# Indirect Evidence for the Presence of Secondary Phosphorus in Continental Fine Aerosol

**Krisztina Krassován[1], Zsófia Kertész[2], Kornélia Imre[3], András Gelencsér[1,3*]**

[1] *Institute of Environmental Sciences, University of Pannonia, PO Box 158, Veszprém, H-8201, Hungary*
[2] *Institute for Nuclear Research Hungarian Academy of Sciences, Laboratory of Ion Beam Applications, PO Box 51, Debrecen, H-4001, Hungary*
[3] *MTA-PE Air Chemistry Research Group, PO Box 158, Veszprém, H-8201, Hungary*

## ABSTRACT

The role of the atmosphere in the biogeochemical cycle of phosphorus (P) is generally associated with the emission of soil dust, sea-salt particles, bioaerosols and industrial aerosols. Quite independently, a reduced gaseous phosphorus compound (phosphine, $PH_3$) was measured over various sources such as marshes and sewage plants and also in the global troposphere. Given that phosphine is a reactive gas that rapidly yields low-volatility phosphoric acid in the atmosphere, secondary aerosol formation can be an important sink that has never been considered in the global phosphorus cycle. In our study we present mass size-distribution measurements of phosphorus in aerosol samples collected at two locations in Hungary. The bimodal size distribution of phosphorus indicated two distinct formation mechanisms in the fine (d < 1 μm) and coarse modes (d > 1 μm). As expected, the mass concentration of phosphorus was dominated by the coarse particles; the contribution of fine mode phosphorus to the total was in the range of 11–61% (median 19%). The contribution of biomass burning and to a lesser extent bioaerosols to the fine mode phosphorus was inferred from measured ambient potassium (K) concentrations and P/K ratios reported for biomass smoke. It was found that biomass burning accounted for only a small fraction of fine mode phosphorus, the rest of which likely formed as secondary aerosol component from gaseous phosphine. Secondary aerosol phosphorus can be even more important in providing this essential nutrient for remote ecosystems because it is associated with fine aerosol particles which have longer residence time and thus are more prone to long-range atmospheric transport than coarse primary particles.

*Keywords:* Phosphine; Secondary phosphorus; Fine aerosol; PIXE.

## INTRODUCTION

The biogeochemical cycle of phosphorus is mainly restricted to the flow of inorganic phosphorus in the lithosphere and that of organic phosphorus between the lithosphere, biosphere, and hydrosphere (Smil, 2000; Liu, 2008). The atmosphere does not play an important role in the cycle because phosphorus, unlike carbon, nitrogen or sulphur, is not emitted in the form of gaseous compounds at any significant rate. The atmospheric presence and transport of phosphorus was predominantly linked to soil dust, sea-salt particles, bioaerosols and industrial aerosols (Graham and Duce, 1979; Smil, 2000). These primary sources all yield mainly coarse particles (with aerodynamic diameter larger than 1 μm) with relatively short atmospheric

residence time in the lower troposphere. The annual global emission flux of phosphorus was estimated to be in the order of 1.4–4 Tg P/yr (Graham and Duce, 1979; Smil, 2000, Mahowald *et al.*, 2008). Quite recently biomass burning has been suggested to contribute to the global atmospheric phosphorus flux by up to 5%, predominantly due to large scale burning emissions in the tropics (Mahowald *et al.*, 2005, 2008). This primary source is expected to emit predominantly fine particles (with aerodynamic diameter smaller than 1 μm). Over many parts of the world this conventional source may be supplemented with the increasing use of biofuels. Generally ignored in discussion of the global phosphorus cycle, a reduced gaseous phosphorus compound (phosphine, $PH_3$) was found to be emitted at a measurable rate from sewage plants by Dévai and his co-workers (1988). Free gaseous $PH_3$ has been detected in marsh gas (Dévai and Delaune, 1995), in the air over paddy fields, landfills and animal slurry at concentrations up to several μg/m³ (Glindemann and Bergmann, 1995; Glindemann *et al.*, 1996a; Liu *et al.*, 1999; Han *et al.*, 2000), and at trace concentrations in the lower troposphere (Glindemann *et al.*, 1996b, Liu *et*

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[*] Corresponding author.
 Tel.: 36-88-624-368; Fax: 36-88-624-747
 *E-mail address:* gelencs@almos.uni-pannon.hu

