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# Enhanced Solubility and Ecological Impact of Atmospheric Phosphorus Deposition upon Extended Seawater Exposure

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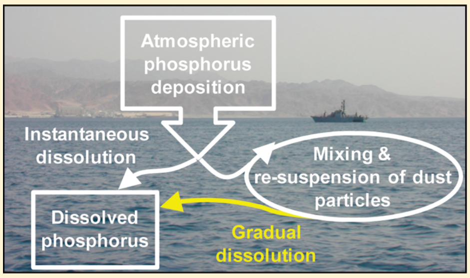
*Supporting Information*

**ABSTRACT:** Atmospheric P solubility affects the amount of P available for phytoplankton in the surface ocean, yet our understanding of the timing and extent of atmospheric P solubility is based on short-term leaching experiments where conditions may differ substantially from the surface ocean. We conducted longer- term dissolution experiments of atmospheric aerosols in filtered seawater, and found up to 9-fold greater dissolution of P after 72 h compared to instantaneous leaching. Samples rich in anthropogenic materials released dissolved inorganic P (DIP) faster than mineral dust. To gauge the effect of biota on the fate of atmospheric P, we conducted field incubations with aerosol samples collected in the Sargasso Sea and Red Sea. In the Sargasso Sea phytoplankton were not P limited, and biological activity enhanced DIP release from aerosols, and aerosols induced biological mineralization of dissolved organic P in seawater, leading to DIP accumulation. However, in the Red Sea where phytoplankton were colimited by P and N, soluble P was rapidly consumed by phytoplankton following aerosol enrichment. Our results suggest that atmospheric P dissolution could continue over multiple days once reaching the surface ocean, and that previous estimates of atmospheric P deposition may underestimate the contribution from this source.



## INTRODUCTION

Atmospheric deposition of nutrients to the surface ocean is of considerable ecological interest because it affects primary productivity,[1,2] nitrogen fixation,[3] and phytoplankton community composition.[4] The flux of macronutrients like nitrogen (N) and trace metals like iron (Fe) from atmospheric deposition contributes significantly to nutrient inventories in open ocean[5−7] and coastal waters.[8−10] Recently, atmospheric phosphorus (P) deposition has received attention, particularly in regions where P limits phytoplankton growth.[10−14]

Phosphorus solubility is lower and more variable than that of N[10,15] and is linked to the mineralogy, chemical composition, and source of atmospheric particles containing P, as well as the acidity of the aerosols. Aerosol acidity is affected by aerosol source and chemical reactions that occur during transport.[2,16] Particle load may also impact P solubility.[15] For crustal phosphate minerals, solubility decreases with soil age and is lower for calcium and magnesium minerals than for phosphate associated with aluminum and iron.[17] Organic P compounds, which may be of natural or anthropogenic origin, also display a range of solubilities.[18]

Another factor likely to affect reported P solubility is the leaching procedure used to release P from aerosol particles. A variety of methods have been used in which solvent, duration, particle to solution-ratio, and mechanical agitation have varied. In addition to variability in the duration of leaching,[10,19] aerosol extraction protocols can include vacuum filtration without agitation,[19] gentle shaking,[10,20] or sonication.[13,21] The choice of solvent used for leaching also has a profound effect on the solubility of P compounds.[16,18] Pure water or buffers that approximate rainwater chemistry (e.g., buffered acetate solutions) are commonly used (18, and referenced therein); however, P solubility in these solvents is typically higher than in seawater.[21] Moreover, several studies have demonstrated that P solubility is generally lower in seawater than in freshwater for aerosols[21] and soils.[20] Sequential leaching procedures that expose aerosols to progressively stronger solvents ranging from fresh water to ashing in strong acids have been applied and used to evaluate operationally defined aerosol P fractions.[18]

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Importantly, the various methods described above may not accurately mimic P dissolution processes in the surface ocean. The time scales for aerosol leaching methods is typically in the range of seconds[19] to hours,[10,13] much shorter than would occur for aerosol particles suspended in the ocean's mixed layer, where they can be retained for days to weeks depending on particle size and the degree of mixing.[22] For example, in the Atlantic Ocean, the residence time of dissolved and particulate Fe derived from aeolian sources is 6–62 days.[23]

To characterize the dissolution of P from Sahara soil, which is the source material for Sahara dust, Ridame and Guieu (2002) conducted dissolution experiments in which leaching time was varied up to one week.[20] They found that ~50% additional P was released from the soil after one week compared to 6 h of leaching. The increased solubility of soil P over time implies that longer soaking could also lead to greater P release from atmospheric deposition. However, several important differences render atmospheric particles chemically distinct from soils. First, atmospheric deposition is a complex mixture of particles with crustal origin, anthropogenic emissions, ash from fires and biomass burning, biological particles, sea spray, and many other sources, each likely contributing its own unique P solubility.[2] Second, as aerosols get transported through the atmosphere, they are exposed to numerous physical and chemical processes, such as acid addition and dissolution in rain, which can impact the solubility of P in the aerosol.[16]

In light of these differences, we investigated P solubility of natural atmospheric deposition samples over environmentally relevant time scales. In this study, we use longer-term (up to 3 day) laboratory leaching experiments to quantify the timing and extent of P released. Three days is a time scale commensurate with phytoplankton nutrient uptake and bloom initiation. We use air mass back trajectory analysis to identify P solubility trends related to anthropogenic and natural source materials. Finally, in two field incubation experiments, we show that the nutritional status of phytoplankton helps determine the extent of P accumulation or drawdown from atmospheric deposition.

