic Emission Spectometry; IRIS Advantage TJA
206 Solutions, THERMO) at the IDAEA-CSIC laboratory. During all analytical runs, blank
207 values corresponding to blank Millipore filters (mean TPP concentration of
208 blanks=0.0004 μmol L^{-1}; min=0.0002 μmol L^{-1} and max=0.0009 μmol L^{-1}; n=8) were
209 subtracted from measured concentrations. Certified reference materials (1633b, and
210 reference samples SO-1-dust, MAG-1-marine mud) were run throughout the different
211 analytical runs. Accuracy was 8-10% of certified values which ranged between 0.23 and
212 1.0% P concentration. Repeated replicate analysis demonstrated precision within 10%.

213

214 2.3.2 Wet and dry soluble P

215 At the Radiobiogeochemistry Laboratory of the University of South Carolina,
216 TDP and SRP were analyzed in 40 African rain samples representing 29 weeks of
217 deposition, and including replicate field samples (from 2-4 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 500ºC 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,

242 http://rapidfire.sci.gsfc.nasa.gov/; TOMS AI Index, http://toms.gsfc.nasa.gov/). To
243 classify a weekly sample as being from an African provenance, the day (or days) of
244 precipitation within the weekly bulk or wet deposition sample were identified and back
245 trajectories, satellite images, dust models and atmospheric synoptic patterns were
246 screened for the rain days. The week was considered "African" when all of the
247 combined evidence suggested an African outbreak. For dry deposition, different air
248 mass provenances may contribute to the particulates deposited within a week, and here
249 it is more probable that some mixing occurred. These weeks were classified as African
250 if at least one African intrusion lasting for 2-4 days determined by back trajectories,
251 satellite images, dust models and synoptic patterns occurred within the week long
252 period. Synoptic patterns associated with African intrusions were identified as described
253 in Escudero et al. (2005).

254

255 2.5. Statistical analyses

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

262

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

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

$$Y_i = a_0 + a\ B \cos(2 + \pi/365\ t + \Phi) \qquad \text{(equation 1)}$$

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^{TM}) 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+0.74TSP, r=0.67; $p< 0.001$, with TPP in nmols 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).

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

288 again suggests that atmospheric P is derived from a mixture of sources (crustal,
289 biogenic and biomass burning).

290 Aluminium is often used as indicator of the crustal origin of aerosols, and for
291 Saharan aerosols a P/Al ratio of 0.013 has been reported (Guieu et al., 2002). Excess P
292 concentration relative to P/Al in the Saharan dust end-member is assumed to represent
293 the fraction of P derived from anthropogenic activities. At Montseny, P was
294 significantly correlated with Al. A considerable overlap was found between African and
295 non-African sources so that the respective regressions were not significantly different
296 (Fig. 3a). This may indicate that African dust interacts with anthropogenic derived
297 pollutants, producing a mixing of mineral dust with industrial emissions and biomass
298 burning. However, the mean P/Al ratio for non-African events was higher than for
299 African (0.11±0.021 *vs.* 0.04±0.030) and the % anthropogenic contribution for non-
300 African events (73.4±1.7) was significantly higher than for African (58.5±2.45; $p<0.05$).
301 The anthropogenic contribution for all samples was inversely related to TSP levels (r= -
302 0.40; $p<0.01$).

303 Mean TSP levels at Montseny in the period March 2002 – December 2003 were
304 24.7±0.99 μg m^{-3}, ranging from 3 to 80 μg m^{-3} (Table 2). Mean TPP concentration in
305 TSP-aerosols was 0.74±0.035 nmols m^{-3} (range: 0.016-2.13 nmols m^{-3}, Table 2). There
306 was a marked seasonal pattern for the particulates and their TPP content, with minimum
307 concentrations in winter and higher values in summer (Fig. 4). Spring and early summer
308 of year 2003 were highly affected by African intrusions; this seasonality is usual, but
309 year 2003 was specially affected. The summer of 2003 was affected by high pressures
310 over Europe, which induced a heat wave in Western Europe from June to August. This
311 may have influenced the aerosol load (with a local and regional contribution besides

312 African transport) over Montseny. Back trajectory analysis shows that most of the
313 African intrusions occurred during 2003 summer. Since TPP concentrations in aerosols
314 were higher in the African episodes compared to non-African ones (0.99 nmols m^{-3} *vs*.
315 0.58 nmols m^{-3}, $p<0.05$), this suggests that African influence determined the cycle.
316 However, the seasonal model (equation 1) showed the highest TPP correlation (r=0.74;
317 55% variance explained) with the seasonal trend of non-African episodes, while the
318 inclusion of African events decreased the correlation (r=0.68; 46% variance explained),
319 indicating a seasonal trend irrespective of the occurrence of African episodes.

