

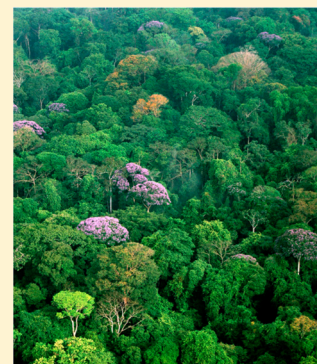
# Tracing the Sources of Atmospheric Phosphorus Deposition to a Tropical Rain Forest in Panama Using Stable Oxygen Isotopes

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**ABSTRACT:** Atmospheric dust deposition can be a significant source of phosphorus (P) in some tropical forests, so information on the origins and solubility of atmospheric P is needed to understand and predict patterns of forest productivity under future climate scenarios. We characterized atmospheric dust P across a seasonal cycle in a tropical lowland rain forest on Barro Colorado Nature Monument (BCNM), Republic of Panama. We traced P sources by combining remote sensing imagery with the first measurements of stable oxygen isotopes in soluble inorganic phosphate ( $\delta^{18}\text{O}_\text{P}$ ) in dust. In addition, we measured soluble inorganic and organic P concentrations in fine ( $<1\ \mu\text{m}$ ) and coarse ( $>1\ \mu\text{m}$ ) aerosol fractions and used this data to estimate the contribution of P inputs from dust deposition to the forest P budget. Aerosol dry mass was greater in the dry season (December to April,  $5.6\text{--}15.7\ \mu\text{g m}^{-3}$ ) than the wet season (May to November,  $3.1\text{--}7.1\ \mu\text{g m}^{-3}$ ). In contrast, soluble P concentrations in the aerosols were lower in the dry season ( $980\text{--}1880\ \mu\text{g P g}^{-1}$ ) than the wet season ( $1170\text{--}3380\ \mu\text{g P g}^{-1}$ ). The  $\delta^{18}\text{O}_\text{P}$  of dry-season aerosols resembled that of nearby forest soils ( $\sim 19.5\%$ ), suggesting a local origin. In the wet season, when the Trans-Atlantic Saharan dust belt moves north close to Panama, the  $\delta^{18}\text{O}_\text{P}$  of aerosols was considerably lower ( $\sim 15.5\%$ ), suggesting a significant contribution of long-distance dust P transport. Using satellite retrieved aerosol optical depth (AOD) and the P concentrations in aerosols we sampled in periods when Saharan dust was evident we estimate that the monthly P input from long distance dust transport during the period with highest Saharan dust deposition is  $88 \pm 31\ \text{g P ha}^{-1}\ \text{month}^{-1}$ , equivalent to between 10 and 29% of the P in monthly litter fall in nearby forests. These findings have important implications for our understanding of modern nutrient budgets and the productivity of tropical forests in the region under future climate scenarios.



## 1. INTRODUCTION

The productivity of terrestrial ecosystems often depends on aeolian inputs of nutrients such as phosphorus (P).<sup>1–3</sup> This is especially true for many tropical forests, which grow on highly weathered soils in which P availability represents a major constraint on primary productivity.<sup>4,5</sup> However, atmospheric P inputs to tropical forests remain poorly characterized for two reasons. First, long-term measurements of atmospheric aerosols in tropical forests are scarce and rarely involve P analysis. Second, P concentrations in aerosols depend on their origins, with marked variation in soluble P between regions,<sup>6,7</sup> yet an adequate technique for identifying the terrestrial sources of atmospheric aerosol P has been developed only recently.<sup>8</sup>

In tropical forests that experience a strong dry season, the origins of atmospheric P may shift seasonally between local and external sources. During the dry season, deposition can be dominated by local sources such as biomass burning, primary biogenic particles, and particles emitted from local soils.<sup>6,9</sup> During the wet season, when emissions from local sources are reduced (e.g., soils are wet, wind speeds lower, reduced biomass burning), long-range transport of aerosols might become the dominant P source. This is particularly true in tropical forests of the Americas, which are located downwind of the Saharan desert,<sup>1,3,10,11</sup> the most important source of dust on earth.

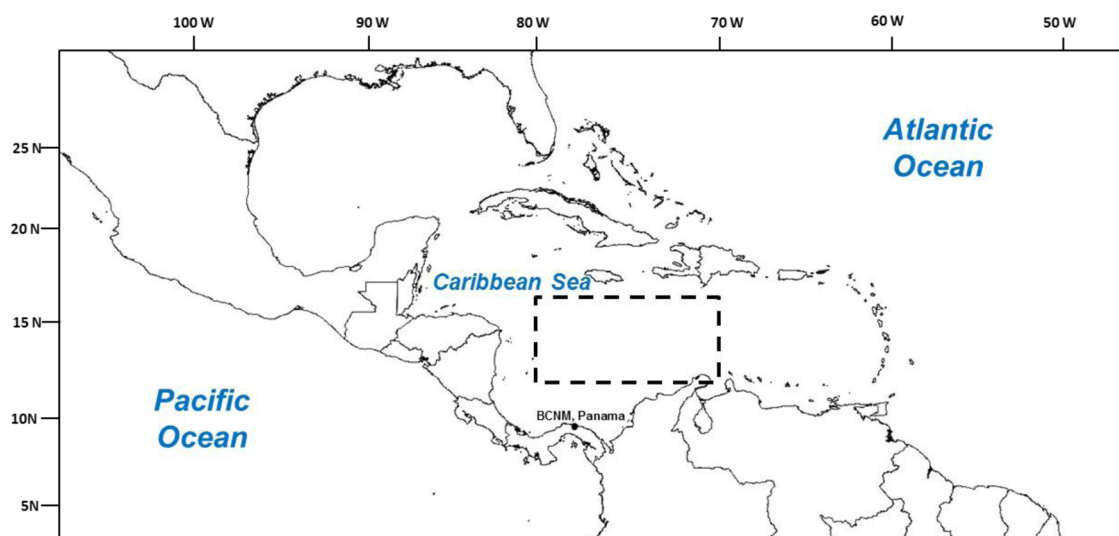
Here we present results from aerosol measurements across a seasonal cycle in lowland tropical forest on Barro Colorado Nature Monument, Republic of Panama (Figure 1). The area supports semideciduous moist tropical forest,<sup>12</sup> with a strong four month dry season between December and April.<sup>13</sup> Forest productivity in the area responds to experimental addition of P as well as other nutrients,<sup>14</sup> but there is little information on atmospheric aerosol deposition. To establish the contribution of atmospheric P inputs from long distance dust transport to the forest P budget, we first aimed to identify the origins of the aerosol P, as this has a marked effect on soluble P concentrations.<sup>6,15</sup> To do this, we took advantage of the natural variation of stable oxygen isotope ratios in phosphate (expressed as  $\delta^{18}\text{O}_\text{P}$ ). These ratios can be used to partition atmospheric P sources, because the isotopic signature of the source is preserved in the atmosphere.<sup>8,15</sup>

