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Title

Missed atmospheric organic phosphorus emitted by terrestrial plants, Part 2: Experiment of volatile phosphorus

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Abstract

The emission and deposition of global atmospheric phosphorus (P) have long been considered unbalanced, and primary biogenic aerosol particles (PBAP) and phosphine (PH_3) are considered to be the only atmospheric P sources from the ecosystem. In this work, we found and quantified volatile organic phosphorus (VOP) emissions from plants unaccounted for in previous studies. In a greenhouse in which lemons were cultivated, the atmospheric total phosphorus (TP) concentration of particulate matter (PM) was 41.8% higher than that in a greenhouse containing only soil, and the proportion of organic phosphorus (OP) in TP was doubled. ^{31}P nuclear magnetic resonance tests (^{31}P-NMR) of PM showed that phosphate monoesters were the main components contributed by plants in both the greenhouse and at an outside observation site. Atmospheric gaseous P was directly measured to be 1–2 orders of magnitude lower than P in PM but appeared to double during plant growing seasons relative to other months. Bag-sampling and gas chromatography mass spectrometry (GCMS) tests showed that the gaseous P emitted by plants in the greenhouse was triethyl phosphate. VOP might be an important component of atmospheric P that has been underestimated in previous studies.

Key words

Growing seasons; Volatile organic phosphorus; Bag-sampling; Gas chromatography mass spectrometry; ^{31}P nuclear magnetic resonance

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1. Introduction

Phosphorous (P) plays an important role in ecosystems as a major nutritional element that is necessary for the building blocks of living systems and participates in the physiological and chemical processes of life (Chen et al., 2016). The biogeochemical cycle of phosphorus mainly involves the lithosphere, pedosphere, hydrosphere, biosphere and anthroposphere, and the burden and flow of P in the cycle has been studied (Ruttenberg et al., 2003). P emissions through the atmosphere have been estimated to be 3.5 Tg yr^{-1} (Wang et al., 2014), which is approximately 5% of the global total P flow, but atmospheric P could be the dominant limiting element for some ecosystems (Mahowald et al., 2005, Krom et al., 2010). For example, transoceanic dust from deserts and arid areas could be an important P source for some tropical forests and remote islands (Graham et al., 1981).

In previous studies, the main sources of atmospheric P were combustion (including anthropogenic and natural combustion), mineral dust, primary biogenic aerosol particles (PBAP), sea salt and small amounts of Phosphine (PH_3) from freshwater wetlands and rice paddies (Wang et al., 2014). Several problems in global atmospheric P studies remain. In fact, we have a poor understanding of the chemical speciation of atmospheric P, especially organic phosphorus (OP) compounds (Violaki et al., 2017). Therefore, it is difficult to verify the emissions, immigration, transformation, and deposition mechanisms of atmospheric P without knowing its exact forms and properties. There might be an internal circulation of P in some terrestrial ecosystems, such as the Amazon, in which plants are able to make full use of P with limited atmospheric P input and violent loss by runoff; however, this remains unknown to date (Yu et al., 2015).

Based on the limited knowledge of atmospheric P, previous studies have estimated the global atmospheric P cycle by approximate sectors and approaches. This estimation has

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caused an imbalance between global P emission/deposition observations (3 - 4 TgP yr^{-1}, Graham et al., 1979, Smil et al., 2000, Tipping et al., 2014, Wang et al., 2014) and emission estimations from the earth's surface (1.39 TgP yr^{-1}, Mahowald et al., 2008).

Atmospheric P from the organisms in terrestrial ecosystems has been regarded to be only PBAP (0.16–1.00 TgP yr^{-1}) and PH_3 (0.2 GgP yr^{-1}), which provide a small part of the total P flow (Wang et al., 2014). However, this value was considered simply proportional to the biomass of the plants (Mahowald et al., 2008). This strategy might introduce large system biases if the types and emission mechanisms for different types of vegetation and other biogenic aerosols related to bacteria, fungi, and pollen are not considered (Myriokefalitakis et al., 2016).

In addition, studies of atmospheric P in a gas phase have mostly focused on PH_3 from wetlands or rice paddies (Han et al., 2000, 2011), which contribute much less to the total P flow (0.2 Gg yr^{-1}, Wang et al., 2014). Few stable gaseous P compounds have been reported but some other studies have proposed a mechanism of P emission in gas (Beck et al., 2005). This aspect of P was not included in the global atmospheric P inventory.

Based on the poor understanding of P from plants in ecosystems, we posited that plants were able to emit P compounds into the atmosphere and could be the missing part of atmospheric P measured in deposition. Other plants could use this part of P and decrease the losses by water or dust. In this research, we first established the P concentration of particulate matter (PM) in greenhouses by measurements. Then, ^{31}P nuclear magnetic resonance (^{31}P-NMR) tests were used to distinguish the forms of P in PM, especially several kinds of OP from different sources. Then, the molybdenum blue spectrophotometric method and gas chromatography mass spectrometry (GC-MS) tests were used to directly analyse the atmospheric P in the gas phase. Finally, bag sampling and corresponding measurements on

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plants in a greenhouse provided a quantitative result for gaseous P emitted by plants. From the results obtained, we identified a previously overlooked biogenic volatile organic phosphorus (BVOP) compound that may lead to a new understanding of the global P cycle.

2. Materials and Methods

2.1. PM Sampling conditions and analysis method.

PM is an important form of atmospheric P, and dry/wet deposition of PM has a great impact on P transportation (Decina et al., 2018). In this work, we collected and analysed the P concentration in PM in a greenhouse experiment.

The sampling site was in Beijing, China, which is in a northern hemisphere warm temperate semi-humid monsoon climate zone and is over 110 km from the nearest marine environment, the Bohai Sea. The annual average temperature is 11 - 13°C, with altitudes of below 50 m. In the downstream of cold air from Siberia, the coldest month in Beijing is January. In cold seasons, cold air cyclones from inner Mongolia regions carry sand and dust from parts of North and Northwest China. As the cyclones move eastward and southward, the dust affects the Beijing area. The average number of sandstorm days in 2017-2018 was 6.9 according to the National Meteorological Data Centre online dataset. Precipitation in summer, ~600 - 800 mm with the north Pacific monsoon, accounts for approximately 3/4 of the annual precipitation. The zonal vegetation is warm temperate deciduous broadleaf forest and warm coniferous forest. The greenhouse is located in Beianhe, a suburban area with relatively low population density approximately 30 kilometres from the centre of Beijing and approximately 500 metres from the nearest roads. The sheds of the greenhouses were used for fruit and vegetable farms, and the vegetation coverage was ~68% (Hu et al, 2018). Peking University (PKU) is located between the 4th and 5th ring roads of the city and has an

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average vegetation coverage of 48%. Evergreen trees, deciduous trees, flower thickets and hedges are all present (Xu et al., 2011). Industrial activities in Beijing were moved outward according to the air management policy, and we found that there were almost no industrial emissions within a 10-kilometre area around the sampling sites. The main influence of atmospheric conditions is the traffic (Luo et al., 2016).