*al.*, 1999) and in the remote troposphere (Glindemann *et al.*, 2003; Zhu *et al.*, 2007). Phosphine is known to be a reactive trace gas, but only sporadic information is available on its atmospheric oxidation reactions. The rate constant of phosphine oxidation by atomic oxygen was measured to be $5 \times 10^{-11}$ cm$^3$/s (Nava and Stief, 1989). Direct atmospheric photolysis of phosphine is not possible in the low troposphere where the low spectral limit of light is 300 nm (Glindemann *et al.*, 2003). The most likely oxidation pathway is the reaction with OH-radicals, with a rate constant of $1.4 \times 10^{-11}$ cm$^3$/s (Frank and Rippen, 1987). By assuming an average concentration of OH-radicals in the lower troposphere to be $5 \times 10^5$ molecule/cm$^3$, an atmospheric residence time of 28 h can be obtained, similar to that of NO$_x$. After the initial reaction between phosphine molecule and an OH-radical, the reactions proceed as follows:

$$PH_{2.} + O_2 \rightarrow PH_2O_{2.} \xrightarrow{NO} PH_2O \xrightarrow{O_2, OH, H_2O, ...} H_3PO_{4(g)}$$

$$PH_3OH \xrightarrow{O_2} PH_2OH \xrightarrow{O_2, OH, H_2O, ...} H_3PO_{4(g)}$$

The only product of the photooxidation of phosphine is gaseous phosphoric acid (H$_3$PO$_4$) (Frank and Rippen, 1987). Its atmospheric fate—though not discussed explicitly in any of the above publications—can be inferred from its physico-chemical properties, by analogy of the atmospheric oxidation products of SO$_2$ and NO$_x$. Since the saturation vapour pressure of phosphoric acid (6 Pa at 25°C) is about 60 times higher than that of sulphuric acid and more than 3 orders of magnitude lower than that of nitric acid, it can be expected that phosphoric acid can directly condense on pre-existing aerosol particles, and then become at least partially neutralized with atmospheric ammonia.

Thus the resulting particulate-phase phosphorus is of secondary origin and generally associated with fine-mode aerosol particles, just like primary combustion-derived phosphorus (Beck *et al.*, 2005). Secondary particulate phosphorus has never been considered in the global cycling of phosphorus. In spite of there are various available phosphine measurements in the global troposphere (Glindemann *et al.*, 2003), a global inventory of phosphine emissions is still lacking. A back-of-the-envelope calculation indicated that this source may not be negligible (Morton and Edward, 2005). Apart from its allegedly low share in the global atmospheric phosphorus budget secondary phosphorus can be disproportionately more important because it is associated with fine aerosol particles which have much longer residence time and thus are more prone to long-range atmospheric transport than coarse particles. In other terms, for remote ecosystems secondary phosphorus may represent an important pathway for the atmospheric supply of this essential nutrient. However, due to its low mass concentration its ability to influence atmospheric processes such as nucleation or cloud droplet activation is probably limited.

The objective of this study is to establish the potential significance of particulate-phase secondary phosphorus for the first time in atmospheric sciences. This is done experimentally by size-selective aerosol sampling and measurements of P, K and calcium (Ca) at urban and rural locations. From the results the regional importance of secondary aerosol phosphorus is also assessed.

## METHODS

### Sampling

Aerosol samples were collected at two different locations in Hungary in the summer of 2003 (Dobos, 2004). K-puszta is an established regional background monitoring station in Hungary and the part of the European Monitoring and Evaluation Programme (EMEP). It is located about 70 km south-east from Budapest, and 15 km from the nearest town Kecskemét. The vicinity of the site is a protected game reserve covered with coniferous forest (62%), deciduous forest (28%) and grassland (10%) (EMEP). The sampling site in Budapest is at the site of the Hungarian Meteorological Office, being part of the National Air Quality Monitoring Network. The air quality in Budapest as in any other large city is strongly affected by transportation and residential activities, public amenities and industrial activities in the city and the surrounding region. The locations of the sampling sites are shown in Fig. 1. The sampling details are given in Table 1.
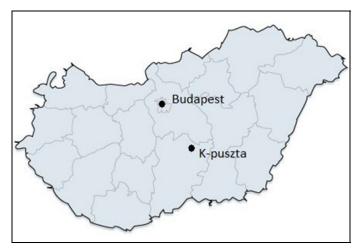