We hypothesized that the aerosol mass concentrations and their P sources would vary between the dry and wet seasons, as shown previously for lowland tropical forest in the Yucatan Peninsula.<sup>11</sup> We expected that local P sources would dominate

Received: October 8, 2015

Revised: December 14, 2015

Accepted: December 28, 2015



**Figure 1.** Location map of the western Caribbean sea and Central America, showing the sampling station at BCNM, Panama (black dot). Spatial extent of MODIS AOD products used to estimate dust transport is indicated with the dashed box.

in the dry season, when dust is mobilized from the local dry soils by strong trade winds.<sup>13</sup> In the wet season, when the Trans-Atlantic Saharan dust belt moves north just over Panama,<sup>16</sup> we expected that external sources such as long-range dust transport would dominate. To address this, we collected a total of 114 filters of dry aerosol particles, with six size fractions, and measured aerosol mass concentrations and their soluble P content and  $\delta^{18}\text{O}_p$  values. We focused on soluble inorganic and organic P in the aerosols, since these are likely to be relatively bioavailable following deposition. Based on these data, we estimated the relative contribution of local and long-range dust to the forest P budget.

## 2. MATERIALS AND METHODS

**2.1. Study Site.** The study was performed in semideciduous rain forest, on Barro Colorado Nature Monument (BCNM), Republic of Panama (9.063°N; 79.50°W, Figure 1). The tropical monsoon (Köppen system) climate has a mean annual temperature of 27 °C and mean annual rainfall of 2600 mm.<sup>13</sup> Approximately 90% of annual rainfall occurs in the wet season between May and December.<sup>8</sup> The rainfall, wind direction and wind speed at BCNM differ markedly between wet and dry seasons.<sup>17</sup> In the wet season Panama is affected by easterly winds, whereas northerly winds prevail in the dry season. Nearby soils are characterized by extremely low readily available phosphate concentrations ( $<1 \text{ mg P kg}^{-1}$ ; determined by extraction with anion-exchange membranes),<sup>18</sup> which are broadly representative of forest soils in central Panama.

**2.2. Aerosols Sampling.** A total of 19 complete cascade impactor sets (that separated the sampled particles according to their size) were sampled continuously from September 2012 to August 2013 (Table 1), on the roof of the field research station in BCNM, resulting in a total of 114 aerosols samples. The particles were collected on quartz fiber filters (QM-A, Whatman, Pittsburgh, PA), placed on a high volume air sampler (Tisch Environmental, OH) operating with a volumetric flow rate of  $1.13 \text{ m}^3 \text{ minute}^{-1}$  and equipped with five stage cascade impactor cutoff device. The cutoff device separated the sampled particles into five size fractions (0.5–1.1  $\mu\text{m}$ , 1.1–1.7  $\mu\text{m}$ , 1.7–3.4  $\mu\text{m}$ , 3.4–8  $\mu\text{m}$ ,  $> 8 \mu\text{m}$ ) and an additional backup filter that collected particles smaller than 0.5

$\mu\text{m}$ . The particles were divided to fine and coarse fractions: the fine fraction was defined as particles  $<1.11 \mu\text{m}$  and the coarse fraction were defined as particles  $>1.11 \mu\text{m}$ . The air sampler was positioned  $\sim 5 \text{ m}$  above the ground to decrease the contribution of particles from close proximity to the sampling station. Before sampling, the filters were preheated at 40 °C and then weighed. The filters were replaced every 10–30 sampling days, based on the particle load on the filters. After sampling, the filters were dried again at 40 °C to minimize biological activity, reweighed and temporarily stored in sealed plastic bags at 4 °C until analysis. The combination of drying and low temperature minimize potential changes in the isotopic composition of the aerosol P through biological activity during storage.<sup>8,19</sup>

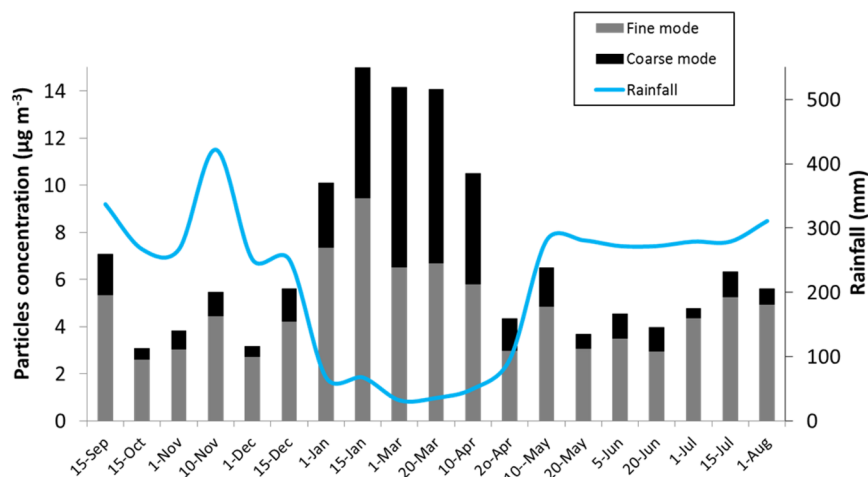
**2.3. Aerosol P Determination.** We measured soluble inorganic P and soluble organic P in the aerosol mass fractions of all the 19 filter groups (a total of 114 filters). Subsamples of 6.7% of filter area were cut from each filter for P determination. The measurements were performed on duplicates from the same filter. For the determination of soluble inorganic P, filters were shaken for 16 h on an orbital shaker with 45 mL of double deionized water (DDW). Phosphorus concentrations in the solution were determined colorimetrically<sup>20</sup> on a subsample of the extracting solutions in duplicates. For soluble organic P determination, the filters were shaken in sealed quartz test tubes under UV irradiation (18 UV-C lamps, 30W each) for 16 h with 40 mL of DDW and 5 mL of phosphate-free  $\text{H}_2\text{O}_2$  following the method of Zamora et al.<sup>21</sup> This procedure hydrolyses soluble organic P compounds and therefore approximates the total soluble P in the sample. The total soluble P was determined colorimetrically as described above. Soluble organic P was calculated as the difference between total soluble P and soluble inorganic P. Blank values from unused filters were subtracted from measured values. For filters with low aerosol dry mass, P concentrations were close to blank values, so we report values only for filters that contained at least 10 mg of dust. The concentrations of total, inorganic and organic soluble P were measured for both the fine ( $<1.11 \mu\text{m}$ ) and coarse ( $>1.11 \mu\text{m}$ ) fractions.