## ■ MATERIALS AND METHODS

**Atmospheric Particulate Matter Collection and Analysis.** Atmospheric particulate matter was collected at three geographically distinct coastal locations, including the Red Sea (Eilat, Israel), the Sargasso Sea (Tudor Hill, Bermuda), and Monterey Bay (Elkhorn Slough, CA). Red Sea samples were collected on polycarbonate filters on a total suspended particle high volume sampler (HVS) operating at approximately 1.2–1.5 $m^3h^{-1}$ as described previously.[13] Monterey Bay samples were collected on quartz filters using a total suspended particulate (TSP) air sampler operating at 84 $m^3h^{-1}$. Sargasso Sea samples were collected on quartz filters on a custom-made sampler operating at 53–78 $m^3h^{-1}$ as described previously.[24,25] Collection was set such that local emissions from the island were not included, contingent on wind speed (>1 m/s) and direction (210–315°). All samplers collected bulk total suspended particulates without size fractionation or exclusion. All filters were acid washed before use. Once samples were collected on the filters, filters were stored frozen until analysis. Air mass back trajectories (AMBTs) were generated using the HYSPLIT model provided by the National Oceanographic and Atmospheric Administration Air Resources Laboratory.[26,27]

**Laboratory Dissolution Experiment.** To quantify the amount of P released from atmospheric deposition and its dependence on leaching time, a dissolution experiment was performed with natural aerosol samples and filtered seawater. The amount of aerosol added to each bottle varied between sites depending on the filter type, size, and duration of sample collection. Aerosol corresponding to ~200 $m^3$ air, ~1000 $m^3$ air, and ~1200 $m^3$ was used for the Red Sea, Sargasso Sea, and Monterey Bay, respectively. This resulted in a more similar aerosol mass in the various bottles, since the aerosol concentrations (mg $m^{-3}$ of air) differed between sites. Supporting Information (SI) Table S1 identifies the source and amount of aerosol used in the laboratory dissolution experiment. The amount of aerosol added per bottle was higher than would occur during a natural deposition event, but similar to the aerosol-to-solvent ratio typically used in other laboratory extraction experiments,[13,19] allowing our results to be compared with prior studies.

Aerosol samples were added to plastic bottles containing 300 mL of 0.2 $\mu$m filtered seawater. All materials used in the experiment were acid cleaned (10% hydrochloric acid soak for 48 h at 65 °C), and sampling was performed in a laminar flow hood in a class-100 clean room. Operational blanks included four seawater-only bottles, three polycarbonate filter blanks, and three quartz filter blanks. Operational blanks were processed identically to the aerosol samples. Bottles were placed on a shaker and gently swirled at 21 °C. Aliquots were taken at four time points over the course of 3 days; immediately (within 10 min) after the filter was added (t0), at 6 h (t6), 1 day (t24), and 3 days (t72). At each time point, sample bottles were shaken vigorously and 40 mL sample water was removed and syringe filtered (0.2 $\mu$m polypropylene) into plastic centrifuge tubes. The magnesium induced co-precipitation method (MAGIC[28,29]) was used to concentrate DIP as described below.

Particle–water ratios have been observed to affect nutrient solubility from soils[20] and atmospheric deposition samples.[15] To determine how particle–water ratios affected P solubility in this study, for select samples we soaked different amounts of aerosol in the same seawater volume. For the Red Sea samples, amounts corresponding to 30, 60, and 90 $m^3$ air were used. In the Sargasso Sea amounts of 250 and 500 $m^3$ air were used, and in Monterey Bay 1000 and 2000 $m^3$ air were used.

**Field Incubation Experiments.** To determine the fate of atmospheric P in seawater containing natural phytoplankton populations, incubation experiments were conducted in the Red Sea and the Sargasso Sea. At each site, locally collected atmospheric deposition samples were added to bottles with surface seawater and incubated under in situ temperature conditions for three days in the Sargasso Sea and four days in the Red Sea. These experiment durations were determined based on prior experiments to be sufficient to observe clear growth responses while minimizing bottle effects, and they are likely shorter than the residence time of particles in the mixed surface layer.[23] SI Table S2 provides information about the aerosol samples used in each experiment and the treatment identification codes used in Figure 5. In the Sargasso Sea, three types of aerosol samples were used (Dust 1, 2, or 3). For Dust 1 and Dust 2, three amounts of dust were tested that simulated the annual average deposition rate for the Sargasso Sea ("low" deposition), the annual average deposition rate for the equatorial North Atlantic ("medium" deposition), or a high deposition event equivalent to 10-fold higher than the annual average deposition rate for the Sargasso Sea ("high" deposition)[30] (SI Table S2). Only the "low" level was tested for Dust 3. Aerosol concentrations in the bottles were 5, 25, and 50 $\mu$g TSP $L^{-1}$ for the low, med, and high treatments respectively. In the Red Sea three types of dust were tested based on AMBT: Dust "A" originated over Africa, Dust "E" originated over Europe, and Dust "L" originated from the surrounding local deserts. All three types were added at a concentration equivalent to a high deposition event 10-fold higher than the annual average deposition rate for the region, corresponding to an aerosol concentration of 167 $\mu$g TSP $L^{-1}$ in the bottles.