Two sheds in the greenhouse and three PM collectors were used in this study, as shown in Figure 1. The area of one shed is approximately 150 m^2, and the temperature is approximately 24°C during the daytime, with ventilation through a reserved air seam. A high-flow atmospheric particle collector was used, the Laoying type 2031 (with a 1 m^3 min^{-1} flow and 25*20 cm glass fibre filter; produced by Qingdao Yingying Environmental Technology Co., Ltd., Qingdao, China). Each instrument was run for 48 h to obtain one PM sample. We collected total suspended particles (TSP) as our PM samples in this experiment. The sampling site at PKU was on the roof of a 7-floor campus building, approximately 24 metres above the ground and approximately 50 metres from the nearby street, and the instrument was the same as those used in the greenhouses.

The shed where we placed the first PM collector was used for lemon cultivation (Improved Meyer, *Citrus limon* (L.) Burm. F.). There were approximately 48 individual lemon trees 1.5 metres in height in the shed, which we called it “Tree” shed. The other shed, where we placed the second PM collector, contained the same soil but no plants were cultivated; we called it “No-Tree” shed. The third PM collector was located outside the greenhouse in the open environment; we called it the “Background”.

During January 18th to April 16th in 2018, we collected 13 samples from the “Tree”, 13 samples from the “Background” and 6 samples from the “No-Tree” available for analysis. In addition, samples from the PKU site for the same period were brought for comparison. (We

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collected the PM on the roof of a 7-floor building on the PKU campus, approximately 24 metres above the ground and approximately 50 metres from the nearby street from 3rd November 2016 to 20th March 2019 for atmospheric P observation).

The following analysis for PM used the molybdenum blue spectrophotometric method. In general, we measured the total phosphorus (TP) and inorganic phosphorus (IP) of every sample, and OP was calculated as the difference between them (Ministry of environmental protection of China, 2011). Equilibrating the samples to the temperature and humidity of the analysis condition, they were divided into two parts. One part was added to excessive potassium persulfate, which had been acidified using sulfuric acid and dissolved in an autoclave at 120°C for 2 h. The other part was added to the same volume of sulfuric acid and was dissolved in an ultrasonic port for 1 h. The two samples were each added to the same amounts of sodium sulfite and sodium thiosulfate to reduce any remaining oxidants and were then added to ascorbic acid, ammonium molybdate and antimony potassium tartrate for coloration. After a 1 h incubation, a spectrophotometer was used at 700 mm wavelength, and the samples were compared with a standard P solution consisting of a monopotassium phosphate solution of known concentration. The concentrations of total phosphorus (TP) and inorganic phosphorus (IP) were then calculated from the two samples, and the concentration of organic phosphorus (OP) was calculated as the difference between the TP and IP concentrations. The various P levels in the atmospheric environment could be calculated according to the sampling volume.

The digestion solution for one part of one sample was sulfuric acid (H_2SO_4, 2.55 $molL^{-1}$, 2 mL), potassium persulfate ($K_2S_2O_8$, 0.50 g) and deionized water (H_2O, ~85 mL). The reduction solution (5 mL) was sodium sulfite (0.74 $molL^{-1}$) and sodium thiosulfate ($9.3*10^{-2}$ $molL^{-1}$). The coloration solution (4 mL) was sulfuric acid (H_2SO_4, 2.55 $molL^{-1}$), ascorbic

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acid ($5.4*10^{-2}$ $molL^{-1}$), ammonium molybdate ($6.0*10^{-2}$ $molL^{-1}$), and antimony potassium tartrate ($4.1*10^{-4}$ $molL^{-1}$). The standard P solution was monopotassium phosphate (0.2194 g exact weighing after drying at 120°C for 1 h) and deionized water (1,000 mL). The standard solution was made in 50 mL volumetric flasks in a gradient series from 0.0 mL to 2.0 mL with intervals of 0.1 mL; these solutions covered the range of colorization of samples used in this study. The concentrations of TP and IP of the samples could be calculated according to the sample volume.

2.2. ^{31}P-NMR

A ^{31}P-NMR test was used to determine the forms of P in PM based on the method of soil analysis (Jarosch et al., 2015). Tree, No-Tree, Background and PKU PM samples were collected as above, and all samples were tested. The PKU samples were collected from the 26th to 28th September 2017 (within the growing seasons). The samples from the greenhouses were collected from 9th to 11th January 2018. Additionally, one sample of soil collected from the Tree shed was tested for comparison. We collected the soil sample by a soil auger of diameter 38 mm and height 20 cm, then thoroughly mixed the soil and dried it for 24 h in a drying oven. Finally, 5 g of soil was used in the ^{31}P-NMR test. The following preprocess were the same as the PM samples.

The PM samples (on glass filters) were digested with NaOH (0.25 $molL^{-1}$) and EDTA (0.05 $molL^{-1}$) at 20°C for 16 h before being purified by negative-pressure filtration and lyophilization. After the powder was dissolved in deionized water, we injected D_2O to lock the agent, adjusted the pH to 14 by adding a NaOH solution, and centrifuged the mixture at 10,000 $rmin^{-1}$ for 1 h. The clear liquid in the upper layer was extracted for ^{31}P-NMR analysis. We used a 400 MHz ^{31}P-NMR instrument (produced by the Bruker Corporation, Germany)

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with a pulse of 12 μs, 3.00 db, a P frequency at 161.9 MHz, and a relation delay pf 2 s, scanning at least 24,000 times at 25°C. For comparison, we collected one sample of soil from the "Tree", preprocessed it the same as the PM samples, and tested it with ^{31}P-NMR We were thus able to find the different P compounds between PM in the atmosphere and the soil particles.

2.3. Atmospheric P in the gas phase

We were able to collect and directly analyse the gaseous P in the atmosphere, avoiding the degradation (oxidization into phosphate) or immigration (adsorption on PM) of decreasing gaseous P. The method used was based on the technology of collecting biogenic volatile organic compounds (BVOC). We collected atmospheric P in the gas phase at the same locations as the PM (the PKU site and greenhouse sites) during September 5th, 2018 to April 10th, 2019. The instrument, a Laoying type 2033, used a 90 mm-diameter glass fibre filter to remove PM from the air and a polyurethane foam (PUF) filter to capture any remaining organic compounds. The collector operated every 48 h for each sample. The PUF was cleaned by Soxhlet extraction with acetone (16 h) and dichloromethane (16 h) followed by vacuum drying before it was installed in the instrument. After sampling, the PUF was hermetically stored under a Teflon plug at -10°C and was analysed within one week. In this work, we collected 22 samples for analysis. The molybdenum blue spectrophotometric method was also used to measure the TP of the samples.

