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2 **Missed atmospheric organic phosphorus emitted by terrestrial plants, Part 2:**3 **Experiment of volatile phosphorus**4
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28

29 **Abstract**

30 The emission and deposition of global atmospheric phosphorus (P) have long been
31 considered unbalanced, and primary biogenic aerosol particles (PBAP) and phosphine (PH₃)
32 are considered to be the only atmospheric P sources from the ecosystem. In this work, we
33 found and quantified volatile organic phosphorus (VOP) emissions from plants unaccounted
34 for in previous studies. In a greenhouse in which lemons were cultivated, the atmospheric
35 total phosphorus (TP) concentration of particulate matter (PM) was 41.8% higher than that in
36 a greenhouse containing only soil, and the proportion of organic phosphorus (OP) in TP was
37 doubled. ³¹P nuclear magnetic resonance tests (³¹P-NMR) of PM showed that phosphate
38 monoesters were the main components contributed by plants in both the greenhouse and at
39 an outside observation site. Atmospheric gaseous P was directly measured to be 1–2 orders
40 of magnitude lower than P in PM but appeared to double during plant growing seasons
41 relative to other months. Bag-sampling and gas chromatography mass spectrometry (GCMS)
42 tests showed that the gaseous P emitted by plants in the greenhouse was triethyl phosphate.
43 VOP might be an important component of atmospheric P that has been underestimated in
44 previous studies.

45

46 **Key words**

47 Growing seasons; Volatile organic phosphorus; Bag-sampling; Gas chromatography mass
48 spectrometry; ³¹P nuclear magnetic resonance

50 Phosphorous (P) plays an important role in ecosystems as a major nutritional element
51 that is necessary for the building blocks of living systems and participates in the
52 physiological and chemical processes of life (Chen et al., 2016). The biogeochemical cycle
53 of phosphorus mainly involves the lithosphere, pedosphere, hydrosphere, biosphere and
54 anthroposphere, and the burden and flow of P in the cycle has been studied (Ruttenberg et al.,
55 2003). P emissions through the atmosphere have been estimated to be 3.5 Tg yr^{-1} (Wang et al.,
56 2014), which is approximately 5% of the global total P flow, but atmospheric P could be the
57 dominant limiting element for some ecosystems (Mahowald et al., 2005, Krom et al., 2010).
58 For example, transoceanic dust from deserts and arid areas could be an important P source
59 for some tropical forests and remote islands (Graham et al., 1981).

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

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

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

76 Atmospheric P from the organisms in terrestrial ecosystems has been regarded to be only
77 PBAP (0.16–1.00 TgP yr⁻¹) and PH₃ (0.2 GgP yr⁻¹), which provide a small part of the total P
78 flow (Wang et al., 2014). However, this value was considered simply proportional to the
79 biomass of the plants (Mahowald et al., 2008). This strategy might introduce large system
80 biases if the types and emission mechanisms for different types of vegetation and other
81 biogenic aerosols related to bacteria, fungi, and pollen are not considered (Myriokefalitakis
82 et al., 2016).

83 In addition, studies of atmospheric P in a gas phase have mostly focused on PH₃ from
84 wetlands or rice paddies (Han et al., 2000, 2011), which contribute much less to the total P
85 flow (0.2 Gg yr⁻¹, Wang et al., 2014). Few stable gaseous P compounds have been reported
86 but some other studies have proposed a mechanism of P emission in gas (Beck et al., 2005).
87 This aspect of P was not included in the global atmospheric P inventory.

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

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

101 2. Materials and Methods

102 2.1. PM Sampling conditions and analysis method.

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

106 The sampling site was in Beijing, China, which is in a northern hemisphere warm
107 temperate semi-humid monsoon climate zone and is over 110 km from the nearest marine
108 environment, the Bohai Sea. The annual average temperature is 11 - 13°C, with altitudes of
109 below 50 m. In the downstream of cold air from Siberia, the coldest month in Beijing is
110 January. In cold seasons, cold air cyclones from inner Mongolia regions carry sand and dust
111 from parts of North and Northwest China. As the cyclones move eastward and southward,
112 the dust affects the Beijing area. The average number of sandstorm days in 2017-2018 was
113 6.9 according to the National Meteorological Data Centre online dataset. Precipitation in
114 summer, ~600 - 800 mm with the north Pacific monsoon, accounts for approximately 3/4 of
115 the annual precipitation. The zonal vegetation is warm temperate deciduous broadleaf forest
116 and warm coniferous forest. The greenhouse is located in Beianhe, a suburban area with
117 relatively low population density approximately 30 kilometres from the centre of Beijing and
118 approximately 500 metres from the nearest roads. The sheds of the greenhouses were used
119 for fruit and vegetable farms, and the vegetation coverage was ~68% (Hu et al, 2018).
120 Peking University (PKU) is located between the 4th and 5th ring roads of the city and has an

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

126 Two sheds in the greenhouse and three PM collectors were used in this study, as shown
127 in Figure 1. The area of one shed is approximately 150 m², and the temperature is
128 approximately 24°C during the daytime, with ventilation through a reserved air seam. A
129 high-flow atmospheric particle collector was used, the Laoying type 2031 (with a 1 m³ min⁻¹
130 flow and 25*20 cm glass fibre filter; produced by Qingdao Yingying Environmental
131 Technology Co., Ltd., Qingdao, China). Each instrument was run for 48 h to obtain one PM
132 sample. We collected total suspended particles (TSP) as our PM samples in this experiment.
133 The sampling site at PKU was on the roof of a 7-floor campus building, approximately 24
134 metres above the ground and approximately 50 metres from the nearby street, and the
135 instrument was the same as those used in the greenhouses.