In addition to atmospheric deposition treatments (which only received aerosol dust additions), separate treatments with nutrient additions of inorganic N and/or P were included at levels typical for each site following deep mixing of the water column. These were 0.4 $\mu$mol $PO_4^{3-}$ $L^{-1}$ and 7.5 $\mu$mol $N^-$ $L^{-1}$ (7 $\mu$mol $NO_3^-$ $L^{-1}$ plus 0.5 $\mu$mol $NH_4^+$ $L^{-1}$) in the Red Sea,[31,32] and 0.2 $\mu$mol $PO_4^{3-}$ $L^{-1}$ and 5.4 $\mu$mol $N^-$ $L^{-1}$ (5 $\mu$mol $NO_3^-$ $L^{-1}$ plus 0.4 $\mu$mol $NH_4^+$ $L^{-1}$) in the Sargasso Sea.[33] The inorganic nutrient treatments did not receive aerosol additions. The N+P treatments were intended to relieve growth limitation such that nutrient uptake at high growth rates could be quantified. To that end, the N+P treatment in the Sargasso Sea experiment also included 3 nmol Fe $L^{-1}$ to avoid secondary limitation by this commonly colimiting metal.[3,34] Control bottles contained seawater without any added nutrients or aerosol dust. Incubations were conducted in acid cleaned, sample rinsed, transparent plastic bottles (0.5 L bottles in the Sargasso Sea, and 6 L bottles in the Red Sea). In all experiments irradiance was attenuated by 50% using a neutral density shade cloth. Soluble reactive phosphorus and chlorophyll *a* (chl *a*) were monitored daily throughout the experiments as described below.

**DIP Analysis.** Water samples from the laboratory dissolution experiment were treated with 1.5 mL concentrated (15 M) ultrapure ammonium hydroxide (Optima) to form $Mg(OH)_2$ precipitate. Samples were centrifuged to pellet the precipitate and pellets were dissolved in 1.3 mL concentrated (12 M) ultrapure hydrochloric acid (Optima). These ultrapure reagents contained negligible P. The soluble reactive P (SRP) concentration was determined using the molybdenum blue calorimetric assay.[29,35] Absorption was read at 880 nm on a spectraMax M2 96 well microplate spectrophotometer (Molecular Devices) equipped with a "PathCheck Sensor" to automatically determine path length. The analysis was performed on 3−5 technical replicates for each sample, and the coefficient of variation was <10%. The detection limit based on 3 times the standard deviation of full operational blanks was 0.02 $\mu$M. Aliquots of the sample supernatant were also measured to ensure no residual $PO_4$ remained in the seawater following precipitation of the $Mg(OH)_2$ pellet, and these values were always below detection. Standards were prepared from aged seawater (for supernatant analysis) and pH-adjusted Milli-Q water (for dissolved MAGIC pellet analysis). Both matrices had negligible $PO_4$ content that was below the detection limit of the assay.

SRP samples from the field incubation experiments were analyzed on a flow injection autoanalyzer (FIA, Lachat Instruments model QuickChem 8000) using standards prepared in Milli-Q water. Blanks were prepared from aged seawater with negligible $PO_4$ content, and the detection limit (~0.01 $\mu$mol P $L^{-1}$) was determined from 3 times the standard deviation of the blanks. In this study, all P compounds detected using the molybdenum blue method are operationally defined as "SRP". The majority of SRP in seawater is dissolved inorganic P (DIP),[36] and while other acid labile P compounds may be included in the SRP measurement,[37] we use the term DIP for simplicity throughout the text.

**Chlorophyll a.** The chl *a* content of the field incubation water was measured by concentrating cells from 50 to 250 mL of sample water on glass fiber filters (Whatman). Filters were extracted in 90% acetone in the dark at −20 °C for 24 h, and the chl *a* concentration was determined fluorometrically using an AU-10 fluorometer (Turner Designs) calibrated with chlorophyll standards derived from the cyanobacterium *Anacystis nidulans* (Sigma).

## RESULTS

**AMBT Trends.** Two major AMBTs were identified for each site based on two day trajectories generated using the HYSPLIT model (Figure 1). In the Red Sea, these air masses originated over Europe or Africa, as previously reported by Chen and co-workers.[13] More rarely, samples contained dust predominantly from local regions including the Negev Desert. (A local dust sample, Dust L, was used in the Red Sea field experiment but not in the laboratory extraction experiment due to rarity of this type of sample). In the Sargasso Sea, trajectories originated from North American or Africa. Samples of African origin are dominated by dust from the Sahara Desert.[7] These Saharan trajectories tended to approach from the south, occasionally traversing the Caribbean prior to arriving in