**Fig. 1.** Locations of the sampling sites in Hungary.

**Table 1.** Parameters of sample collection.

| Sampling site | Coordinates and altitude | Site type | Campaign | Collection device | Sampling conditions |
|---|---|---|---|---|---|
| K-puszta | N46°58′ E19°33′ 126 m a.s.l. | rural background | 21 July–03 Aug. 2003 | 7-stage PIXE cascade impactor | flow rate: 1 L/min sampling time: 24 h continuous |
| Budapest | N47°28′26″ E19°3′43″ 106 m a.s.l. | urban | 21 July–01 Aug. 2003 | 7-stage PIXE cascade impactor | flow rate: 1 L/min sampling time: 24 h continuous |

Size-segregated aerosol samples were collected with a 7-stage PIXE (Proton Induced X-Ray Emission) International cascade impactor (Maenhaut *et al.*, 1996). The sampling durations were 24 hours, the sampler heads were installed at a height of 1.5 m and the flow rate was 1 L/min. The cut-off diameters of the impactor stage are given in Table 2.

The samples were collected on paraffin coated Kapton foils and Nuclepore polycarbonate filters with pore size of 0.3 µm were used as end filters.

*Analysis*

The elemental compositions of the samples were determined by PIXE at the Laboratory of Ion Beam Applications of the Institute of Nuclear Research of the Hungarian Academy of Sciences. PIXE is based on the detection of characteristic X-rays induced by a proton beam of 2–3 MeV energy. PIXE is a sensitive (with detection limits in the order of 0.1–100 µg/g) multielemental analytical technique which has been widely used for the analysis of atmospheric aerosol samples (Maenhaut and Malmquist, 2001).

The measurements were carried out at the PIXE vacuum chamber installed on the left 45° beamline of the 5 MV Van de Graaff accelerator of Atomki (Borbély-Kiss I. *et al.*, 1985). The samples were irradiated with a homogeneous proton ($H^+$) beam of 2 MeV energy and of 35–40 nA current. The diameter of the beam spot was 5 mm, which covered the whole aerosol deposit on the impactor stages 1–6. The accumulated charge on each sample was 40–80 µC.

The evaluation of the X-ray spectra was performed with the PIXECOM program code (Szabó and Borbély-Kiss, 1993). The mass of the aerosol on an impactor stage was few micrograms. Therefore for the evaluation the aerosol deposits were considered as thin samples. Concentrations of the following elements were determined: Al, Si, P, K, Ca and Fe. For calculation of the concentration values blank corrections were carefully taken into consideration, too. The concentration values were given in ng/m³. In this work the results are based on the analytical data of P, K and Ca. The minimum detection limits of these elements were 0.46, 0.17 and 0.13 ng/m³, respectively. The uncertainties of the determination of P and K were on average 7.5% and 4%, respectively.

**RESULTS AND DISCUSSION**

The results of the mass concentration measurements of phosphorus lumped into fine (AED < 1 µm, sum of < 0.25, 0.25–0.5, 0.5–1.0 µm) and coarse (AED > 1 µm, sum of 1.0–2.0, 2.0–4.0, 4.0–8.0, 8.0–16.0 µm) modes are listed in Table 3.

As expected, the mass concentration of phosphorus is dominated by coarse particles resulting from resuspended soil dust, primary biogenic particles and industrial processes. The relative mass shares of fine mode phosphorus were in the range of 11–61% (median 19%) and 12–27% (median 19%) of the total for K-puszta and Budapest, respectively. These findings are in reasonable agreement with those of a recent study which found that fine mode phosphorus (< 1 µm) at K-puszta accounted for approximately 30% of the total phosphorus concentration (Vicars *et al.*, 2010).