2.4. Bag sampling

Bag-sampling is an improvement of gaseous P sampling that collects P from a single branch of a plant, as shown in Figure 2. The device consists of 4 parts. Part A is an inflow

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filter made of one glass pipe of 1.8 cm inside diameter, into which we placed a glass-fibre membrane (after heat treatment at 400℃ for 4 h), activated carbon (heat treated at 330℃ for 4 h) and clean PUF (cleaned by Soxhlet extraction with acetone and dichloromethane as described above) in that order. The device was used to remove PM and other gases (such as VOC and gaseous P emitted by the plants) from the inlet air. Part B is a small air flow pump (2 L min^{-1} standard) followed by a flow meter for correction. Part C is a Teflon sampling bag (10 L) with two interfaces. Part D is a pipe for sampling made of another glass pipe with the same size as part A, into which we put cleaned PUF to collect the gas from the sampling bag.

The device was first connected as subplot a of Figure 2. After placing one well-growing lemon branch into the bag and checking for airtightness, we pumped air into the sampling bag for 15 min to exhaust the original air in the bag. Filtered with the glass-fibre membrane, activated carbon and clean PUF, the pumped air was sufficiently clean, with no PM and volatile organic compounds. Then, the device was changed as in subplot b and constituted a closed system so that no air would exchange with the outside atmosphere. During the sampling (6 h), the air in the system was continuously cycled with the BVOP adsorbed by the PUF. After finishing the sampling, the PUF was stored and analysed using the same method described above. A blank comparison test was conducted to ensure that the collected OP was emitted from the plant placed in the bag. A total of 6 samples from similar growth and mass on different Lemon plants were available for the bag-sampling test and the calculations that followed; we used the bag with branches of similar growth and mass on different Lemon plants during the experiment.

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2.5. GC-MS

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A GC-MS test was used to determine the forms of P in the gaseous phase following the method of BVOC (Iijima et al., 2014., Bai et al., 2002, Hardt et al., 2000). Here, we developed a method to distinguish the gaseous P from the gaseous samples we collected from the greenhouse.

The collected PUFs were treated by Soxhlet extraction with dichloromethane for 24 h. Then, the liquid was concentrated by rotary evaporation and nitrogen sweeping and the solvent was switched to N-hexane. The GC-MS system used was a Hybrid Quadrupole-Orbitrap GC-MS/MS System produced by the Thermo Fisher company, which contained Quadrupole in series Orbitrap electrostatic field orbit trap technology with an EI/CI ion source. The parameters of our analysis were as follows: GC temperature key gradient: initial 50°C (hold 1 min), 2.5°C/min to 120°C (hold 0 min), and 20°C/min to 300°C (hold 5 min). Inlet condition: 250°C with no split injection and transmission line at 250°C. Carrier gas: helium at 1.0 mL/min (constant current mode). Injection volume: 1.0 μL. MS method: EI source, 300°C, transmission line 250°C, electron energy 70 eV, full scan mode, and range 40–600 (m/z). Resolution: 60,000 FWHM. Solvent delay: 3 min. For qualitative analysis, we directly tested the samples and searched the library attached by the instrument to distinguish the exact form of the OP compounds in the samples. For quantitative analysis, we used both an internal standard (using trimethyl phosphate) and an external standard method to calculate the concentration of P in the solution.

3. Results

The results of the greenhouse experiment are shown in Figure 3. The TSP concentrations (values at the head of the figure) at the Background and PKU appeared higher than those in the greenhouse. The TP concentration (the sum of each pair of blue and red bars of Figure 3)

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at the Background and PKU also appeared higher, with a large amount of PM. Note that IP in the Tree samples was lower than in the No-Tree samples; plants would affect the IP in the atmosphere. Considering the TP/TSP ratio (values at the head of Figure 3 with units of μg TP/g TSP) to eliminate any disturbance of PM concentration, the Background and PKU ratios were similar ($p>0.40$) but were significantly lower than the Tree ratios.

Figure 4 and table 1 show the results of the ^{31}P-NMR test with PM samples from the Tree, No-Tree and PKU sites. One sample of soil collected from the Tree site was included for comparison. Marks a - e are five symbols for peaks corresponding to orthophosphate, phosphate monoesters, phosphate diester, nucleic acid and pyrophosphate, respectively. The location of the peak was slightly affected by impurities or pH, and the non-negligible noise was caused by the low concentration of phosphorus in the samples. The TP concentration in each sample was different, and the area of the peaks thus could not be exploited for quantitative comparison.

Orthophosphate (peak a, ~5.5 - 6.5 ppm, the main form of IP and the final degradation product of OP) was the dominant component of all PM samples. Except for the No-Tree samples, where we detected only orthophosphate, the average relative concentration of orthophosphate of the other three atmospheric samples was over 60%. In contrast, the soil sample contained more abundant OP components than the PM samples, which led to a lower orthophosphate profile.

Phosphate monoesters (peak b, 3.5 - 5.5 ppm, the P atom is combined with one carbon atom) were detected in all samples except for the No-Tree samples. The content of monoesters of PKU was close to the soil sample, whereas the Tree samples were higher, which suggests that plants serve as major sources of phosphate monoesters.

Only a small amount of Phospholipids (peak c, ~1.0 - 3.0 ppm, a kind of phosphodiester

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released by animals, plants and microbial residues) was detected in the soil sample and none in the four atmospheric samples.

Nucleic acids (peak d, ~2 - 0 ppm, part of phosphodiesters, including nucleic acid and teichoic acid) were detected only in the soil sample and were more abundant than phospholipids.

Pyrophosphate (peak e, ~ -4.5 - -3.5 ppm, active and bioavailable inorganic compounds) was detected in all samples except the No-Tree samples (the line in the figure is cut because of no obvious peak in the high field) and reached a maximum in the PKU sample. The Tree samples had ratios of pyrophosphate similar to those of soil.

Gaseous P at the PKU site was measured as 1.5 ngP m^{-3} during the sampling period, which was ~ 1 - 2 orders of magnitude lower than the TP in PM, although it varied between growing seasons (2.3 ngP m^{-3}) and other months (1.1 ngP m^{-3}, $p<0.01$). In Tree samples, gaseous P was much higher (8.8 ngP m^{-3}, $p<0.01$), approximately 31% of the TP in PM.

The results of the bagging sampling and GC-MS test are shown in Figure 5. The form of P in the gaseous phase is phosphate ester, most likely triethyl phosphate according to the fragments of MS and physical parameters. For quantitative analysis, we obtained 19.9 pgP on average during a 6 h cycle of sampling from one tree branch.

4. Discussion

In this work, we focused on both PM and gas to determine if a P compound was emitted from plants. Considering that there are few avenues for plants to produce PM into the atmosphere other than via PBAP, it is possible for plants to release P in a gas phase, and the compound can be transformed into PM, thus causing the obvious observed deposition of P.

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4.1 Atmospheric P in PM

Wind-transported dust and traffic sources were abundant and contributed most of the atmospheric P in Beijing during the winter because of the cold air cyclone from the inner Mongolia regions and North and Northwest China (National Meteorological Data Centre). The TSP outside the greenhouse was thus much higher than that in each shed.