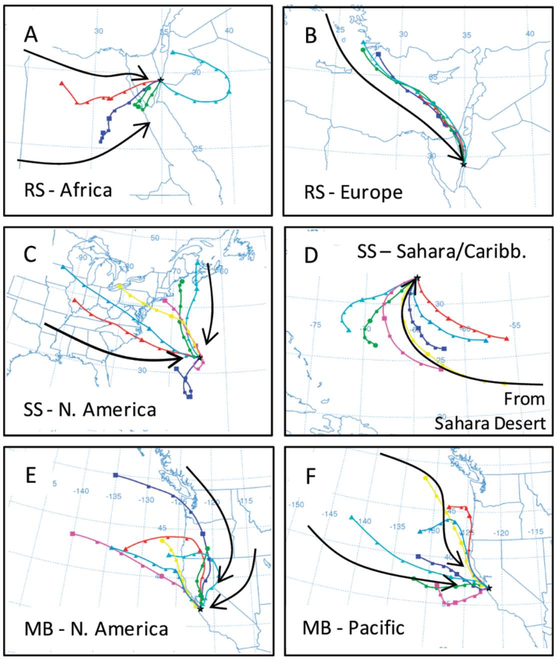

**Figure 1.** Two-day air mass back trajectories from (A) Africa to the northern Red Sea; (B) Europe to the northern Red Sea; (C) North America to the Sargasso Sea; (D) Africa (the Sahara Desert) via the central Atlantic Ocean and the Caribbean to the Sargasso Sea; (E) west coast of North America to Monterey Bay, and (F) Pacific Ocean to Monterey Bay. For each panel, each colored trajectory represents one day of the sampling period over which the sample was collected, and black arrows are shown to emphasize the range of typical trajectories that might be encountered from each source location. The sampling period for each sample ranged from 4 to 7 days depending on location (SI Table S1). RS = Red Sea, SS = Sargasso Sea, and MB = Monterey Bay.

Bermuda. In Monterey Bay, trajectories were categorized as either originating predominantly over the Pacific Ocean, as is common during the summer upwelling season, or as having traversed land immediately prior to arriving at Monterey Bay, more typical of winter samples for this region.[9] Trajectories from the Pacific Ocean originated at various locations, including Alaska and parts of Asia.

**Laboratory Dissolution Experiment.** The dissolution of P from aerosol samples increased with time for all samples tested regardless of source (Figure 2, Figure. 3A). For the Red Sea, 2- to 3-fold more DIP was released 72 h after aerosol addition (t72) compared to initial solubility immediately after aerosol addition (t0). Between 6- to 9-fold more DIP was measured at the final time point than the initial for Sargasso Sea and Monterey Bay samples.

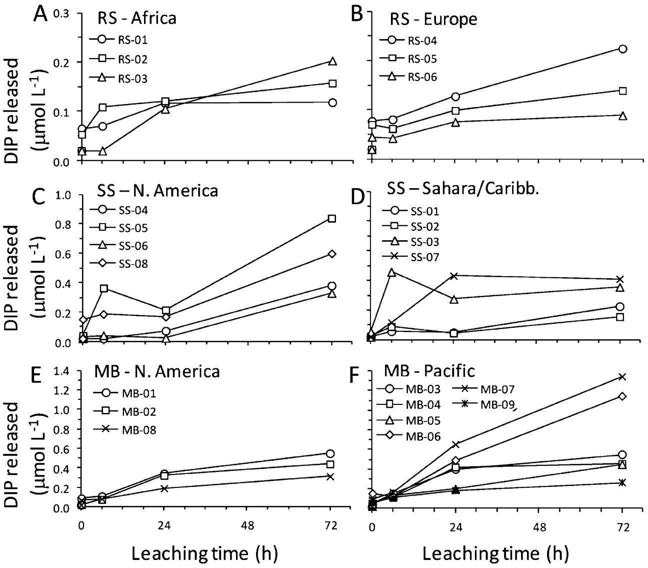

Figure 2. DIP released from atmospheric deposition samples with air mass back trajectories from (A) Africa to the Red Sea, (B) Europe to the Red Sea, (C) North America to the Sargasso Sea, (D) the Caribbean and Sahara Desert to the Sargasso Sea, (E) North America to Monterey Bay, and (F) the Pacific Ocean to Monterey Bay. RS = Red Sea, SS = Sargasso Sea, and MB = Monterey Bay.

The amount of DIP released over the 72 h experiment was similar for samples with African and European trajectories in the Red Sea (Figure 2, Figure 3A). In the Sargasso Sea, samples from North American trajectories released ~2 fold more DIP than samples with trajectories from the Caribbean and/or Sahara Desert. The DIP released from Monterey Bay samples was similar between North American and Pacific trajectories; however, two samples with Pacific trajectories showed ~2-fold greater DIP release than other samples from the region (Figure 2, Figure 3A).

The fraction of instantaneous DIP release, as determined by comparing DIP concentrations at t0 to those at t72, differed by trajectory for each site. A larger fraction of DIP was released more quickly in Red Sea samples from European trajectories, and in Sargasso Sea and Monterey Bay samples from North American trajectories compared to other trajectories (Figure 3B)

**The Effect of Particle Concentration.** In general the solubility of P increased with lower particle concentration (Figure 4), with the exception of the Sargasso Sea sample that originated from North America where solubility was similar for the two loads (Figure 4C). The particle concentration effect was particularly evident in the Red Sea samples, where the smallest particle dose yielded the highest amount of DIP per equivalent volume of air (Figure 4A,B).