320

321 3.2 Dry / wet TPP deposition and African source partitioning

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

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

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

340 For the period July 2002 to December 2003, annual TPP deposition at LC was
341 576 µmols P $m^{-2}y^{-1}$ (Table 3), evenly distributed between wet (285 µmols P $m^{-2}y^{-1}$) and
342 dry deposition (291 µmols P $m^{-2}y^{-1}$). Despite the abovementioned differences in daily
343 mean deposition rates in dry and wet modes, the higher number of dry deposition days
344 compared to wet deposition days resulted in similar total annual deposition in both
345 modes. African weeks accounted for 380 µmols P $m^{-2}y^{-1}$ (66% of annual total, Table 3),
346 with deposition partitioned into 212 µmols P $m^{-2}y^{-1}$ in the wet and 168 µmols P $m^{-2}y^{-1}$ in
347 the dry modes. Therefore, dry deposition accounted for 44% of total TPP deposition in
348 African events, while for non-African ones dry deposition predominated (63%, Table
349 3). Overall, the major contribution to TPP deposition was from wet African weeks (37%
350 of total deposition) followed by dry African deposition (29%) and non-African dry
351 deposition (21%). Wet deposition from non-African weeks only amounted to 13% of
352 TPP deposition.

353

354 3.3 African rain samples from 1996 to 2008

355 Given the importance of African TPP deposition, we examined these inputs
356 more closely by analysing TDP and SRP for African red-rains from 1996-2008. The
357 mean annual TPP deposition in red-rains in this period (29 samples corresponding to red
358 rains between 1996 and 2008) was 217 µmols m^{-2} y^{-1}, a value that falls within the range

359 of TPP African deposition that can be calculated from the P content in the African end
360 member (0.08% Guieu et al., 2002) and the African deposition flux in the western
361 Mediterranean (5-12 kg km^2 y^{-1}), which results in 132-317 μmols P m^{-2} y^{-1}. Because
362 these measurements only refer to African wet weekly samples, we need to correct them
363 for total annual deposition. For this correction, the percent wet African to total
364 deposition for year 2002-03 (37%, Table 3) was applied to the 1996-2008 mean TPP
365 red-rain deposition, producing an estimate of 588 μmols m^{-2} y^{-1} TPP for the period
366 1996-2008, which closely compares with the wet deposition obtained for the period
367 2002-2003 (576 μmols m^{-2} y^{-1}, Table 3). For African rainfall samples, there was a good
368 correlation between TPP and TDP (r=0.65; p<0.0002) and TPP *vs.* SRP deposition
369 (r=0.88; p<0.0001). On a weekly basis, TDP accounted for 11.2 % of TPP, while SRP
370 was only 2.2% of TPP (Table 4).

371

372 4. Discussion

373 4.1 Seasonality and provenances

374 TPP in aerosols and dry deposition during 2002-2003 was well correlated with a
375 seasonal model (r=0.68 and 0.59, respectively), but wet deposition showed a more
376 irregular seasonal pattern (r=0.38). TPP wet deposition was not correlated with
377 precipitation (r= -0.021; p=0.89); rather, it was much more influenced by the sporadic
378 occurrence of African events (Fig. 5), similarly to findings of Morales-Baquero et al.,
379 (2006) in Sierra Nevada, southern Spain, and Bergametti et al., (1992) in Corsica.
380 Bergametti et al. (1992) found higher P concentrations in aerosols from North-Africa
381 than from European trajectories (0.57 nmols m^{-3} *vs.* 0.33 nmols m^{-3}). At Crete and
382 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 nmols m^{-3} and 0.6-0.7 nmols 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 nmols m^{-3} for African and 0.58 nmols 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):

$$F_d = C_a \cdot V_d \qquad \text{(equation 2)}$$

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 e 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