TP in Tree samples was 41.8% higher than that in the No-Tree samples in the greenhouse, and the OP/TP ratio was doubled. Therefore, atmospheric P was emitted both from plants and soil, and there should be an important source of TP in the Tree samples. P emitted from plants had a higher OP profile than that from soil. The higher ratio of TP in TSP also indicated the contribution of plants to P in PM. Noting the fact that IP in the Tree shed was lower than that in the No-Tree shed, this result illustrated that the appearance of plants may decrease the atmospheric P emissions from soil by some reason such as humidity.

The OP/TP ratios of Background and PKU samples were lower, although the TP concentration was approximately 30% higher than the greenhouse samples. Moreover, there was no significant difference in OP/TP ratio between No-Tree, Background and PKU samples (No-Tree vs. Background $p>0.29$ and No-Tree vs. PKU $p>0.25$). This result indicated that atmospheric P values for Background, PKU and No-Tree samples were contributed by dust with low TP concentrations and low OP/TP ratios, with Background and PKU samples mixed with traffic sources. In addition, we inferred that the OP profile in the Background and PKU samples might be influenced by other sources such as combustion, in which a small amount of OP produced at high temperature was caught by the sampling instrument before its degradation. However, P compounds in the two former samples might be emitted and kept in an open environment for a relatively long time, and more OP was degraded into IP, whereas samples in the greenhouse could only stay for a relatively short

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time before collection by the instrument. Therefore, Background samples had a higher ratio of OP, and their compositions were intermediate between samples from the Tree and outside sites.

Bioderived atmospheric P is an important nutrient that is part of the ecosystem, although details of its mechanisms are still unclear. Gregory et al., 1986 found that vegetation-derived PM was important for P nutrition in a tropical forest, and atmospheric PO_4^{3-} concentrations above the trees showed a decreasing trend from the centre of the forest (157 ng m^{-3}) to the nearest coastal area (20 ng m^{-3}). Lawson et al., 1979 measured P dry/wet deposition in a South American rain forest and inferred that there was a local P internal circulation within the ecosystem via aerosols. P imported by dust from the Sahara Desert was considered to be the main P source for the Amazon basin because the P in the soil of the local tropical rainforest ecosystem was exhausted (Gross et al., 2015). However, other studies found that the dust over the Atlantic Ocean only accounted for 13% of the amount of P deposition in the Amazon, approximately the same amount of P exported by runoff from the Amazon. Therefore, there might be an internal circulation of P in the ecosystem as stated in the introduction.

4.2 ^{31}P-NMR tests

Comparing the samples of Tree and No-tree origin, phosphate monoester appears to be an important OP source from plants in PM, and we inferred that the P emitted from plants may have a structure similar to that of phosphate monoester. This compound is mainly found in inositol phosphoric acids, single nucleotide and partial degradation products of nucleic acids, and it is able to degrade into phosphate in the environment (Reitzel et al., 2007). Soil contributed both OP and IP with different constitutions, and we could distinguish the P

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emissions of inorganic dust from soil in the inventory. Comparing the samples from the greenhouse with those from PKU, a similar emission profile indicated that both urban and suburban areas emitted biogenic OP because of high vegetation coverage in the PKU campus.

Based on Zhang et al., 2012 and Turner et al., 2003, the ^{31}P-NMR method has been widely used for P analysis of environmental samples, such as soil, aquatic sediments and animal manures, since its first application in 1980 (Newman et al., 1980). It is quite difficult to apply this method directly to PM analysis because of the small mass of the samples compared with the soil or sediment used (approximately 5 g for one sample). We prolonged our sampling time and merged two samples together for one test to obtain a sufficient amount for testing. The results were searched against a spectrum library (Cade-Menun et al., 2014).

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Turner et al., 2003 showed that orthophosphate and phosphate monoester stayed stable during the process of storage and analysis treatment, without obvious deterioration within two weeks. DNA is more stable than RNA and phospholipids, and phospholipids can easily decompose into phosphate monoesters. The extraction of OP from soil by the NaOH-EDTA method might be selective, and the recovery rate of some kinds of OP components might be as low as 63%, which would lead to an underestimation of the PM (Giles et al., 2016). Other studies also agree with the OP loss during the preprocessing of samples (Jarosch et al., 2015).

^{31}P-NMR is a relatively simple method used to classify the compounds into several types that is used when the species are not known beforehand; however, the approach is constrained by the quantity and concentration of the samples. For analyses of soil, fertilizer, retardants and pesticides, gas chromatography (GC) and high-performance liquid chromatography with mass spectrum (HPLC-MS) have been widely applied and have a much lower detection limit, on the order of pg P mL^{-1}, but the target species to be quantitatively analysed must be known. Proton-transfer-reaction-mass-spectrometry (Ruuskanen et al., 2011) and silicone tubes (Ooki et al., 2008) are also common methods for VOC analysis.

Recently, a single-particle mass spectrometry method has been used to demonstrate that the particle size of biogenic sources is distributed at ~0.2 - 3 μm (Zawadowicz et al., 2017), which accounts for ~0.04% - 2% of the total amount of the particles in the range, and a biological aerosol may exist in the form of internal mixing. The P in PM may have 2%~17% derived from biogenic sources. It is necessary to determine the specific components and develop a method of testing.

4.3 P in gaseous phase

In addition to the evidence of plants being a source of atmospheric P in PM from the PKU and greenhouse sites, we also detected and directly analysed the P compounds in the gas phase. Since we treated the samples with the method of IP, there was no obvious signal of P for the PUF. However, the method of TP worked, and we could thus conclude that the materials on the PUF were almost all OP.

Our bag-sampling device was developed from a method used for collecting BVOC from the atmosphere. There are some more-widely used methods to collect and analyse BVOC (Iijima et al., 2014). Active carbon has been used in previous studies (Uzmez et al., 2015), with good repeatability and acceptable accuracy, but the sampling time is relatively long, and the interruption by temperature and humidity is thus considerable. Fewer studies use active carbon in precise and trace VOC analysis. Solid-phase microextraction (SPME) fibres have

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become popular in recent studies (Uzmez et al., 2015) because of the method’s strong capacity of extraction for a wide range of compounds, its high recovery rate and high accuracy and its short sampling and analysis time; however, the shortages are expensive for the column and preprocess device. This would be ideal method for BVOC analysis but we did not use this method due to instrumentation limitations. PUF is widely used in the measurement of polycyclic aromatic hydrocarbons and has a good capacity in the adsorption of VOC (Ho et al., 2009). In this work, it met the needs of our sampling conditions (a long time and cycled airflow in bag-sampling) and was comparable with our analysis method of P in PM, and we chose PUF to enrich the gaseous P in our experiments. This result could be used to estimate the emission factor of the plants.

We inferred that the plants emitted gaseous P that was rapidly converted to a solid phase, which resulted in little P remaining in the gas phase because there are almost no stable compounds of P in gas phases according to previous studies (Beck et al., 2005). Our results suggest that plants emit P not only in the form of PBAP as reported in previous studies (Heald et al., 2009) but also in some volatile compounds via a gas phase. We suggest that atmospheric P emissions from plants is a common and relatively wide phenomenon that increases the atmospheric P flux depending on the type of land use. Emission rates and constituents might vary for different plant species.