**2.4.  $\delta^{18}\text{O}_p$  Determinations.** To obtain sufficient particulate matter for the determination of the aerosol P  $\delta^{18}\text{O}_p$  values,<sup>22</sup>

**Table 1. Aerosols Mass Concentrations and Their Soluble Organic and Inorganic P Concentrations of 19 Cascade Impactor Sets That Were Collected Continuously During September 2012 to September 2013**

rain (mm)	group	sampling period	coarse fraction mass <sup>a</sup> (mg)	fine fraction mass <sup>a</sup> (mg)	TSP <sup>a</sup> (mg)	coarse fraction conc in air <sup>b</sup> ( $\mu\text{g m}^{-3}$ )	fine fraction conc in air <sup>b</sup> ( $\mu\text{g m}^{-3}$ )	total soluble-P conc in air <sup>b</sup> ( $\text{ng m}^{-3}$ )	soluble inorganic-P conc in coarse fraction ( $\mu\text{g P g}^{-1}$ )	soluble inorganic-P conc in fine fraction ( $\mu\text{g P g}^{-1}$ )	soluble organic-P conc in coarse fraction ( $\mu\text{g P g}^{-1}$ )	soluble organic-P conc in fine fraction ( $\mu\text{g P g}^{-1}$ )
340	1	15/9/12	29.5	91.4	120.9	1.7	5.3	12.4	708 ± 15	2096 ± 580	84 ± 44	ND
270	2	15/10/12	11.5	67.3	78.8	0.4	2.6	6.4	ND	2458 ± 650	64 ± 5	ND
270	3	1/11/12	26.5	103.9	130.2	0.8	3.0	10.7	895 ± 211	3305 ± 380	100 ± 30	ND
420	4	10/11/12	19.7	86.3	106.0	1.0	4.4	8.1	ND	1833 ± 260	81 ± 4	98 ± 60
250	5	1/12/12	16.7	105.6	122.3	0.4	2.7	6.8	ND	2511 ± 630	102 ± 7	ND
250	6	15/12/12	50.6	156.6	207.2	1.4	4.2	9.8	1361 ± 260	1877 ± 100	151 ± 57	ND
70	7	1/1/13	99.9	270.5	370.4	2.7	7.4	9.5	829 ± 276	979 ± 240	260 ± 110	ND
70	8	15/1/13	69.2	104.5	173.7	6.3	9.5	13.0	506 ± 310	1043 ± 240	89 ± 51	161 ± 110
32	9	1/3/13	249.1	212.7	461.8	7.6	6.5	9.1	669 ± 420	610 ± 480	199 ± 125	453 ± 200
36	10	20/3/13	327.6	299.2	626.8	7.3	6.7	7.6	530 ± 320	547 ± 210	285 ± 150	619 ± 320
50	11	10/4/13	166.3	206.0	372.3	4.7	5.8	9.1	888 ± 480	852 ± 320	196 ± 95	363 ± 115
95	12	20/4/13	37.8	82.6	120.4	1.4	3.0	8.7	1640 ± 520	2158 ± 430	ND	112 ± 4
280	13	10/5/13	61.7	182.1	243.8	1.6	4.8	10.9	1637 ± 400	1703 ± 50	176 ± 22	233 ± 120
280	14	20/5/13	21.6	109.8	131.4	0.6	3.1	5.9	999 ± 350	1745 ± 580	ND	125 ± 64
270	15	5/6/13	37.3	126.1	163.4	1.0	3.5	14.5	865 ± 350	3878 ± 1100	122 ± 64	ND
270	16	20/6/13	41.6	120.0	161.6	1.0	2.9	6.0	2510 ± 800	1174 ± 400	ND	ND
280	17	1/7/13	15.1	165.0	180.1	0.4	4.4	9.7	1160 ± 150	2122 ± 280	ND	170 ± 80
280	18	15/7/13	36.8	178.4	215.2	1.1	5.2	12.3	1218 ± 240	2101 ± 310	172 ± 72	ND
310	19	1/8/13	20.8	158.1	178.9	0.7	4.9	10.8	ND	2184 ± 390	153 ± 8	ND

<sup>a</sup>Analytical standard error of <3%. <sup>b</sup>Analytical standard error of <1%.



**Figure 2.** Aerosol mass concentrations of the fine (gray) and coarse (black) fractions observed at the sampling station at BCNM, Panama, operated continuously from September 2012 to September 2013. Rainfall during the study period (mm) is given in light blue line.

several filter groups were pooled together to create six date-range groups. Due to the limited amount of coarse material, isotopic determinations were performed only on the fine size fraction. Currently, reliable  $\delta^{18}\text{O}_p$  measurements can be performed only on inorganic P fractions (in soils or aerosols).<sup>15</sup> Most of the soluble P in our samples was inorganic, with only minor contribution of organic P (see results). To measure  $\delta^{18}\text{O}_p$  of soluble inorganic P, phosphate was extracted by shaking filters with 5 L of DDW for 24 h with anion exchange resin membranes.<sup>8</sup> The extracted phosphate (resin P) was then precipitated as cerium phosphate to remove other oxygen containing compounds, and then precipitated as silver phosphate. All isotopic values are given in the delta-notation versus Vienna standard mean ocean water (VSMOW). The standard deviation of three replicate analyses of the same sample was between 0.9 and 1.2‰.