406 s^{-1} was obtained for all samples in 2002-2003. When accounting for air-mass
407 provenance, a significantly lower V_d of 1.07±0.13 cm s^{-1} was found for non-African
408 events (n = 45), compared to 3.1±0.80 cm s^{-1} for African weeks (n = 16; p=0.00025),
409 indicating higher settling velocities for coarser desert dust particles. Indeed, a particle
410 size mass distribution study for dust at Crete found that 85% of dissolved P was
411 associated with particle diameters between 1-10 μm and showed a similar distribution to
412 Ca, a tracer of crustal material (Markaki et al., 2003). Measurements of the grain size
413 distribution (particle diameter measured with a Coulter LS100 counter) of 4 African rain
414 samples collected at Montseny indicated a median particle diameter of 9.8 μm, which is
415 similar to that obtained for the particulate phase of 7 Saharan rains collected at Corsica
416 (median of 8 μm; Guieu et al., 2002), thus confirming large particle diameters for
417 African aerosols.

418

419 4.3 Mean aerosol and deposition values

420 TPP mean concentration in aerosols (0.74±0.035 nmols m^{-3}) was similar to
421 values in Corsica (0.33-0.63 nmols m^{-3}, Bergametti et al., 1992) and the Eastern
422 Mediterranean (0.43-0.77 nmols m^{-3} at Crete and Turkey, respectively; Markaki et al.,
423 2003), but lower than in southern France (1.65 nmols m^{-3}, in Cap Ferrat; Migon et al.,
424 2001), though this later study was only for a one-month period. The mean daily TPP
425 deposition fluxes were 4.64±1.28 μmols $m^{-2}d^{-1}$ and 0.95±0.17 μmols $m^{-2}d^{-1}$, for the wet
426 and dry modes respectively. Migon et al., (2001) estimated lower dry deposition fluxes
427 in the range of 0.15-0.7 μmols TPP $m^{-2}d^{-1}$, an estimate that was obtained from the
428 product of aerosol concentrations and V_d values from the literature (0.1-0.5 cm s^{-1}; Duce
429 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 µmols 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 8-15% 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 to 23 µmols 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 µmols 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 μmols L^{-1} P and 0.27±0.03 μmols 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 5.6-7.0, 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 μmols 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 x 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: SRP-TPP correlations 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.

503 SRP concentrations measured in this study were ~50% lower than the
504 concentrations measured by Markaki et al., (2010), but within the range obtained by
505 Herut et al., (1999) using similar methods. DOP concentrations were similarly lower,
506 only ~ 6 % as opposed to the 13–19 % measured in eastern Mediterranean (Carbo et al.,
507 2005). We hypothesize that our lower %SRP and DOP are due to the strong influence of
508 African dust, and is consistent with the solubility results reported by Ridame and Guieu
509 (2002). These differences between TDP, DOP, and SRP concentrations highlight the
510 importance of determining the P source and speciation in establishing the P pools
511 bioavailable for planktonic uptake following deposition.

512 TPP deposition values for the period 2002-2003 (for which the wet and dry
513 partitioning in background and African weekly samples were measured) were converted
514 to dissolved P fluxes using average solubility percentages for African (11.2%) and
515 background events (30-50%, from literature references). This produced wet+dry soluble
516 P fluxes of 43 μmols m^{-2} y^{-1} for African rain samples and 59-98 μmols m^{-2} y^{-1} for non-
517 African ones, and thus a total deposition of ~100-140 μmols m^{-2} y^{-1} (Table 6). When
518 splitting data into wet and dry deposition, TDP deposition was estimated as 46-60
519 μmols m^{-2} y^{-1} in the wet mode and 56-80 μmols m^{-2} y^{-1} in the dry mode (Table 6). Dry
520 deposition from background polluted air masses, with higher solubility, explain the
521 increased P contribution of the dry deposition mode. A compilation of data from the
522 literature on soluble P deposition (measured predominantly as DIP) around the
523 Mediterranean indicates that dissolved fluxes at Montseny are similar to those measured
524 at Crete, but higher than those determined at a closer coastal site in southern France
525 (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 0.13-0.18 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 Chiaverini (2002) and Morel & 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.