Most gaseous P emission studies have focused on phosphine. Glindemann et al., 1996 found that the PH_3 concentration appeared higher at night than in the daytime, higher in the lower terrestrial troposphere than at high altitudes, and higher in urban areas than in rural areas, and the authors noted several observations of PH_3 around Germany in the range of 0.04–157 ngPH_3 m^{-3}. Liu et al., 1999 found that PH_3 appeared more in specific areas around Beijing, China, such as reservoirs and landfills, and a maximum of 65 ngPH_3 m^{-3} in the

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summer was noted. In general, PH_3 is related to reducing atmospheres, such as wetlands and marine areas, which are suitable for the survival of microorganisms. Plants are not able to directly release PH_3, and the estimates of their PH_3 emission are rather small.

Other P compounds found in the gas phase were not included in the estimation of global atmospheric P emissions. Wang et al., 2014 explained that the imbalance between global atmospheric P emissions and deposition was caused by underestimation of combustion sources. However, this estimation of combustion-related P emissions contains large uncertainties (0.5–4.4 TgP yr^{-1} with a 90% confidence interval). Wang's method depended on the P concentration in fuel and ash as well as the conditions of combustion; however, there are studies that proposed gaseous P emission in flue gases from combustion (Beck et al., 2005). Ahl et al., 1988 inferred that gaseous P consisted of soluble orthophosphate (H_3PO_4) and tetraphosphine oxide (P_4O_{10}) and that these compounds condensed and mixed with other particles in a short time given their unstable chemical properties at normal temperatures, which resulted in concentrations of P in particles of small size that were much higher than those in particles of larger size. There is a considerable concentration of phosphorus on particulate matter smaller than 0.05 μm during coal combustion but it is difficult to correlate this concentration to the concentration of fly ash PM. Raison et al., 1985 found that volatile P was important during combustion and inferred the forms as P_4O_{10} and P_4O_6. Volatile P condensed and mixed with other particles in a short time due to its unstable chemical properties at normal temperatures, which resulted in the concentration of phosphorus in particles of a small size being much higher than that in large particles. This result indicated that there could be large uncertainties when we estimated the P emissions by Wang's method and that the emission estimation could be improved with respect to this sector.

Moreover, there were several sources of atmospheric P not included in the previous

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inventory because of the small amount of emissions and the complexity of human activity. For example, organophosphate pesticides (Degrendele et al., 2015, Coscollà et al., 2011) appeared at a 12 pgm^{-3} concentration in agricultural land. Gaseous organophosphate ester-flame retardants (OPE) are an abundant source of OP (Castro-Jiménez et al., 2016) and were measured as 0.04–0.8 ng m^{-3} (Pagels et al., 2009). However, the fluxes and burden of these sources are difficult to estimate and could be considered in future work.

We designed our experiment using a single species of plant, lemon trees, and a single sampling area in Beijing in this research, which might not be representative of global emissions. For example, the TP concentrations in PM might vary with the climatic zones, length of the growing seasons and plant types. In addition, we did not distinguish OP emitted by plants from that of combustion. This limitation might have resulted in an overestimation of OP from plants. It is necessary to consider these variables when we refine the global emission inventory of P.

5. Conclusions

In this work, we found a contribution of atmospheric P emitted by plants in an OP form. ^{31}P-NMR testing showed that the main composition provided by plants is phosphate monoesters. The P in the gas phase was measured directly and appeared to be 1 - 2 orders of magnitude lower than the TP concentration in PM but was higher during plant growing seasons. According to the bag-sampling and GC-MS tests, we inferred that the atmospheric P emitted by plants was in the form of triethyl phosphate. Due to the instability of this substance, triethyl phosphate might rapidly transfer onto PM and then be counted as PBAP in aerosol studies. More research into the mechanisms and measurements of atmospheric P emissions should be conducted without neglecting this biogenic source.

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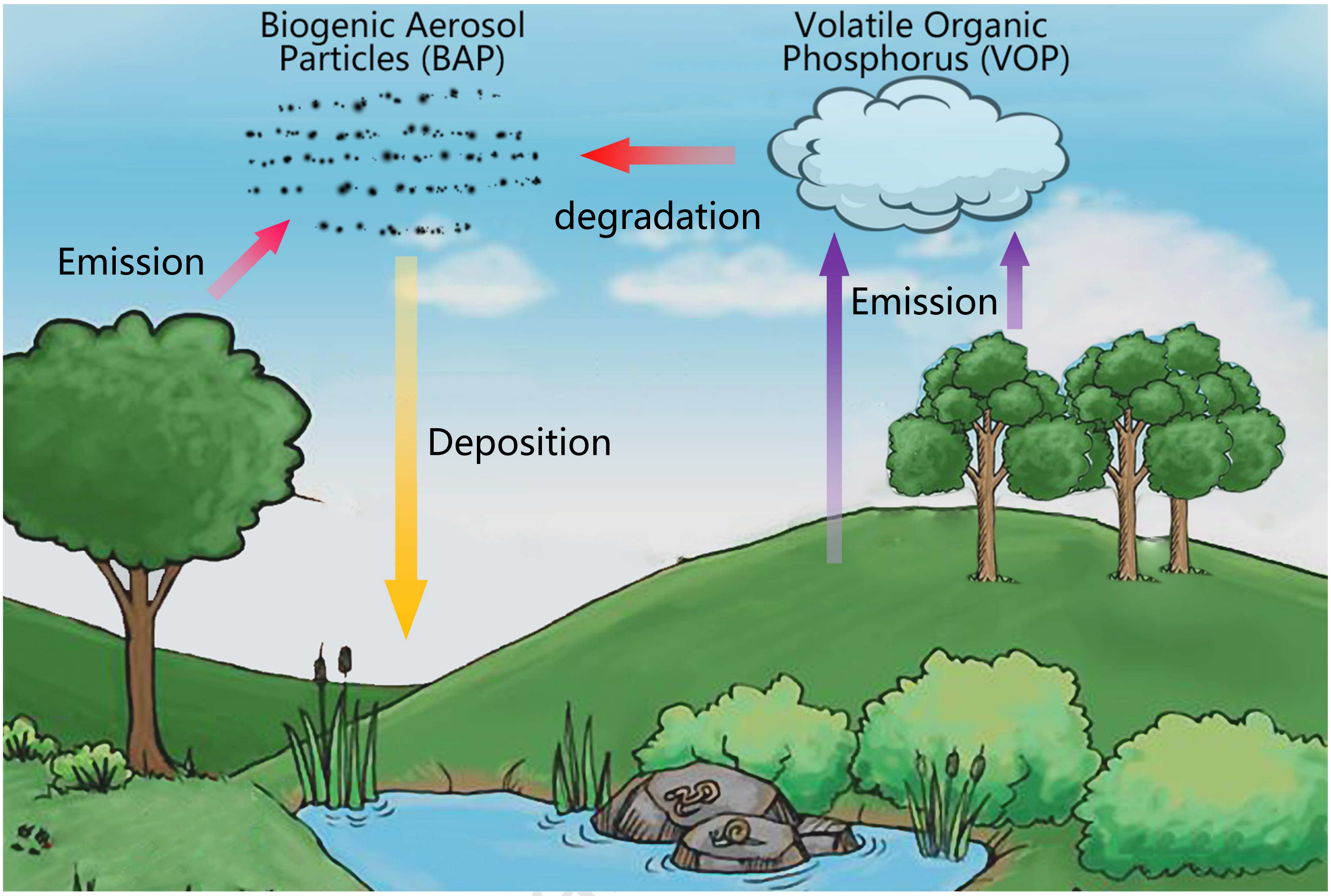
Graphical abstract