In order to estimate the relative contribution of biomass burning to submicron phosphorus the mass concentrations of potassium were determined as listed in Table 4. Potassium is commonly used as a tracer element for biomass burning since all plants contain potassium a part of which is emitted with submicron smoke particle. However, there are only a few studies in the literature which determined both phosphorus and potassium concentrations in biomass smoke, the average ratio was found 0.0288 (gP)/(gK) for cereal waste burning (Ortiz *et al.*, 2000), 0.0309 (gP)/(gK) for olive oil waste burning (Jiménez and Ballester, 2005), 0.0548 (gP)/(gK) for wood burning in fireplace and woodstove (Alves *et al.*, 2011) and 0.0239 for savanna burning (gP)/(gK) (Echalar and Gaudichet, 1995). Although mass emission factors of elements are typically expected to vary significantly with the type of biomass burned and the conditions of burning, the reported relative emission factors of the two elements showed surprisingly low variations (i.e., within a factor of 2). In our calculations we used 0.0127 and 0.0565 (gP)/(gK) (p = 0.05) as the low and high bound of the relative mass emission ratio, respectively. Primary biogenic particles are not expected to be present in fine mode particles in great abundance, and moreover they contain both phosphorus and potassium so that they are likely accounted for in the estimated contribution of biomass burning. Based on the measured total concentrations of phosphorus and potassium and their relative emission factors we estimated the concentrations of excess phosphorus (i.e., likely not related to biomass burning particulates/bioaerosols, by analogy of excess sulphate in sea salt aerosols). And its contribution to the total fine mode phosphorus for both sampling locations as given in Table 5. The estimated median contribution of biomass burning to fine mode phosphorus was 19% (53% RSD) and 3% (21% RSD) for aerosol samples collected in Budapest and K-puszta, respectively. The significantly higher estimated contribution of biomass burning in Budapest may

**Table 2.** The cut-off diameters of the impactor stages.

| Stages | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| 7-stage cut-off diameter (µm) | < 0.25 | 0.25 | 0.5 | 1 | 2 | 4 | 8 | 16 |

**Table 3.** Mass concentrations of phosphorus P (ng/m$^3$) in fine (< 1 µm) and coarse (> 1 µm) aerosol measured in aerosol samples collected at a rural (K-puszta) and urban site (Budapest).

| Sampling date | K-puszta | | Budapest | |
|---|---|---|---|---|
| | Fine mode | Coarse mode | Fine mode | Coarse mode |
| 21.07.2003 | 16.3 | 86.6 | 3.2 | 11.8 |
| 22.07.2003 | 14.9 | 77.0 | 2.6 | 9.67 |
| 23.07.2003 | 18.1 | 69.4 | 3.1 | 13.9 |
| 24.07.2003 | 23.9 | 65.9 | 1.7 | 12.6 |
| 25.07.2003 | 23.1 | 88.1 | 3.0 | 10.8 |
| 26.07.2003 | 14.2 | 71.7 | 3.5 | 13.1 |
| 27.07.2003 | 15.1 | 65.8 | 2.8 | 13.5 |
| 28.07.2003 | 14.9 | 62.3 | 3.1 | 13.2 |
| 29.07.2003 | 10.8 | 7.0 | 4.3 | 11.8 |
| 30.07.2003 | 2.72 | 11.1 | 3.6 | 14.7 |
| 31.07.2003 | 1.47 | 11.8 | 3.3 | 17.1 |
| 01.08.2003 | 2.92 | 14.6 | 2.2 | 13.1 |
| 02.08.2003 | 3.70 | 8.56 | - | - |
| 03.08.2003 | 5.20 | 10.8 | - | - |

**Table 4.** Measured mass concentrations of potassium K (ng/m$^3$) in the fine mode (< 1 µm).

| Date | K-puszta (rural) | Budapest (urban) |
|---|---|---|
| 21.07.2003 | 25.0 | 31.9 |
| 22.07.2003 | 14.3 | 30.7 |
| 23.07.2003 | 26.2 | 34.9 |
| 24.07.2003 | 5.3 | 22.5 |
| 25.07.2003 | 19.4 | 6.9 |
| 26.07.2003 | 7.7 | 15.7 |
| 27.07.2003 | 7.9 | 19.7 |
| 28.07.2003 | 6.5 | 11.9 |
| 29.07.2003 | 2.3 | 7.1 |
| 30.07.2003 | 7.0 | 11.8 |
| 31.07.2003 | 13.5 | 21.3 |
| 01.08.2003 | 36.8 | 21.6 |
| 02.08.2003 | 15.2 | - |
| 03.08.2003 | 18.2 | - |

be attributed to specific local sources such as food preparation (frying), biofuel use, residential burning or waste incineration. It is also possible that there are other emission sources of potassium (e.g., abrasion, fossil fuel combustion, industrial activity) (Andreae, 1983). At K-puszta the estimated contribution of biomass burning was low, in accordance with a previous study which reported very low incidence of biomass burning for the same site in summer based on aerosol tracer (levoglucosan) and radiocarbon measurements (Gelencsér *et al.*, 2007).