Conclusions

The results of this study show that dry deposition accounted for ~50% of total annual particulate phosphorus deposition which amounts to 576 μmols 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 north-eastern 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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777

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

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

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785 Table 2. Statistics for total particulate phosphorus (TPP) concentrations in aerosols
786 (total suspended particles, TSP) at La Castanya, Montseny (NE Spain) from March
787 2002 to December 2003.

788

	TSP $\mu g\ m^{-3}$	TPP in TSP (all samples) nmols m^{-3}	TPP in TSP (non-African) nmols m^{-3}	TPP in TSP (African) nmols 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

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Table 3. African, non-African, and annual total particulate phosphorus (TPP) deposition (in μmols 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 (μmols m^{-2} $week^{-1}$) for TPP, TDP, SRP and DOP at La Castanya (Montseny, NE Spain) for red-rain weekly samples from 1996-2008. DOP estimated from TDP-SRP.

	TPP	TDP	SRP*	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

*Calculated without values below detection limit[a1]

806 Table 5. Annual deposition (μmols m^{-2} y^{-1}) for TPP, and TDP or DIP from references around the
807 Mediterranean and from this study.
808

	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*		588*	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

809 * Mean TPP deposition for wet African events corrected from wet Africa percent to total annual, from
810 Table 3.
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812

Table 6. Estimation of the dissolved P inputs (μmols 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

820 Figure captions

821 Figure 1. Map of Montseny study site, NE Spain.

822 Figure 2. Aerosol total particulate phosphorus (TPP) plotted against Total Suspended
823 Particles (TSP). Regression lines for African (filled dots) and non-African (white dots)
824 are also shown. *** indicates significance of regression $p<0.001$ and ** indicates
825 $p<0.01$.

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

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

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

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

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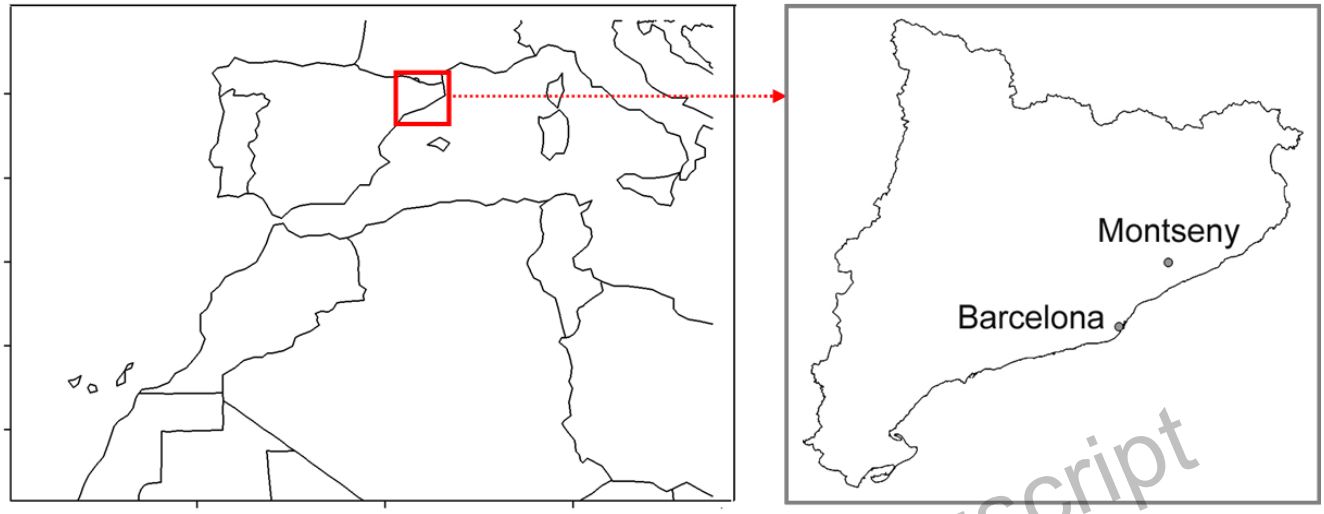
844 Fig.1