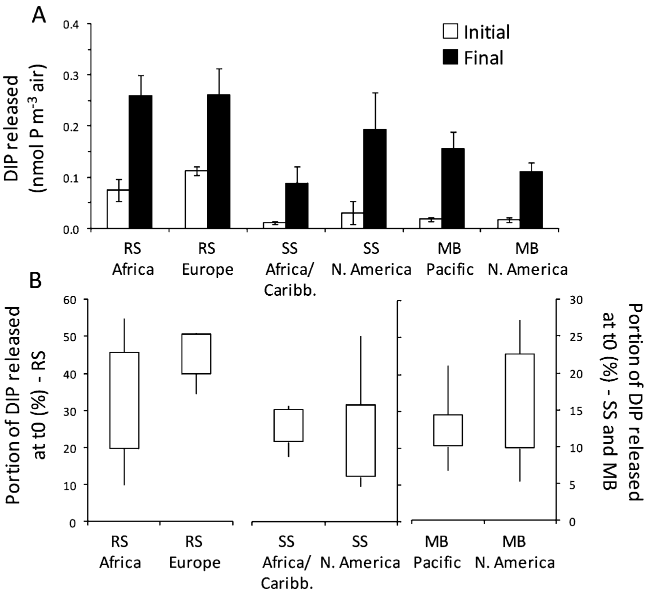

Figure 3. Comparison of instantaneous and prolonged DIP release showing (A) amount of DIP released normalized to air volume at the initial time point (t0, white bars) and final time point (t72, black bars). Error bars show standard error. (B) The percentage of DIP released at the initial time point relative to the total released over 72 h. Upper and lower box edges depict mean ± SE, and lines show range. RS = Red Sea, SS = Sargasso Sea, and MB = Monterey Bay. In general, samples from AMBTs with greater anthropogenic influence (e.g., RS Europe, SS N. America, and MB N. America) released a greater portion of their DIP at t0.

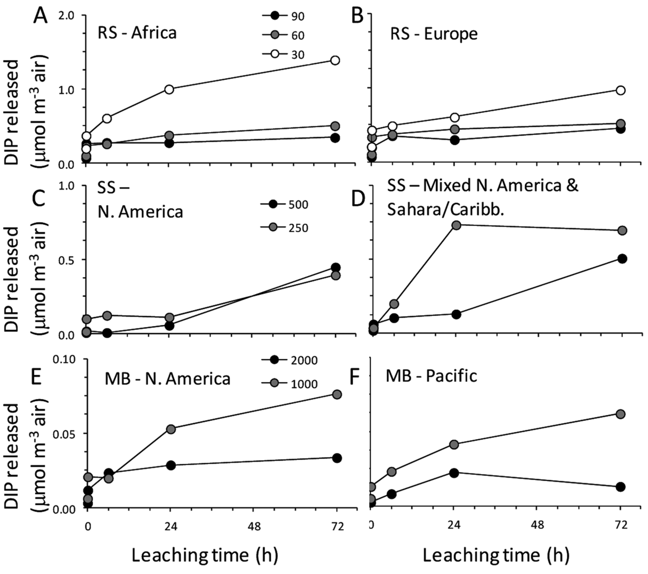

Figure 4. Particle concentration effect on P solubility. Each panel shows DIP released normalized to air volume for different amounts of the same aerosol sample. Trajectories are as described in Figure 1 except for the sample in (D), which had mixed trajectories from North America and the Caribbean/Sahara. Legends in (A,C,E) denote the amount of air contained in the sample in units of $m^3$. RS = Red Sea, SS = Sargasso Sea, and MB = Monterey Bay.

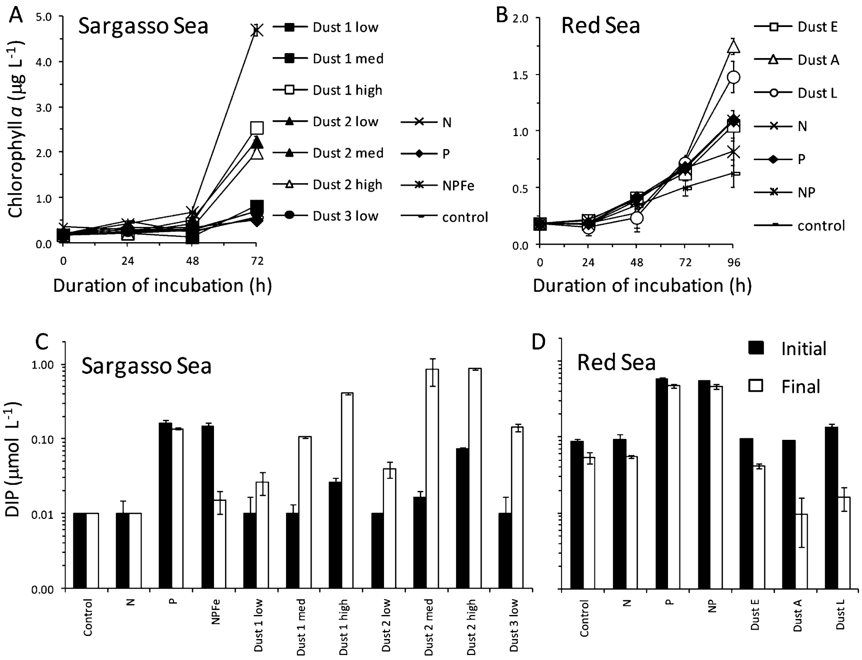

**Figure 5.** (A, B) Growth responses of phytoplankton during the field incubation experiments in (A) the Sargasso Sea, and (B) the Red Sea. (C, D) Initial (black bars) and final (white bars) DIP concentrations in the field incubation experiment in (C) the Sargasso Sea, and (D) the Red Sea.