**2.5. Satellite Retrieval of Carbon Monoxide (CO) Concentrations.** Carbon monoxide (CO) concentrations (in ppbv) in the troposphere, which are indicative of anthropogenic activity and biomass burning, were retrieved from the Measurements of Pollution in the Troposphere (MOPITT) sensor on board the Terra polar orbiting satellite. The retrieval method is described in Deeter et al.<sup>14</sup> We used level 3-monthly mean CO surface concentrations that are available at 1° horizontal resolution. The CO concentrations for each month were averaged over an area of about 300 × 300 km (i.e., 9 pixels) around the location of the site. Only the daytime retrievals were considered because sensitivity is generally greater than the sensitivity for the night time retrievals.

**2.6. Isotopic Mass Balance Calculations.** The percent contribution of Saharan dust-P in the wet season can be calculated using a simple two source isotopic mass balance:

$$P_{\text{Sahara}} = \frac{\delta^{18}\text{O}_{\text{Pmeasured}} - \delta^{18}\text{O}_{\text{Plocal}}}{\delta^{18}\text{O}_{\text{Psaahara}} - \delta^{18}\text{O}_{\text{Plocal}}} \quad (1)$$

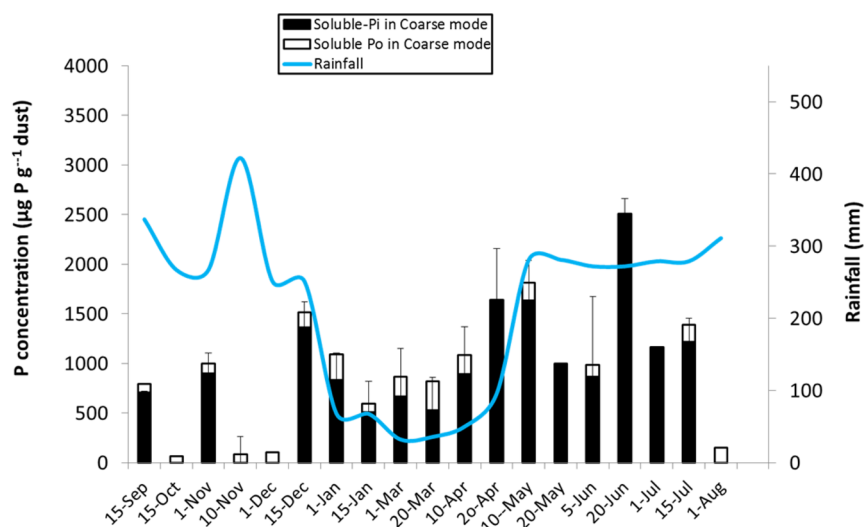
where  $\delta^{18}\text{O}_{\text{Pmeasured}}$  is the measured  $\delta^{18}\text{O}_p$  value in the atmospheric aerosols in our study,  $\delta^{18}\text{O}_{\text{Plocal}}$  is the  $\delta^{18}\text{O}_p$  value of local sources (19.5‰)<sup>24</sup> and  $\delta^{18}\text{O}_{\text{Psaahara}}$  is the average  $\delta^{18}\text{O}_p$  value of Saharan dust-P (14‰).<sup>15</sup>

**2.7. Dust-P Inputs.** To estimate P deposition based on satellite retrieved AOD products we adopted the method of Das et al. (2013).<sup>11</sup> The Dust Mass Path (DMP) was calculated

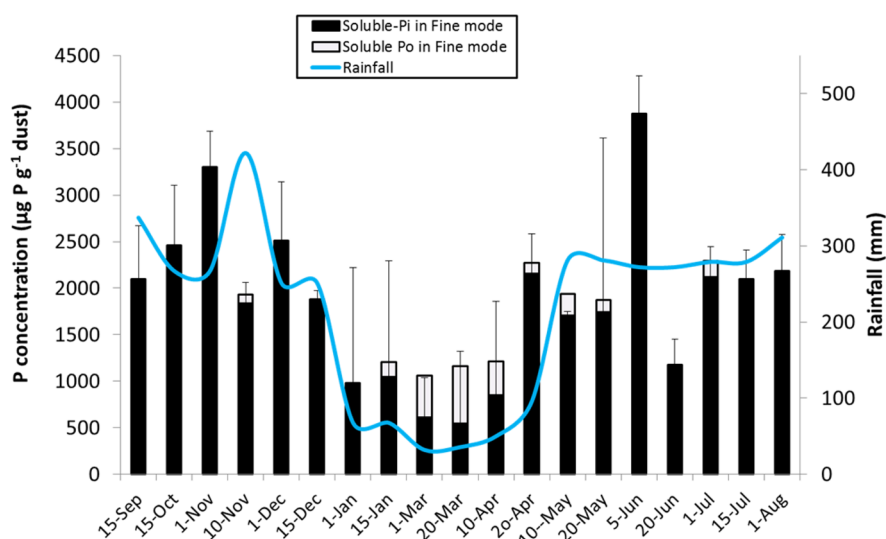
and its divergence over a specific area was converted to monthly cumulative dust deposition. We used AOD and fine mode AOD from collection 6 level 3 MODIS data together with wind speed data from ECMWF (European Centre for Medium-Range Weather Forecasts) reanalysis, both with spatial resolution of 1 × 1 degree. The monthly averaged dust deposition rates were estimated by calculating the zonal flux divergence of the DMP, assuming that decreasing flux in the westward direction is due to deposition to the surface. We considered only the divergence in the zonal direction because meridional wind is minor in this area, especially between May and August when African dust transport to the region occurs. Ideally, this calculation would be performed directly over Panama, but this was not possible because fine mode fraction AOD is not available over land in the most updated MODIS level 3 collection 6 data set. Therefore, dust deposition amounts were calculated over the Caribbean sea, northeast of Panama, over an area between 70 and 80°W and 12–17°N (Figure 1), assuming that deposition in this area is indicative of deposition over Panama. During most of the months that were analyzed we noticed spots of higher AOD values in the Caribbean Sea that caused noise to the DMP estimations. June was the month in which the dust belt was the most pronounced, ranging from Africa to Central America, implying a significant and continuous transport of Saharan dust to the area of Panama. This strong gradient of AOD in June, assumed to be caused by the transport of Saharan dust, allowed us to capture the signal of the dust and estimate the amount of deposition. In addition, our isotopic and chemical analyses indicated that the particles collected during June-July contained the largest proportion of P originating from remote sources. Therefore, the most reliable estimation of the monthly P inputs from dust in the course of this study was calculated by multiplying the dust deposition amounts with the dust P concentration measured during June.