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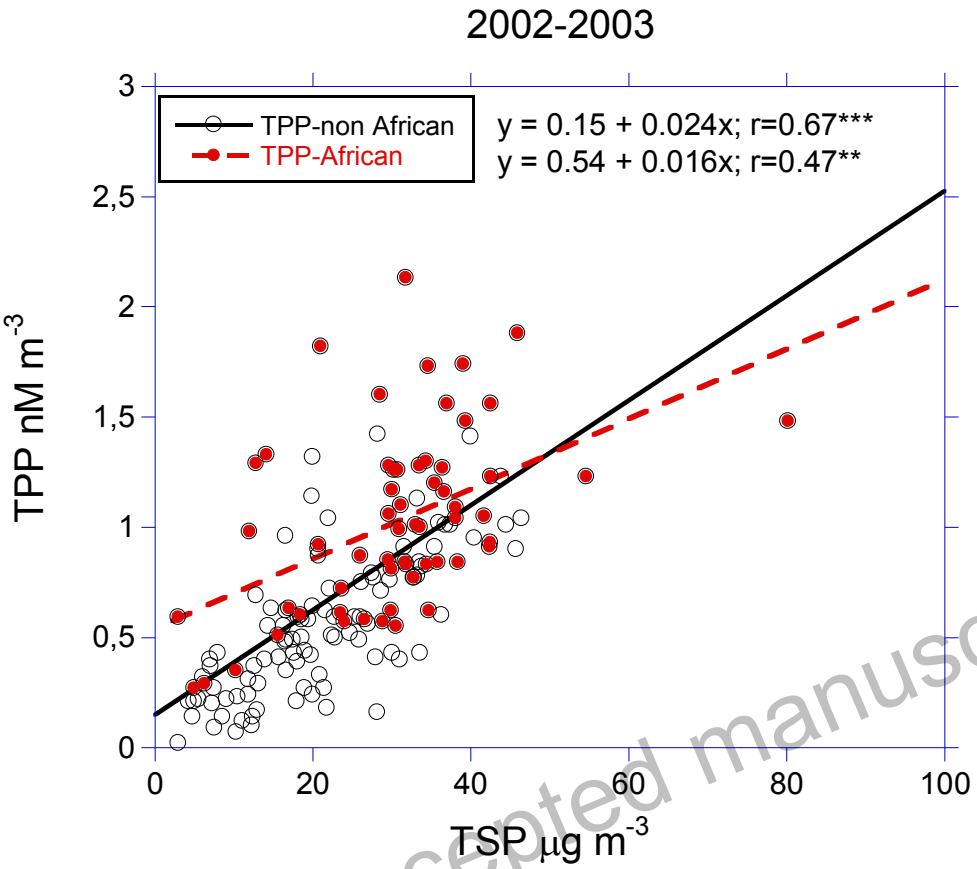
853 Fig. 2