**Field Incubation Experiments.** *Sargasso Sea.* The growth response of the phytoplankton community to nutrient and AD additions was monitored via chl *a* concentrations. Initial chl *a* concentrations were 0.18 $\mu$g L$^{-1}$. The strongest growth occurred when N, P, and Fe were added together (reaching 4.7 $\mu$g L$^{-1}$; Figure 5A), followed by Dust 1 high and Dust 2 medium and high (~2−2.5 $\mu$g L$^{-1}$). All other treatments (Dust 1 low, Dust 1 medium, Dust 2 low, Dust 3 low, N alone, and P alone) showed minimal growth similar to the untreated control (range 0.50−0.81 $\mu$g L$^{-1-}$).

The background DIP level in the Sargasso Sea incubation water was at the detection limit of ~0.01 $\mu$M. In bottles receiving aerosol additions, DIP concentrations increased in proportion to the amount of aerosol added to the bottles (Figure 5C). For example, treatments Dust 1 high and Dust 2 high had 0.03 $\mu$M and 0.07 $\mu$M DIP respectively immediately following aerosol addition. DIP in the incubation water increased an order of magnitude for all aerosol treatments over the course of the experiment (Figure 5C), reaching 0.41 $\mu$M and 0.88 $\mu$M by the final day of incubation for Dust 1 high and Dust 2 high respectively. In general the amount of additional DIP released between the initial and final time points was proportional to the amount of aerosol added to the bottles. However, the relationship was not linear, as can be seen in the "Dust 2 medium" and "high" treatments, which both appeared to saturate at ~0.85 $\mu$M even though twice as much dust was added in the high treatment compared to the medium treatment. DIP concentrations did not change over the course of the experiment in the untreated control bottles, or when N or P were added independently. However, DIP was drawn down by 0.14 $\mu$M when N and P were added together.

*Red Sea.* The initial concentration of chl *a* in the incubation water was 0.18 $\mu$g L$^{-1}$. By the end of the experiment, phytoplankton growth was greatest in bottles receiving Dust A (1.75 $\mu$g L$^{-1}$) followed by Dust L (1.48 $\mu$g L$^{-1}$; Figure 5B). Growth was elevated to similar levels in bottles treated with P alone, N and P together, as well as Dust E (~1.1 $\mu$g L$^{-1}$). Smaller increases in chl *a* occurred in the untreated control and in bottles receiving N alone.

The background DIP level in the Red Sea incubation water was ~0.09 $\mu$M. Immediately following addition of aerosol, DIP levels remained at the background level for Dust A and E, but increased to 0.14 $\mu$M for Dust L (Figure 5D). By the final day of the experiment DIP concentrations had declined between 0.03 and 0.12 $\mu$M in all treatments. More DIP drawdown occurred in bottles that received additions of P or Dust, compared to bottles receiving N alone or the untreated control. The largest drawdown was observed in bottles receiving Dust L (0.12 $\mu$M) and P alone (0.10 $\mu$M).

## DISCUSSION

The solubility of atmospheric P affects the P available for biological uptake in the surface ocean, yet our understanding of the timing and extent of atmospheric P solubility is based largely on short-term solubility experiments in which the conditions may differ substantially from those in the surface ocean.[10,11,15,18,20] The goal of this study was to quantify P solubility using real atmospheric deposition samples in seawater over time scales in which phytoplankton growth could affect, and be affected by, aerosol P dissolution. The use of filter-sterilized seawater in the leaching experiments allowed us to differentiate purely chemical processes from biological influences (e.g., uptake, remineralization, and scavenging) that likely occurred in the unfiltered incubation water.

**DIP Solubility over Environmentally Relevant Time Scales.** In the laboratory dissolution experiment, longer aerosol leaching led to greater DIP dissolution compared to instantaneous leaching, indicating that a greater portion of the total P in atmospheric deposition could be bioavailable to phytoplankton than previously suggested based on short-term leaching experiments. Atmospheric DIP deposition is calculated from DIP solubility estimates together with modeled deposition fluxes for atmospheric particles.[2] In their model of global P deposition, Mahowald et al.[2] estimated the oceans receive 96.5

Gg of $PO_4^{3-}$ per year. If all of this $PO_4^{3-}$ was utilized by phytoplankton (and other essential nutrients like N were not limiting), it would support ~3.8 Tg C $y^{-1}$of new primary production assuming a Redfield uptake ratio of 106C:1P. This estimate assumes variable aerosol P solubility; for example, 10% solubility for mineral dust and 50% for anthropogenic aerosols based on data obtained from short-term extractions reported in the literature. However, our results suggest that the solubility of P in mineral and anthropogenic aerosols may be more similar provided longer extraction times more relevant to the environment are used. This may be because more time is available for kinetic processes of P dissolution to occur, allowing equilibrium to be reached. In addition P is associated with different phases and minerals (organic and inorganic, adsorbed and within crystal structure, etc.) and each of these components will have a different time scale for dissolution. The very soluble phases may be leached first and other less soluble phases will gradually add to the dissolved fraction over time.