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List of Tables and Figures

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Table 1. A summary result of the ^{31}P-NMR test. It shows the normalized area ratio of five signal peaks in every sample. Names of each sample are given in the first column. Tree represents the sample from the shed under lemon cultivation. No-Tree represents the sample from the shed without plants. Soil is one soil sample collected from the Tree shed. PKU is the long-term observation. Mark a ~ e are 5 symbol signal peaks, representing orthophosphate, phosphate monoesters, phospholipid, nucleic acid and pyrophosphate, respectively.

Name	a	b	c	d	e
Soil	38.4%	27.5%	10.5%	16.8%	6.7%
PKU	59.5%	25.6%	0.0%	0.0%	14.9%
Tree	100.0%	0.0%	0.0%	0.0%	0.0%
No-Tree	58.0%	35.1%	0.0%	0.0%	6.9%

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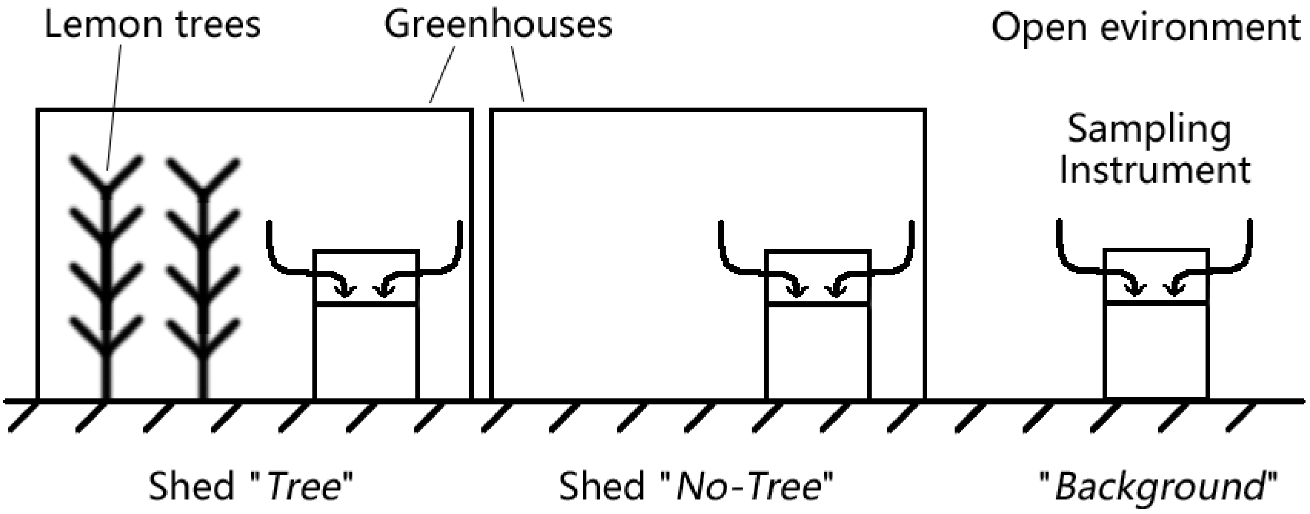

Figure 1. The sampling condition used in the greenhouse experiment. The first shed of the greenhouse is used for lemon cultivation (shed Tree), while the other shed contained the same soil but no plants (shed No-Tree). One PM collector was placed in each shed. The third PM collector was located outside the greenhouse, exposed to the open environment (Background).

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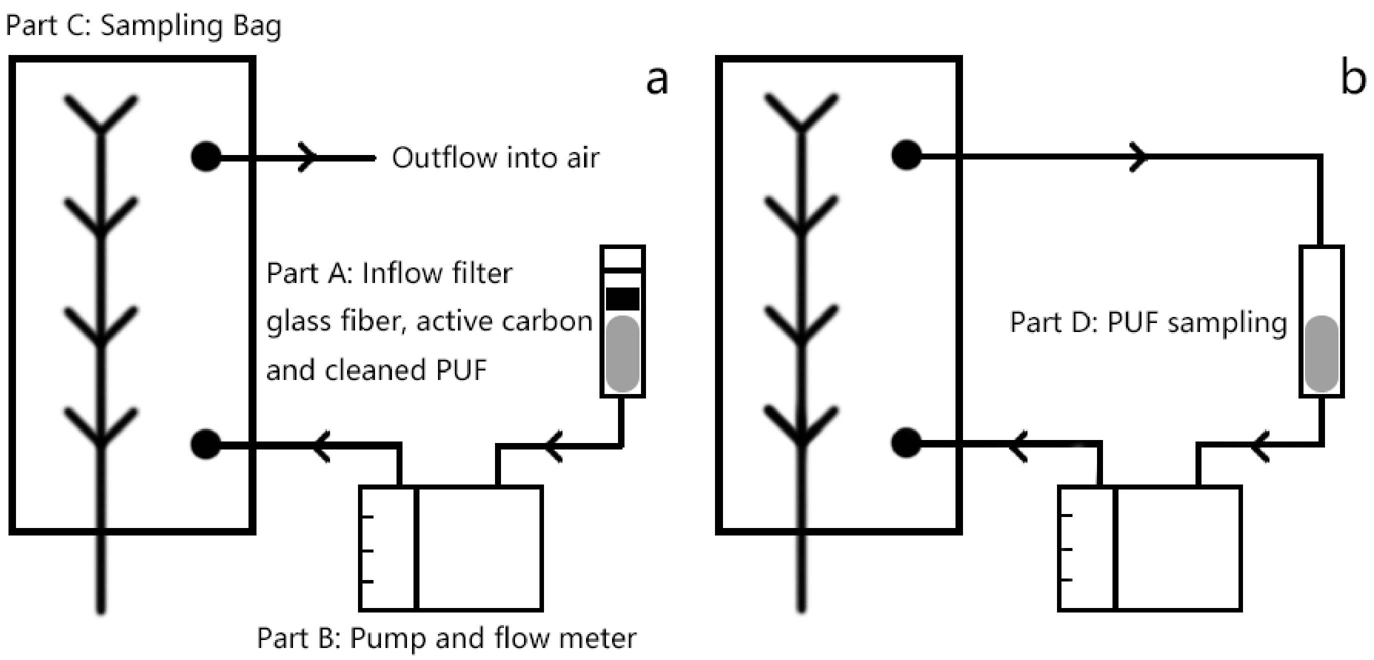

Figure 2. Construction of the bag-sampling device. Subplot a and b is the two successive steps of sampling on one single branch of plant. Part A: an inflow glass pipe filter with a glass-fiber membrane, activated carbon and cleaned PUF to remove PM and other gas from the inlet air. Part B: a small air flow pump and a following flowmeter for correction. Part C: the Teflon sampling bag with two interfaces. Part D: a sampling glass pipe with cleaned PUF to collect the gas from the sampling bag.