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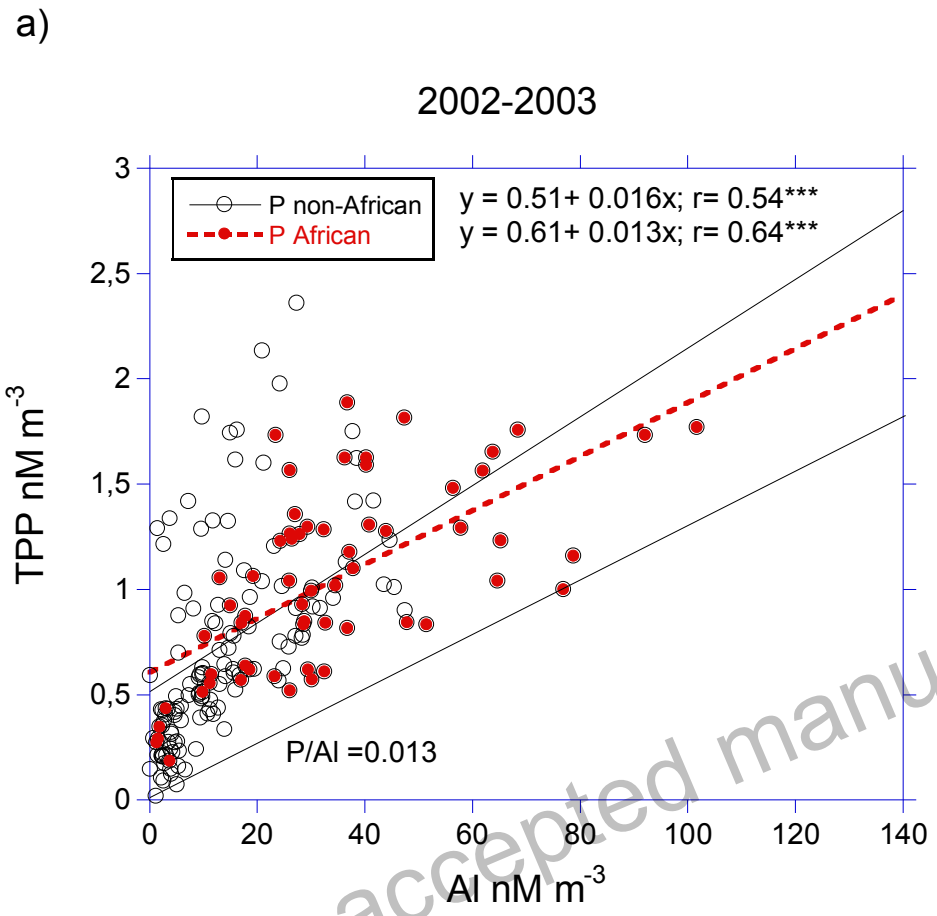
858 Fig. 3



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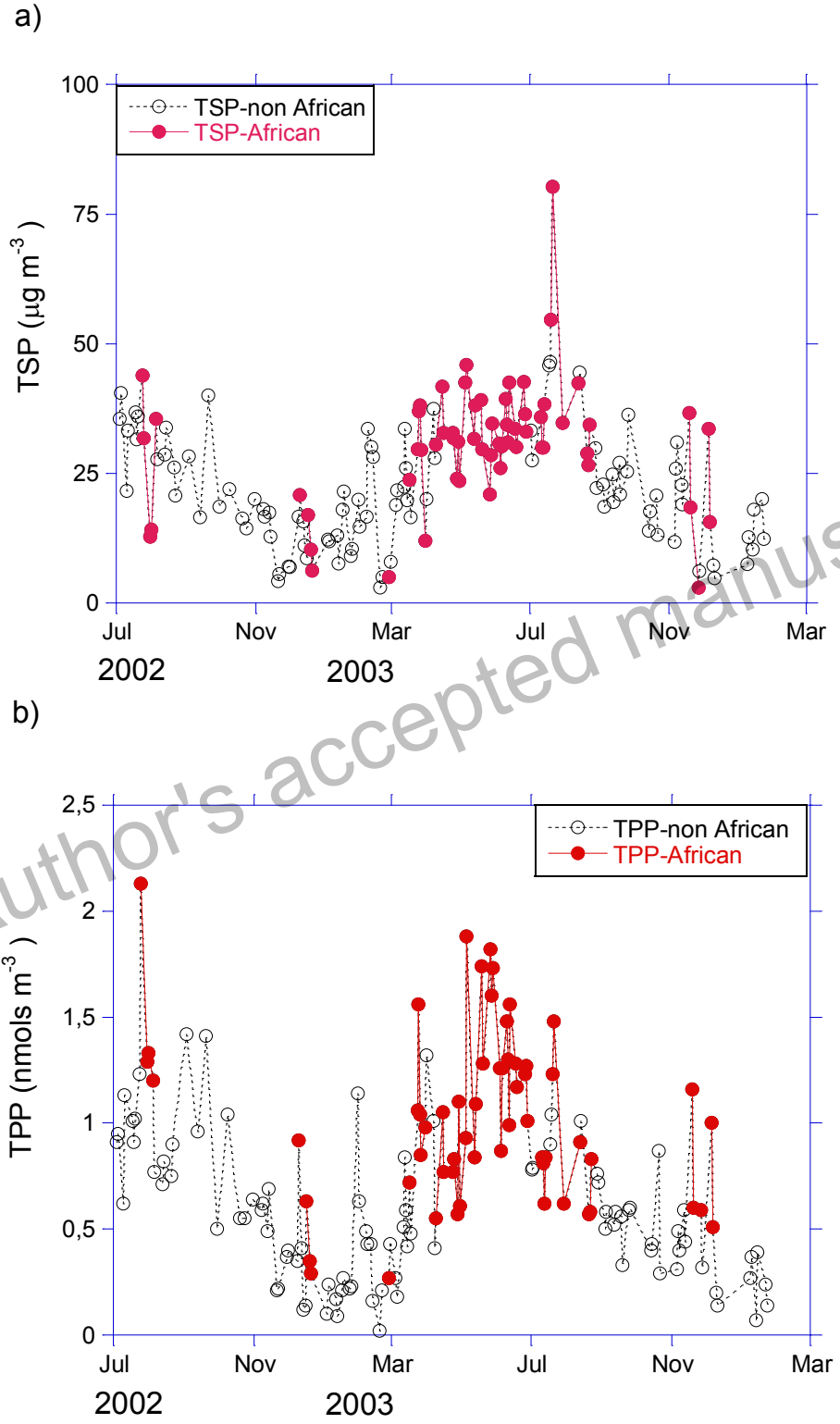
862 Fig. 4