## RESULTS

**3.1. Atmospheric Aerosols Mass Concentrations.** The aerosol mass concentrations changed seasonally and were significantly greater in the dry season in both the fine and coarse particles sizes (Table 1 and Figure 2,  $p < 0.05$ ). The mass concentration of the coarse fraction ranged from 2.7 to 7.6  $\mu\text{g m}^{-3}$  in the dry season and from 0.4 to 1.7  $\mu\text{g m}^{-3}$  in the



**Figure 3.** Soluble inorganic and organic P concentrations (black and white, respectively) in the coarse fraction of aerosols collected on BCNM, Panama, between September 2012 and September 2013. The rainfall during the study period (mm) is given in light blue line. Error bars are standard deviations of duplicate samples.



**Figure 4.** Soluble inorganic and organic P concentrations (black and white, respectively) in the fine fraction of aerosols collected on BCNM, Panama, between September 2012 and September 2013. The rainfall during the study period (mm) is given in light blue line. Error bars are standard deviations of duplicate samples.

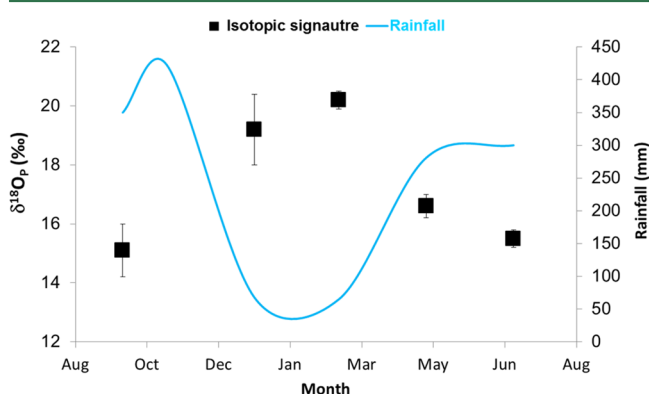
wet season. The mass concentration of the fine fraction were generally greater, ranging from 4.2 to 9.5  $\mu\text{g m}^{-3}$  in the dry season and from 2.6 to 5.3  $\mu\text{g m}^{-3}$  in the wet season. The total suspended particle concentration (TSP) ranged from 5.6 to 15.7  $\mu\text{g m}^{-3}$  in the dry season, peaking in January 2013, and from 3.1 to 7.1  $\mu\text{g m}^{-3}$  in the wet season, being lowest in September 2012.

**3.2. Aerosol Soluble P Concentration.** **3.2.1. Aerosol Soluble P Concentration in the Coarse Fraction.** Total soluble P concentrations in the coarse fraction ranged between 790 and 2510  $\mu\text{g P g}^{-1}$  particles (Table 1 and Figure 3). The soluble inorganic P concentrations ranged between 708 and 2510  $\mu\text{g P g}^{-1}$  particles and the soluble organic P concentrations ranged from undetectable to 285  $\mu\text{g P g}^{-1}$  particles, indicating that most of the soluble P was inorganic. Organic P concentrations ranged from undetectable to  $285 \pm 150 \mu\text{g P g}^{-1}$  particles in the dry season and from undetectable to  $176 \pm 22 \mu\text{g P g}^{-1}$  particles in the wet season (Figure 3).

**3.2.2. Aerosol Soluble P Concentration in the Fine Fraction.** Soluble P concentrations in the fine fraction were generally greater than in the coarse fraction. The total soluble P concentrations in the fine fraction varied seasonally, being significantly greater in the wet season ( $p < 0.05$ ). A much weaker seasonal effect was apparent for the coarse particles because total soluble P concentrations did not change significantly between the dry and wet season. Total soluble P concentrations ranged between 1174 and 3378  $\mu\text{g P g}^{-1}$  particles in the wet season (with a peak in June 2013) and between 979 and 1877  $\mu\text{g P g}^{-1}$  particles in the dry season, being lowest in January 2013 (Table 1 and Figure 4). As for the coarse fraction, most of the soluble P in the fine fraction was inorganic with concentrations that ranged between 1174 and 3378  $\mu\text{g P g}^{-1}$  particles. The soluble organic P concentrations ranged from undetectable to  $233 \pm 120 \mu\text{g P g}^{-1}$  particles in the wet season and from undetectable to  $619 \pm 320 \mu\text{g P g}^{-1}$

particles in the dry season, although these differences were not statistically significant (Figure 4).

**3.3. Aerosol Soluble P  $\delta^{18}\text{O}_\text{P}$  Values.** The  $\delta^{18}\text{O}_\text{P}$  values of soluble inorganic P varied seasonally ( $p < 0.05$ ). Values ranged between  $19.2 \pm 1.2$  and  $20.2 \pm 0.3$  ‰ in the dry season and between  $15.1 \pm 0.9$  and  $16.6 \pm 0.4$  ‰ in the wet season (Figure 5).



**Figure 5.**  $\delta^{18}\text{O}_\text{P}$  (in ‰ vs SMOW) of soluble inorganic P in the fine fraction of aerosols collected on BCNM, Panama, between September 2012 and September 2013. The dashed line is the resin-P  $\delta^{18}\text{O}_\text{P}$  value of the local soils in BCNM.<sup>24</sup> The rainfall during the study period (mm) is given in light blue line. Error bars indicates standard deviations of three replicates of the same sample.