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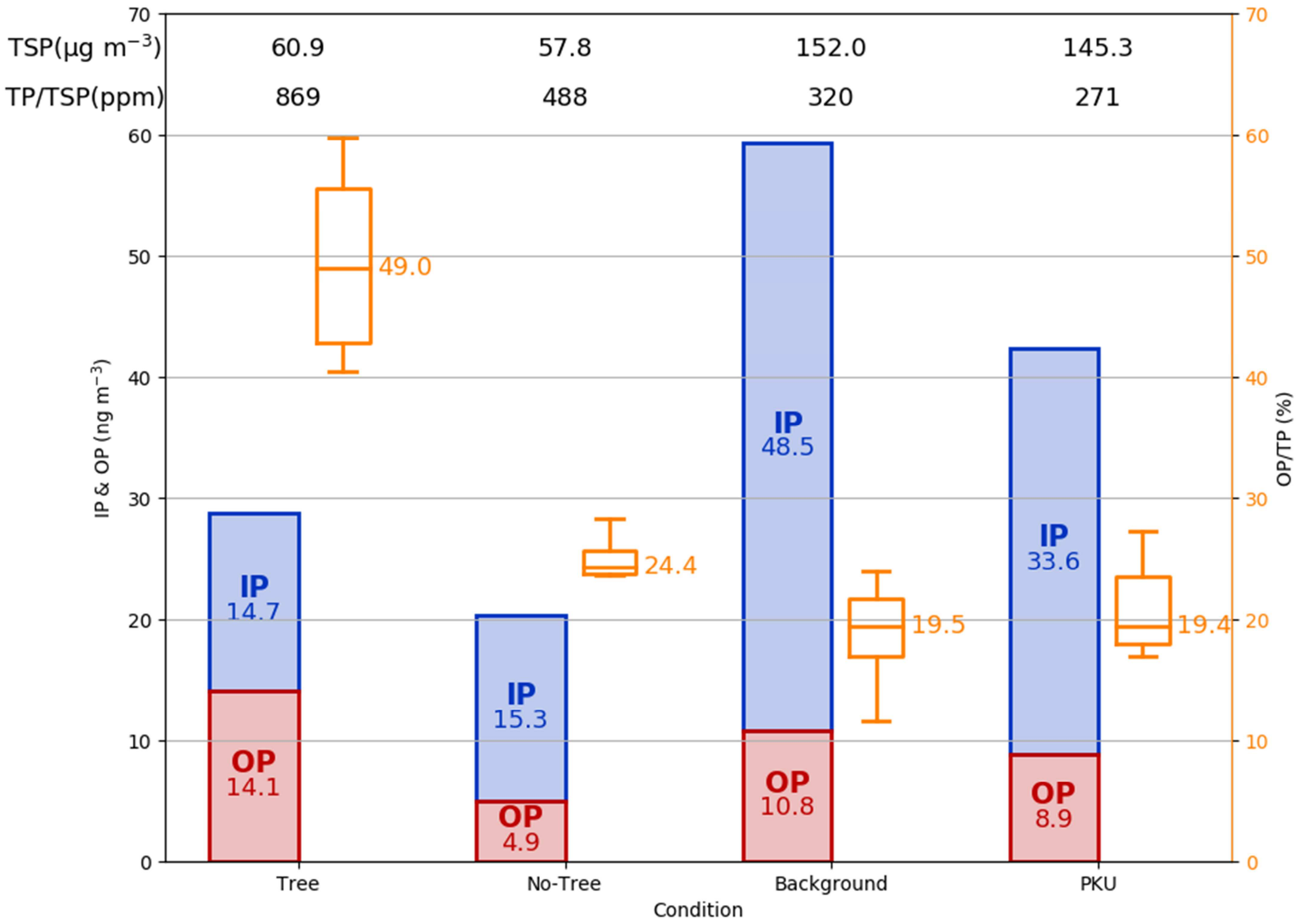

Figure 3. The results of the greenhouse experiment. The blue and red bars represent the IP and OP concentration (ngP m^{-3}, using the left Y-axis) in PM, respectively, and the orange boxes represent the OP/TP ratio (%, using the right Y-axis); the upper error bar, upper edge, middle line, lower edge and lower error bar of a box are the maximum, 75% 50%, 25% quantiles and minimum of the OP/TP ratios, respectively. Tree, No-Tree and Background represent the three sampling conditions in the experiment. PKU represents the results of observation at the PKU site during the same period as the greenhouse experiment (25th December 2017 to 6th April 2018) for comparison.

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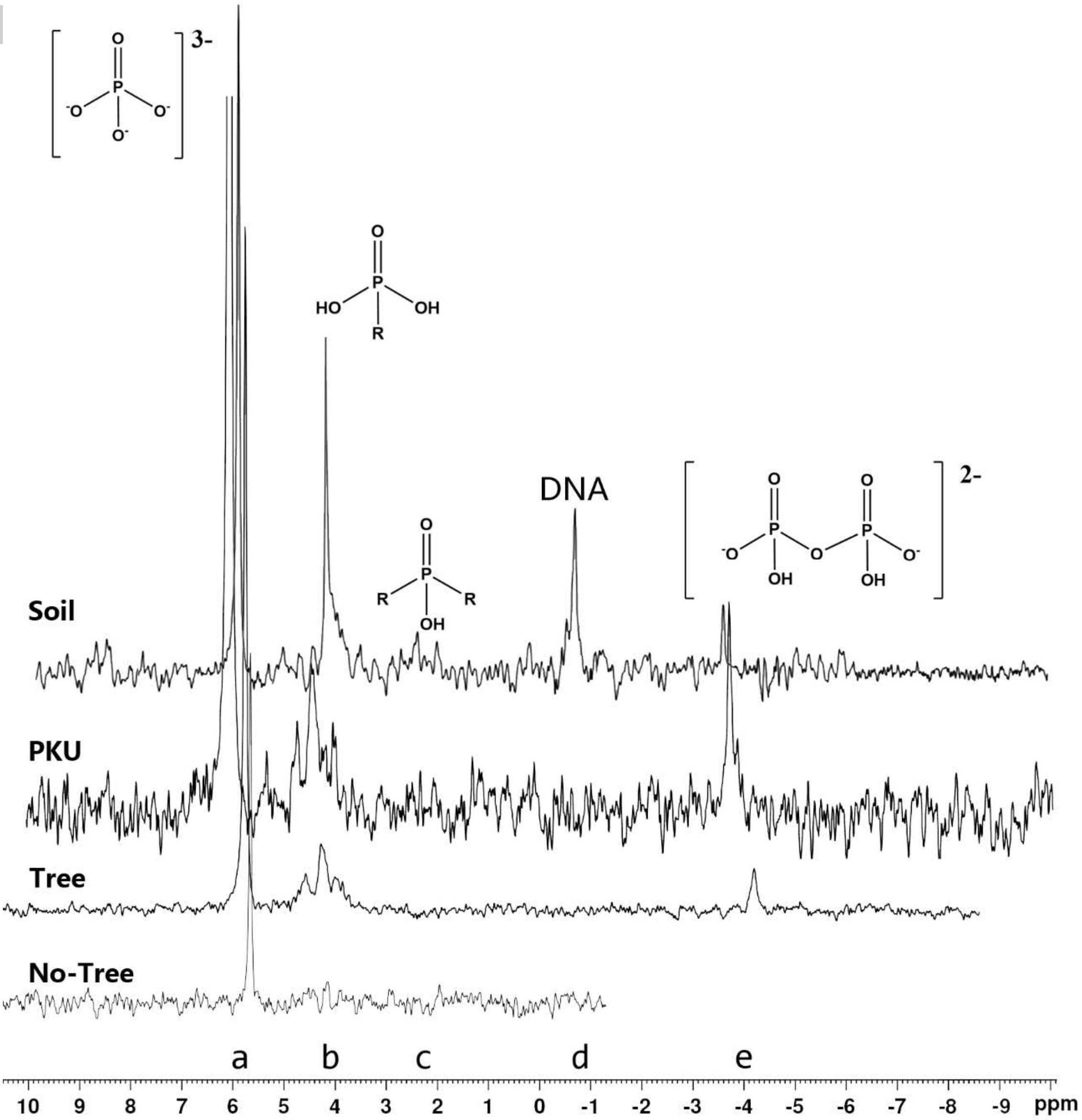