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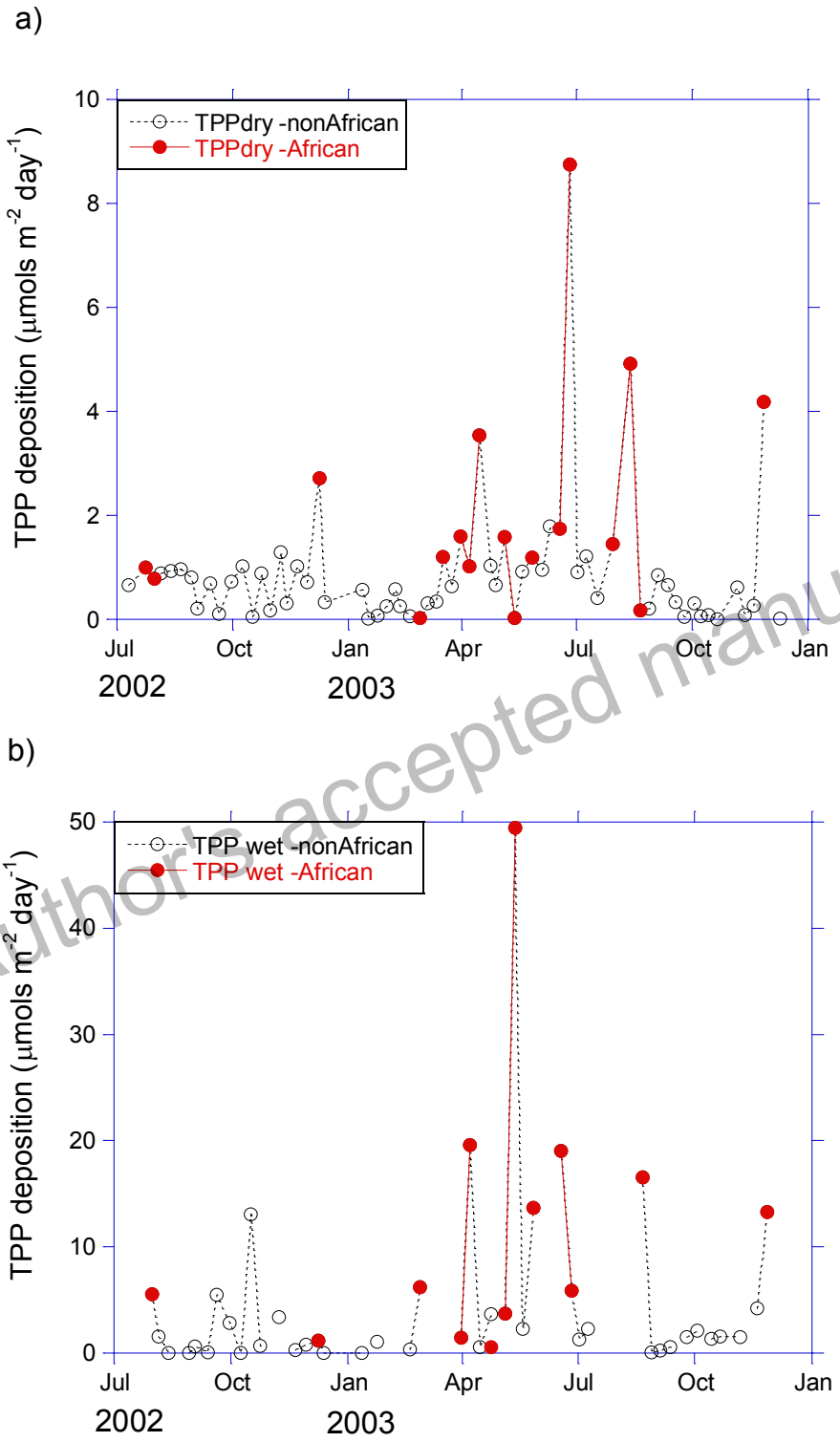
865 Fig. 5.