**3.4. Isotopic Mass Balance Calculation.** We use eq 1 to calculate the relative contribution of P from long distance dust transport during our study period, adopting the  $\delta^{18}\text{O}_\text{P}$  values we measured during our study period (ranging from 15.1–16.6‰ in the wet season and from 19.2–20.2‰ in the dry season). Our calculation shows that Saharan dust contributes between 53 and 80% of the atmospheric P in Panama in the wet season (with peaks during June–July and September–October which are positively correlated with the peaks in the aerosols soluble P concentrations (Figure 4)) but makes no significant contribution in the dry season.

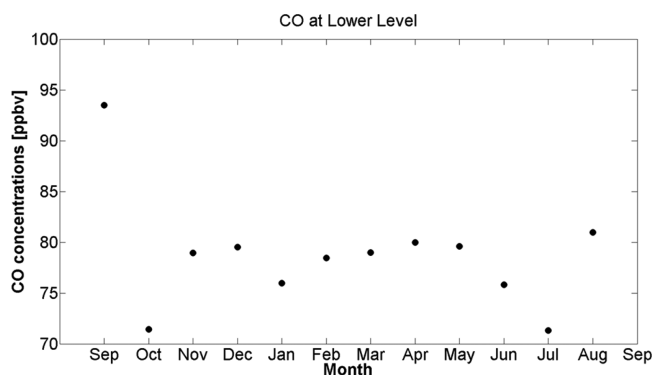
**3.5. Dust P Inputs.** To estimate the monthly P inputs from the deposition of long distance dust transport we multiplied the monthly cumulative dust deposition amounts during June (when the contribution of Saharan dust was maximal) with the soluble P concentrations in dust we measured in the aerosols sampled during June ( $2440 \mu\text{g P}^{1-} \text{g}^{-1}$  dry weight). Our calculation shows that the monthly P inputs from the deposition of long distance dust transport when the Saharan dust flux to Panama peaks is  $88 \pm 31 \text{ g P ha}^{-1} \text{ month}^{-1}$ . The overall uncertainty of the deposition estimation is reported to be 35%, based on the combined uncertainties in dust column concentrations and wind speed.<sup>25</sup> This P influx accounts for between 9.6–28.5% of monthly P inputs from litter at a nearby site ( $3700\text{--}11\,000 \text{ g ha}^{-1} \text{ yr}^{-1}$ ).<sup>14</sup>

**3.6. Phosphorus Concentration in Air.** The total soluble P concentration in aerosols per unit volume of air, which is defined as the aerosol mass concentration multiplied by the aerosol P concentration, ranged between  $6.5$  and  $27.3 \text{ ng P m}^{-3}$  (Table 1 and Figure 8). The greatest concentrations occurred in March 2013 (dry season) and the lowest in October 2012 (wet season). The total soluble P concentration was mainly associated with the fine aerosol fraction, which contributed between  $3.5$  and  $13.6 \text{ ng P m}^{-3}$  in the wet season and between

$7.9$  and  $11.4 \text{ ng P m}^{-3}$  in the dry season. The coarse fraction contributed up to  $3.1 \text{ ng P m}^{-3}$  in the wet season and up to  $6.0 \text{ ng P m}^{-3}$  in the dry season. Overall, the concentrations were slightly higher in the dry season, but did not show any statistically significant seasonal differences.

## 4. DISCUSSION

The total aerosol dry mass concentrations in our study (ranging from  $5.6$  to  $15.7 \mu\text{g m}^{-3}$  in the dry season and  $3.1$  to  $7.1 \mu\text{g m}^{-3}$



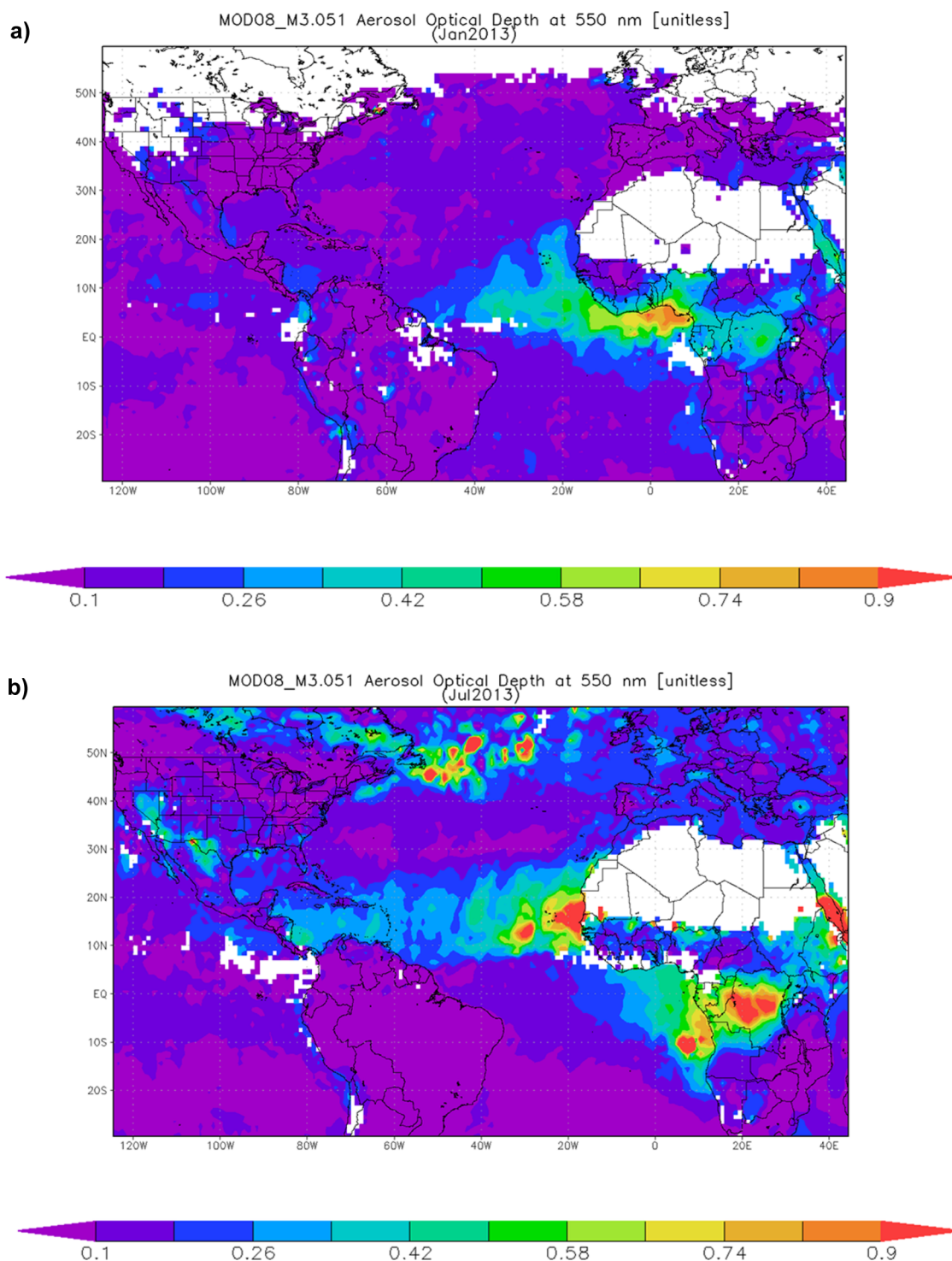
**Figure 6.** Monthly mean surface concentrations of tropospheric carbon monoxide (CO, ppbv), which are indicative for anthropogenic activities such as biomass burning. The concentrations were retrieved from the Measurements of Pollution in the Troposphere (MOPITT) sensor on board the Terra polar orbiting satellite.