Figure 4. The results of the ^{31}P-NMR test of the three PM samples and one soil sample. The X-axis is the chemical shift of the signals. Tree and No-Tree represent two sampling conditions in the experimental plants. There was no obvious peak showing in the high field of the No-Tree sample, and it was removed automatically by the instrument. PKU represents the results of observation at the PKU site from 26th to 28th September. 2017 (within the growing season) for comparison. Soil is one soil sample collected from Tree. Marks a to e are five signal peaks, presenting orthophosphate, phosphate monoesters, phosphate diester, nucleic acid and pyrophosphate, respectively.

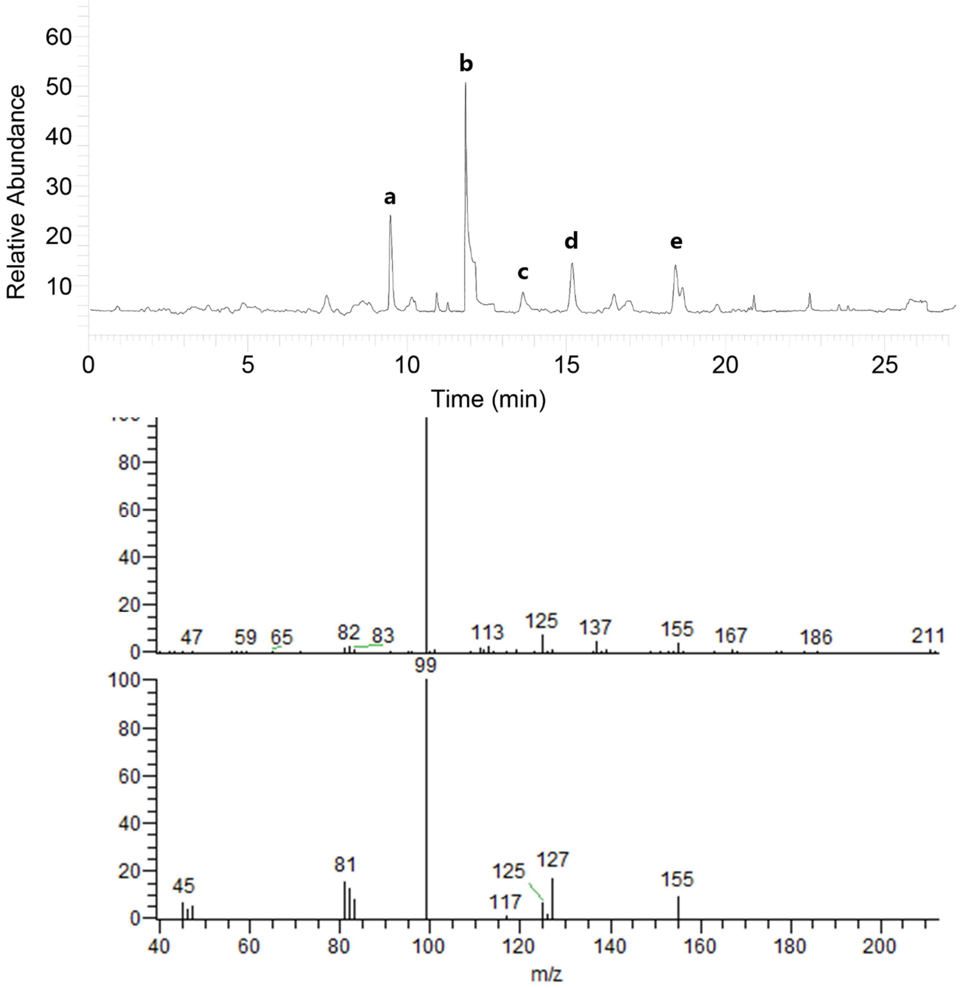

Figure 5. The results of the GC-MS test of one bag-sampling analysis in the shed Tree. The upper subplot is the GC result, in which the X-axis is the retention time in GC and the Y-axis is the relative abundance of the signal. The 5 peaks represent compounds, while we ignored the other compounds, such as BVOC at a low concentration or without P. The 5 compounds are: β-pinene, d-limonene, triethyl phosphate, citronellal, and dipropyl phthalate. The lower subplot is the comparison of the results of the GC-MS test and standard data attached to the instrument. The X-axis shows the mass-to-charge ratio (m/z) in the MS test, and the Y-axis is the relative abundance of the signal. The upper subplot is the result of the sample, and the lower subplot is the data of triethyl phosphate in the database.

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- Atmospheric total phosphorus and organic phosphorus on particulate matter was higher while plants were present.
- Phosphate monoesters is the main form of phosphorus in PM contributed by plants.
- Atmospheric gaseous P is 1-2 orders of magnitude lower than P in particulate matter.
- Atmospheric gaseous P appeared to double during plant growing seasons relative to other months.
- P emitted by plants is identified as triethyl phosphate.

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There is no conflict of interest in this study.

Journal Pre-proof

Journal Pre-proof

Wei Li: Conceptualization, Methodology, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing

Bengang Li: Conceptualization, Methodology, Project administration, Funding acquisition

Shu Tao: Conceptualization

Philippe Ciais: Writing - Review & Editing

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Bo Fu: Investigation, Data Curation, Validation

Tianya, Yin: Writing - Review & Editing

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Jie An: Investigation

Yunman Han: Investigation

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