Based on the leaching experiment, the amount of DIP released from atmospheric deposition may be 2- to 9-fold larger than previously estimated based on short duration seawater leaching procedures (Figure 3B). Taking this additional DIP into account and using the conservative value of a 2-fold increase in DIP solubility, the amount of primary production supported by atmospheric DIP would be at least 7.6 Tg C $y^{-1}$. (This calculation provides a maximum estimate of productivity under P limited conditions as assumed by Mahowald et al;[2] however, colimitation for N and/or trace metals would likely limit additional growth in highly oligotrophic waters).[38] Seawater extraction protocols that use short extraction times may underestimate the amount of bioavailable DIP that can be supplied to the ocean through atmospheric deposition, yet extractions in fresh water or acidified buffer may overestimate this amount. Longer-term measurements of aerosol DIP solubility in seawater would permit comparisons between these methods and clarify the true extent of atmospheric DIP release in the natural environment.

The ecological consequences of greater P solubility over time extend beyond supporting primary production. For example, atmospheric deposition is known to support $N_2$ fixation by relieving limitation for P and Fe in diazotrophs in the oligotrophic ocean.[3,39] The greater dissolution of aerosol P with time could favor diazotroph growth since more P is supplied in concert with Fe,[3] a nutrient required in high quantities for the nitrogenase enzyme.[40] In addition the gradual, sustained dissolution of atmospheric P as the dust remains suspended in the mixed layer could support slower growing phytoplankton with high affinity P uptake capabilities, rather than favoring bloom forming species that would tend to benefit if high levels of DIP were released in a large pulse all at once following deposition.

**Sources of Variability.** Solubility can be related to aerosol source, and specifically to the relative proportions of anthropogenic and mineral compounds in the aerosol. The degree of anthropogenic influence has been shown to strongly increase the solubility of elements like Fe and copper in aerosols.[41,42] The solubility of P (i.e., the amount of soluble DIP relative to total P in the sample) may also be related to anthropogenic versus mineral dust influence. Based on short-term leaching studies, P solubility in Sahara mineral dust is significantly lower than the overall average P solubility of anthropogenic aerosols reaching the Atlantic Ocean[15] and Mediterranean Sea.[10] However, for Red Sea and Sargasso Sea AMBTs considered in the present study, the observed difference in P solubility based on short-term leaching experiments for aerosols from anthropogenic and mineral sources is not statistically different[13,43,44] (SI Figure S1).

In the present study, the fraction of DIP immediately released at t0 was generally higher for anthropogenic sources (i.e., European trajectories in the Red Sea, and North American trajectories in the Sargasso Sea and Monterey Bay) compared to samples from less anthropogenic sources collected at the same site (Figure 3B), although the difference was not statistically significant (*t* test, $p < 0.05$). While solubility generally increased in all samples by t6 relative to t0 (Figure 2), the portion of soluble P still did not differ significantly by source at this time point (*t* test, $p < 0.05$). In the Red Sea at t0, an average of 45% of the total DIP that dissolved was released at the initial time point for European trajectory samples compared to only ~33% for African samples that contain more mineral dust (Figure 3B). Similar, although smaller, responses were observed in the Sargasso Sea and Monterey Bay, where anthropogenic aerosols showed a broader range of instantaneous solubilities due to very high instantaneous solubilities of some samples, compared to the tighter range observed for nonanthropogenic aerosols (Figure 3B).

While the initial rate of P solubility appears to be related to anthropogenic influence, the overall amount of DIP released over longer extraction times did not show a clear relationship with aerosol source (Figure 3A). For the Red Sea samples, the amount of DIP released on the final time point was similar for samples originating from Africa versus Europe. In contrast, more DIP was released from the more anthropogenic North American samples than Caribbean/Saharan samples in the Sargasso Sea, while the Pacific samples released more DIP than the more anthropogenic North American samples in Monterey Bay. Therefore, for longer extractions the amount of DIP released was not consistently higher or lower for samples with greater anthropogenic influence. While the differential solubility (i.e., soluble relative to total P) between mineral and anthropogenic aerosols that has been reported based on short-term extractions is controlled by different chemical characteristics of the aerosols,[10,15] this difference may be accentuated by short-term leaching procedures where the solubility of P in mineral particles could be underestimated.

Aerosol composition and atmospheric processing both affect aerosol P solubility, and the choice of leaching protocol will result in operationally determined variability. Chen et al.[21] observed that the amount of soluble P released from aerosols was significantly lower in seawater (0.4 nmol $m^{-3}$) than freshwater (0.7 nmol $m^{-3}$), a difference they attributed to pH dependent solubility of organic and mineral P compounds in the two solvents. The additional DIP released following longer extraction in the present study could be partially due to the dissolution of these less labile (but still soluble) P compounds, which take longer to dissolve in seawater than they would in freshwater extractions. Moreover, dissolved organic (DOP) was not measured directly in this study, but would contribute additional bioavailable P to phytoplankton via enzyme-mediated reactions. These results highlight the importance of simulating the natural environment as accurately as possible when measuring aerosols P solubility to obtain the most realistic estimates for atmospheric DIP (and DOP) deposition.

In the present study a particle concentration effect was observed in which higher P solubility was linked to lower particle concentrations (Figure 4). This effect has been observed to affect the solubility of P and other elements to varying extents,[20,45−47] and is due to (re)adsorption of dissolved nutrients onto aerosol particles at high particle loads. If particle concentration affects the solubility of atmospheric P in surface seawater in a similar manner to that observed in the laboratory extraction experiment, then this implies small deposition events could have disproportionately large effects on DIP levels. However, it is likely that the particle concentration effect is less prominent or nonexistent for DIP in the surface ocean because of the mixing and increased dilution by water. Direct monitoring of nutrient release following natural deposition events would help determine the importance of this effect in the natural environment.