in the wet season, Table 1 and Figure 2) are typical natural background aerosol concentrations in tropical forests.<sup>26</sup> As hypothesized, the aerosol mass concentration varied seasonally, being significantly higher in the dry season when wind speed was higher<sup>13,17</sup> and the soils are dry.

**4.1. Dry Season.** The coarse to fine fraction ratio was greater in the dry season, in agreement with previous reports for the Amazon.<sup>27</sup> This is expected, since coarse particles originate mainly from local sources within the forest,<sup>26</sup> and dry soils are more susceptible to wind erosion than moist soils. Even though the mass concentration of the coarse fraction varied seasonally, the seasonal effect on the soluble P concentrations of these particles was less pronounced than for the fine particles (Figure 3). This suggests that the origin of the soluble P in coarse particles does not depend on the seasonal climate in Panama. In contrast, the strong seasonal pattern in soluble P concentrations in the fine fraction was correlated with seasonal changes in the  $\delta^{18}\text{O}_\text{P}$  values suggesting that the P sources of the fine fraction varied between the dry and wet seasons (Figure 4). In the dry season, the  $\delta^{18}\text{O}_\text{P}$  values in fine particles ( $19.2\text{--}20.2\%$ , Figure 5) are similar to the resin P  $\delta^{18}\text{O}_\text{P}$  values of soils near BCNM,<sup>24</sup> which points to the dominance of dust P from local soils in the dry season.

The bulk of the soluble P in dust was in inorganic form in both the coarse and fine fractions during the entire study period (Figures 3 and 4). These results suggest that the contribution of P derived from biogenic particles (including pollen, spores, bacteria, fungi, and fragments of leaves, which contain P in predominantly organic form<sup>27</sup>), was generally low during the entire study period.

Since biomass burning is a major source of atmospheric aerosol particles in tropical forests in the dry season<sup>26</sup> we examined its contribution during our study period and discovered that the aerosol mass concentrations in our study

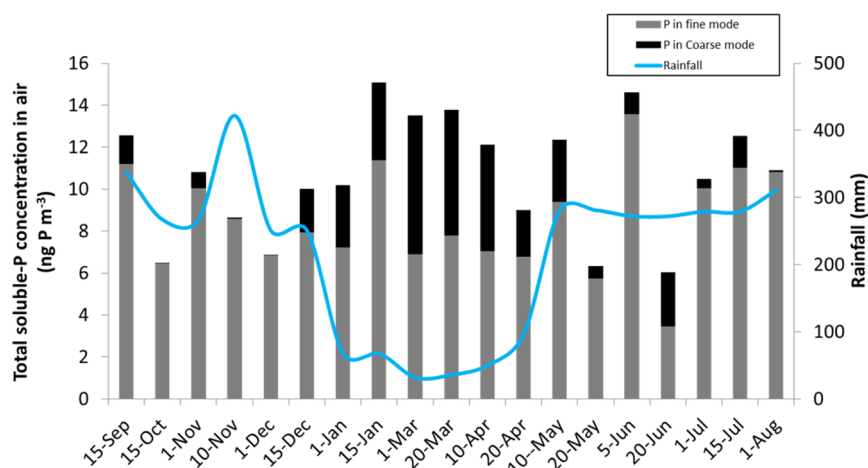


**Figure 7.** Monthly average total Aerosols Optical Depth (AOD) at 550 nm in January (a) and July (b) 2013. The sampling station in BCNM is shown in red circle. Data was derived from MODIS TERRA satellite through Giovanni web interface.

are significantly lower than the typical values under the influence of biomass burning (which can approach  $300\text{--}600\ \mu\text{g m}^{-3}$ ,<sup>27</sup>  $\sim 85\ \mu\text{g m}^{-3}$  on average<sup>28</sup>), indicating that no large fires occurred in proximity to our sampling station. In addition, the monthly mean surface CO concentrations, which are indicative to emissions of anthropogenic particles from biomass burning, showed no seasonal pattern and were not higher in the dry season, even though fires are more likely to occur in this period of the year (Figure 6). Thus, it is fair to assume that the

influence of particles derived from biomass burning is not a major P source in our study. However, we cannot rule out completely that particles derived from biomass burning made some contribution to the total aerosol mass we sampled in the dry season.

**4.2. Wet Season.** In the wet season, the fine to coarse fraction ratio was much higher than in the dry season (Figure 2), probably reflecting lower emissions of coarse particles from local soils due to the high rainfall that occurs on the wet season.