The contribution of soil particles to the submicron excess phosphorus concentrations was estimated from the measured mass concentrations of calcium which forms the most abundant phosphorus-containing mineral (apatite,

$Ca_5(PO_4)_3$) in soils. Our results shows that the soil derived excess phosphorus can be excluded because measured Ca mass concentrations indicate only negligible occurrence of submicron soil particles as shown in Fig. 2.

Thus we hypothesize that the excess phosphorus in the fine mode (i.e., that cannot be attributed to biomass burning or associated sources) is of secondary origin and derives primarily from the photooxidation of gaseous phosphine and subsequent gas-to-particle transformation.

The time series of the measured mass concentrations seems to support our hypothesis, as shown in Fig. 3. In the period between 21 and 29 July 2003 the measured mass concentrations of phosphorus in the submicron mode were significantly higher than those measured in the city of Budapest. This period was characterized with a stagnant high-pressure system over the Carpathian Basin associated with high temperatures and intense global radiation. These conditions were conducive to photochemical smog formation which did occur and the concentrations of atmospheric pollutants were high with only moderate fluctuations. In the morning of July 29, 2003 there was a heavy rainfall with precipitation amounting to 18 mm in the very first hour at K-puszta, followed by another 20 mm in the first half of the day. This heavy rain washed out most particulates very effectively, reducing mass concentrations down to one-fifth of their previous values. Even larger reductions were recorded a day after since the start of sampling did not coincide with the onset of the rainfall. On the next days the global radiation started to rise again and due to the photochemical processes the concentration of fine mode particles also began to increase. However, following the sharp reduction of phosphorus concentrations after 29th July 2003 at K-puszta, the estimated contribution of biomass burning became relatively high (11%) which started to

**Table 5.** Estimated excess phosphorus concentrations (ng/m$^3$) and its fraction of the total phosphorus in the fine mode.

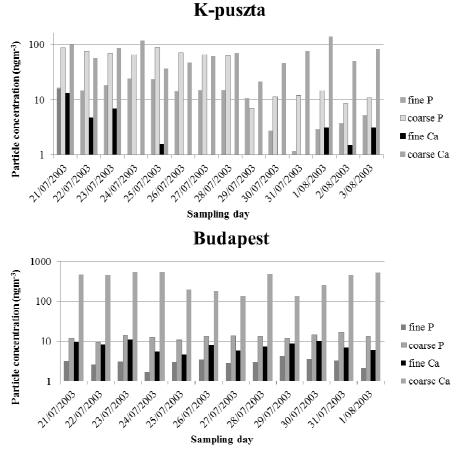| Sampling date | K-puszta | | Budapest | |
| --- | --- | --- | --- | --- |
| | Fine mode excess P | Rate of excess P to fine mode TP (%) | Fine mode excess P | Rate of excess P to fine mode TP (%) |
| 21.07.2003 | 14.9–16.0 | 91.3–98.1 | 1.41–2.81 | 43.9–87.4 |
| 22.07.2003 | 14.1–14.7 | 94.6–98.8 | 0.86–2.20 | 33.1–85.0 |
| 23.07.2003 | 16.6–17.8 | 91.8–98.2 | 1.15–2.68 | 36.8–85.8 |
| 24.07.2003 | 23.6–23.8 | 98.8–99.7 | 0.42–1.40 | 24.9–83.1 |
| 25.07.2003 | 22.0–22.9 | 95.3–98.9 | 2.65–2.95 | 87.2–97.1 |
| 26.07.2003 | 13.8–14.1 | 96.9–99.3 | 2.64–3.32 | 74.9–94.3 |
| 27.07.2003 | 14.7–15.0 | 97.0–99.3 | 1.71–2.58 | 60.6–91.1 |
| 28.07.2003 | 14.5–14.8 | 97.6–99.5 | 2.39–2.91 | 78.1–95.1 |
| 29.07.2003 | 10.7–10.8 | 98.8–99.7 | 3.92–4.23 | 90.7–97.9 |
| 30.07.2003 | 2.32–2.63 | 85.5–96.7 | 2.88–3.40 | 81.3–85.8 |
| 31.07.2003 | 0.71–1.30 | 48.1–88.3 | 2.11–3.04 | 63.7–91.8 |
| 01.08.2003 | 0.84–2.45 | 28.8–84.0 | 0.95–1.90 | 43.9–87.4 |
| 02.08.2003 | 2.84–3.51 | 76.8–94.8 | - | - |
| 03.08.2003 | 4.17–4.97 | 80.2–95.5 | - | - |



**Fig. 2.** Phosphorus and calcium concentrations on each sampling day at both locations.

decrease again with the resumed photochemical smog formation. This finding might be an implication that excess phosphorus can be of secondary origin.