**Fate of Atmospheric P Deposited to the Surface Ocean.** The fate of atmospheric P in the surface ocean is influenced by a number of factors, including mixing, advection, hydrolysis, sorption, and biological uptake and mineralization. In this study, field incubation experiments were conducted with natural atmospheric deposition samples and phytoplankton populations in the Sargasso Sea and the Red Sea to determine how biological activity may impact, and be impacted by, liberated atmospheric DIP. Phytoplankton and bacteria assimilate P during their growth, and are therefore a major sink for DIP in the surface ocean. Phytoplankton and other microbes may also increase the solubility of aerosol P by generating enzymes such as alkaline phosphatase that help mineralize organic P compounds that are more resistant to dissolution.[48,49] These enzymes are stable in filtered seawater for up to ∼40 days if stored in cool, dark conditions, but degrade much faster (on the order of ∼2 days) when stored in the light.[48] The seawater used in our laboratory leaching experiment was stored at room temperature in the light, so it is unlikely that residual alkaline phosphatase activity affected P solubility in our lab experiment. However, microbial mineralization, uptake, and cell surface scavenging[50] of aerosol P were all possible in the field incubation experiments.

In the Red Sea incubation, the strongest growth responses (greatest chl *a* increase) occurred when dust was added, or when inorganic P was added (Figure 5B), suggesting that these cells were primarily P limited. Because dust supported the highest levels of growth (more than additions of P alone or N +P), the dust likely provided P and another colimiting nutrient to phytoplankton as has been shown previously.[14] Concurrent with this phytoplankton growth, DIP was *drawn down* over the 96 h incubation in all three dust treatments (Figure 5D). In this P colimited system,[31] DIP from aerosols was taken up by rapidly by growing cells and/or scavenged onto cell surfaces[50] such that DIP did not accumulate in seawater.

In contrast to the Red Sea, phytoplankton in the Sargasso grew most when N, P, and Fe were cosupplied, but not when N or P were supplied independently (Figure 5A), consistent with the observation that phytoplankton are regularly Fe-limited or colimited in this region.[3,34] Dust also supported growth by supplying N, Fe and possibly P and other nutrients. The amount of N and Fe drawdown was similar in treatments receiving inorganic N+P+Fe or dust (both treatments had ∼2 $\mu$M $NO_3^-$ and ∼2nM Fe drawdown, data not shown). Interestingly, when we compare the initial and final DIP concentrations in the seawater during this experiment, we see that DIP actually *accumulated* over 72 h in the bottles receiving dust (Figure 5C). In the "high" dust treatments, DIP levels reached 0.41 and 0.88 $\mu$M for Dust 1 and Dust 2, respectively. This amount is considerably higher than expected based on dissolution observed in the laboratory leaching experiment where aerosol samples were dissolved in filtered seawater without cells, suggesting that microbial enzymes play a role in solubilizing more resistant P compounds, including organic P. However, the amount of additional DIP that accumulated during the experiment was higher than the amount added from the dust; at most the addition of aerosol P could increase the ambient DIP 4-fold (SI Table S2). The larger DIP increases observed in this experiment therefore suggest that aerosol additions further contributed to DIP accumulation in the seawater by stimulating the mineralization of seawater DOP to DIP by marine microbes. The accumulation of DIP suggests that the amount of DIP generated following aerosol addition was greater than that used by phytoplankton. The 2 $\mu$M $NO_3^-$ drawdown we observed in the high dust treatments would correspond to ∼0.1 $\mu$M P uptake assuming a Redfield uptake ratio of 16N: 1P. Therefore, the P generated following aerosol addition was in excess of the P demands of the phytoplankton during our experiment, resulting in DIP accumulation. The lower P requirements of picocyanobacteria that dominate phytoplankton communities in the Sargasso Sea could also contribute to this effect.[51,52]

From these two field experiments we can see that the gradual solubility of atmospheric P can lead to sustained release of DIP in seawater over biologically relevant time scales. However, whether this DIP accumulates or is consumed is determined by the biological demand of phytoplankton and availability of other potentially colimiting nutrients. If phytoplankton are P limited and their needs exceed the amount of P released from aerosols, then DIP gets taken up upon dissolution, as we saw in the Red Sea experiment. In contrast, if phytoplankton are not P limited or if their P demands are smaller than the amount of DIP released from aerosols, then DIP accumulates, as we saw in this Sargasso Sea experiment.

In this study we sought to elucidate how aerosol P solubility varies under natural conditions over environmentally relevant time scales. From our laboratory dissolution experiments we showed that P solubility increases over time. The rate of solubilization is related to particle composition and source, with anthropogenically impacted sources in general releasing a higher proportion of their soluble P rapidly, and crustal sources taking longer to dissolve. Our field incubation experiments show that accumulation of DIP from dust is strongly regulated by phytoplankton nutritional requirements. Accumulation of P in surface seawater is more likely to occur in systems where phytoplankton are not P limited; otherwise, DIP gets taken up by growing cells immediately upon release from aerosol particles. Based on this study, we suggest that aerosol-seawater leaching protocols that use short leaching times may underestimate the amount of bioavailable DIP that can be supplied to the ocean through atmospheric deposition, as aerosol particles can persist for days to weeks in the mixed layer once they are deposited on the surface ocean.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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## Notes

The authors declare no competing financial interest.

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