**Figure 8.** Total soluble P concentrations in air ( $\text{ng m}^{-3}$ ) in fine (gray) and coarse (black) fractions that were measured on BCNM, Panama, between September 2012 and September 2013. The rainfall during the study period (mm) is given in light blue line.

Since fine particles travel long distances, the increase in the fine fraction in the wet season is an additional indication of the contribution of long-range dust transport during the wet season.<sup>11,21</sup> This is supported by the decrease in the  $\delta^{18}\text{O}_\text{P}$  values of atmospheric P during the wet season (15.1–16.6‰, Figure 5), which suggests a mixing between local P (~19.5‰) and external sources with lower  $\delta^{18}\text{O}_\text{P}$  values. The influence of long-range Saharan dust transport is particularly important in the wet season, since Panama is located within the Trans-Atlantic Saharan dust transport pathway (Figure 7a and b). Thus, the decrease in  $\delta^{18}\text{O}_\text{P}$  in the wet season may reflect inputs of Saharan dust, which can contain extremely high soluble P concentrations (up to  $2300 \mu\text{g P g}^{-1}$ ) with relatively low resin P  $\delta^{18}\text{O}_\text{P}$  values (as low as 6.5‰)<sup>15</sup> with an average annual value of ~14‰.<sup>15</sup>

The high P solubility<sup>6</sup> and low  $\delta^{18}\text{O}_\text{P}$  values<sup>28</sup> we measured in aerosols collected in the wet season could also be attributed to volcanic ash delivered from the numerous active volcanoes in the Caribbean region. However, there were no eruptions during or before our study period. The combination of (1) higher ratio of fine to coarse fraction found in the wet season (Figure 2), (2) increased soluble inorganic P concentrations with lower portion of organic P (which is typical to desert soils, Figure 4) and (3) relatively low  $\delta^{18}\text{O}_\text{P}$  values (Figure 5) provide evidence for the presence of Saharan dust P at BCNM in the wet season. Nonetheless, further geochemical, mineralogical and isotopic characterization of major and rare earth elements is required to confirm this.

Soluble P concentrations in the fine fraction at BCNM during the wet season were even greater than in Saharan dust collected over the Eastern Atlantic Ocean<sup>7</sup> (up to  $3378 \mu\text{g P g}^{-1}$  dry weight in June). As primary mineral phosphate is acid-soluble<sup>29</sup> it seems likely that acidification in the atmosphere enhances dust P solubility during its transport across the Atlantic.<sup>15,30,31</sup>

Overall, our observations from the wet season provide additional evidence for the presence of Saharan dust P over tropical forests in the Americas, as suggested in previous studies conducted in the Yucatan Peninsula<sup>9,11</sup> and the Amazon basin.<sup>3,32</sup> Estimation of the contribution of P inputs from long-distance dust transported to the forest P budget requires reliable data on the amount of dust deposited onto the forest and its P concentrations. Recent advances in remote sensing

imaging greatly improved our ability to quantify the amounts of Saharan dust deposition in tropical forest.<sup>11,33</sup> However, because our current knowledge on the dust P sources to the tropics is lacking, and since the P content in aerosol depends on the P content in the aerosol source, there is no reliable data on the actual P concentrations in dust particles over tropical forests. Modeling studies that aimed to quantify the contribution of dust P inputs to tropical forests<sup>1,6,11,33</sup> used dust P concentrations in the range of 720–880 ppm in their global simulations, but acknowledged that there might be significant variability in this value. Here we found that the average soluble inorganic P concentration in fine dust particles arriving by long distances transport from locations such as the Sahara is  $2440 \mu\text{g P g}^{-1}$  dry weight (taking the P concentration we measured in June when the isotopic mass balance calculation shows the Saharan contribution was highest and only the inorganic P fraction, as dust inputs are assumed to contain mainly inorganic P), which is ~3 times higher than the average P concentrations adopted in previous studies.

The monthly dust P inputs we calculate for the wet season in this study ( $88 \pm 31 \text{ g P ha}^{-1} \text{ month}^{-1}$ ) are slightly higher than the estimations that are based on field observations from Yucatan peninsula in Southern Mexico ( $\sim 40 \text{ g P ha}^{-1} \text{ month}^{-1}$ ).<sup>11</sup> Since this value accounts for 9.6–28.5% of the monthly P inputs to the forest soils from plant litter, which is an important source of bioavailable P in highly weathered tropical soils, our results suggest that in the periods when large amounts of Saharan dust arrives to Panama the contributions of dust P inputs are crucial for the productivity of this P-limited forest. However, since our estimations of dust deposition were performed on an area that is located ~100–1000 km east of the sampling station, the actual dust P deposition in Panama may deviate from the amounts we report here.

Based on the aerosol mass concentrations and their P mass fraction we also calculated the average P concentrations in the air during the entire study period. These calculations shows that P derived from local sources during the dry season ( $12.4 \text{ ng P m}^{-3}$ ) was almost equal to the average P derived from remote external sources (such as the Saharan desert) in the wet season ( $10.1 \text{ ng P m}^{-3}$ ) (Figure 8).

In conclusion, our results highlight that at least in the current climatic conditions, deposition of dust transported from long distances makes significant contribution to the forest P budget.



However, it is important to note that in this study we focused only on dry aerosol deposition, even though atmospheric wet deposition may lead to greater removal of aerosols from the atmosphere, at least in the wet season.<sup>11</sup> Yet, the high contribution of Saharan dust P we report here for dry aerosols has important implications for the future of tropical forests in the region, because their long-term productivity might be sensitive to climatic changes that influence rates of Saharan dust emission and perturb the flow of that dust across the Atlantic Ocean.<sup>1</sup>

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research was supported by a Grant from the Israel Science Foundation (#45/14) and by a Grant from the GIF, the German-Israeli Foundation for Scientific Research (#1139/2011). A.G. was funded by the Israel Ministry of Science and Technology (MOST). We thank Joe Wright and Raul Rios from the Smithsonian Tropical Research Institute and Edward Gryspeerd from Universität Leipzig for their contribution.

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