Further support may come from the measured mass size distribution of phosphorus as shown illustratively for both sampling locations in Fig. 4. The bimodal size distribution of total phosphorus indicates two distinct formation mechanisms in the fine and coarse modes at both sites. It seems that the fine mode phosphorus concentrations are very little affected by the tail of the coarse distribution. The inferred mass size distribution of biomass burning phosphorus (also shown in Fig. 4) implies that it is unlikely that biomass burning contributes significantly to measured fine-mode particulate phosphorus.
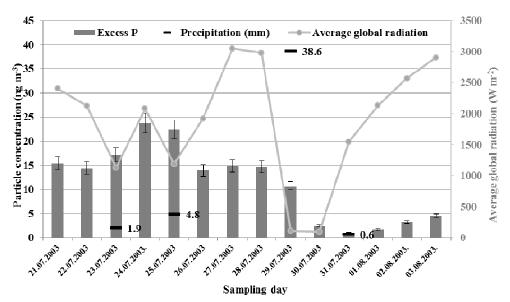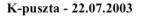
**Fig. 3.** Meteorological parameters (precipitation, average global radiation) affecting the measured phosphorus concentration in the fine mode at K-puszta.
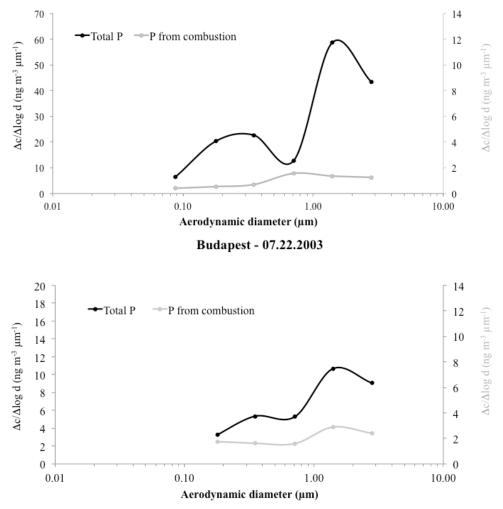


**Fig. 4.** Measured size distribution of phosphorus in K-puszta and Budapest.

The concentrations of free phosphine were reported in the order of 1 ng/m$^3$ at a height of 1–300 m in remote air with peaks of 100 ng/m$^3$ in air in populated areas (Glindemann *et al.*, 1996a, b; Liu *et al.*, 1999; Han *et al.*, 2000; Han *et al.*, 2010). Taking into account the average residence times of free phosphine (28 h) and secondary aerosol phosphorus (6 d) a back-of-the-envelope calculation reveals that typical mass concentrations of secondary P should be in the order up to a few 10 s ng P/m$^3$ excluding other loss mechanisms for phosphine (e.g., dry deposition). The derived excess P concentrations fall into this range lending further support to our hypothesis that secondary aerosol formation may be a plausible explanation for the presence of fine mode excess phosphorus in continental aerosol.

## CONCLUSIONS

Fine mode phosphorus, well in excess of that emitted by biomass burning was found to be an important fraction (up to 20% during the period of intense photochemical smog) of total particulate phosphorus in the collected aerosol samples. We hypothesized that this excess phosphorus is of secondary origin and results from the photooxidation of gaseous phosphine whose atmospheric fate has never been considered explicitly in atmospheric aerosol science. Although the scope of our study was limited to a two-week sampling campaign and the presence of secondary phosphorus was only indirectly established, the evaluation of the results of size-distribution measurements in the light of meteorological data seems to support our deductive hypothesis regarding the atmospheric fate of widely observed gaseous phosphine. Besides being a small, but definitely non-negligible part (up to the order of a few %) of the global biogeochemical cycle of phosphorus, it can be disproportionately more important for phosphorus-limited remote ecosystems. As a matter of course, the limited span of our study does not allow global-scale conclusions to be drawn, further studies are clearly warranted.

## ACKNOWLEDGMENTS

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