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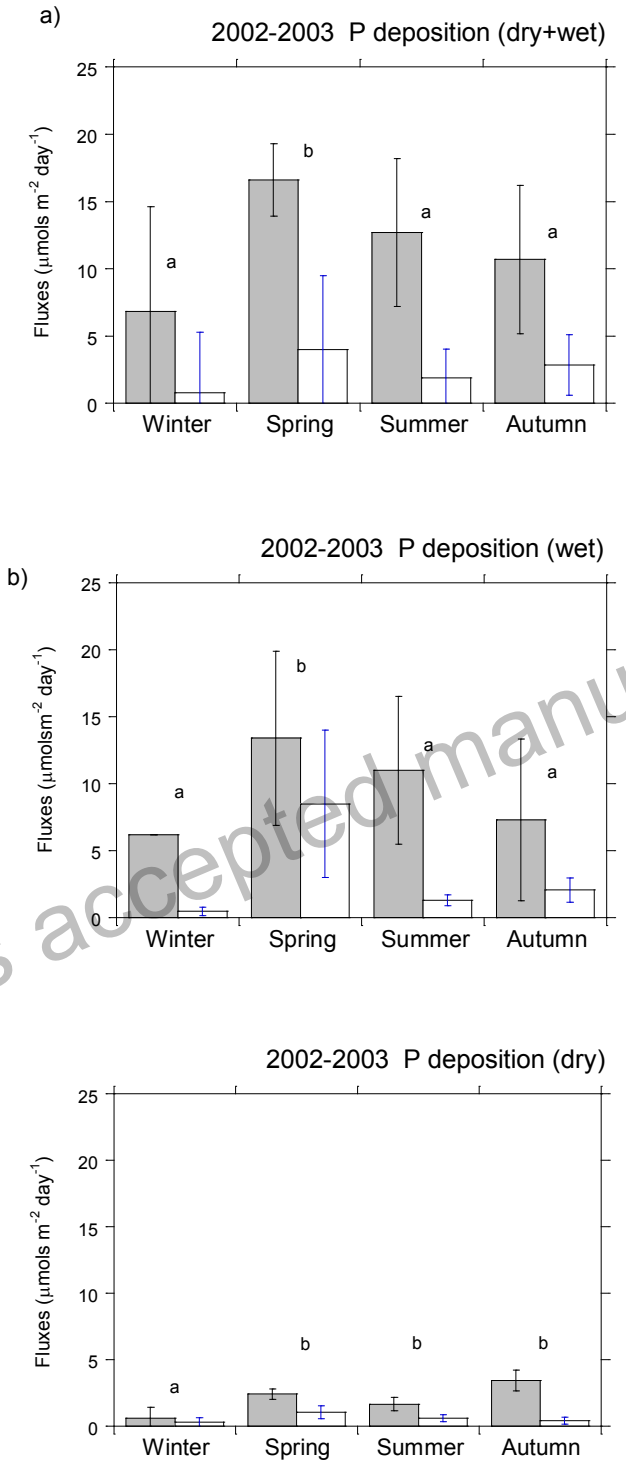
868 Fig. 6.



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