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

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

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

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

165 The digestion solution for one part of one sample was sulfuric acid (H_2SO_4 , 2.55 molL^{-1} ,
166 2 mL), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, 0.50 g) and deionized water (H_2O , ~85 mL). The
167 reduction solution (5 mL) was sodium sulfite (0.74 molL^{-1}) and sodium thiosulfate (9.3×10^{-2}
168 molL^{-1}). The coloration solution (4 mL) was sulfuric acid (H_2SO_4 , 2.55 molL^{-1}), ascorbic

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

177 2.2. ^{31}P -NMR

178 A ^{31}P -NMR test was used to determine the forms of P in PM based on the method of soil
179 analysis (Jarosch et al., 2015). Tree, No-Tree, Background and PKU PM samples were
180 collected as above, and all samples were tested. The PKU samples were collected from the
181 26th to 28th September 2017 (within the growing seasons). The samples from the greenhouses
182 were collected from 9th to 11th January 2018. Additionally, one sample of soil collected from
183 the Tree shed was tested for comparison. We collected the soil sample by a soil auger of
184 diameter 38 mm and height 20 cm, then thoroughly mixed the soil and dried it for 24 h in a
185 drying oven. Finally, 5 g of soil was used in the ^{31}P -NMR test. The following preprocess
186 were the same as the PM samples.

187 The PM samples (on glass filters) were digested with NaOH (0.25 molL^{-1}) and EDTA
188 (0.05 molL^{-1}) at 20°C for 16 h before being purified by negative-pressure filtration and
189 lyophilization. After the powder was dissolved in deionized water, we injected D_2O to lock
190 the agent, adjusted the pH to 14 by adding a NaOH solution, and centrifuged the mixture at
191 $10,000 \text{ rmin}^{-1}$ for 1 h. The clear liquid in the upper layer was extracted for ^{31}P -NMR analysis.
192 We used a 400 MHz ^{31}P -NMR instrument (produced by the Bruker Corporation, Germany)

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

199 2.3. Atmospheric P in the gas phase

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

214 2.4. Bag sampling

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

217 filter made of one glass pipe of 1.8 cm inside diameter, into which we placed a glass-fibre
218 membrane (after heat treatment at 400°C for 4 h), activated carbon (heat treated at 330°C for 4
219 h) and clean PUF (cleaned by Soxhlet extraction with acetone and dichloromethane as
220 described above) in that order. The device was used to remove PM and other gases (such as
221 VOC and gaseous P emitted by the plants) from the inlet air. Part B is a small air flow pump
222 (2 L min⁻¹ standard) followed by a flow meter for correction. Part C is a Teflon sampling bag
223 (10 L) with two interfaces. Part D is a pipe for sampling made of another glass pipe with the
224 same size as part A, into which we put cleaned PUF to collect the gas from the sampling bag.

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

238

239 2.5. GC-MS

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

244 The collected PUFs were treated by Soxhlet extraction with dichloromethane for 24 h.
245 Then, the liquid was concentrated by rotary evaporation and nitrogen sweeping and the
246 solvent was switched to N-hexane. The GC-MS system used was a Hybrid
247 Quadrupole-Orbitrap GC-MS/MS System produced by the Thermo Fisher company, which
248 contained Quadrupole in series Orbitrap electrostatic field orbit trap technology with an
249 EI/CI ion source. The parameters of our analysis were as follows: GC temperature key
250 gradient: initial 50°C (hold 1 min), 2.5°C/min to 120°C (hold 0 min), and 20°C/min to
251 300°C (hold 5 min). Inlet condition: 250°C with no split injection and transmission line at
252 250°C. Carrier gas: helium at 1.0 mL/min (constant current mode). Injection volume: 1.0 µL.
253 MS method: EI source, 300°C, transmission line 250°C, electron energy 70 eV, full scan
254 mode, and range 40–600 (m/z). Resolution: 60,000 FWHM. Solvent delay: 3 min. For
255 qualitative analysis, we directly tested the samples and searched the library attached by the
256 instrument to distinguish the exact form of the OP compounds in the samples. For
257 quantitative analysis, we used both an internal standard (using trimethyl phosphate) and an
258 external standard method to calculate the concentration of P in the solution.

260 3. Results

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

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

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

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

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

287 Only a small amount of Phospholipids (peak c, $\sim 1.0 - 3.0$ ppm, a kind of phosphodiester

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

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

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

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

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

306 4. Discussion

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

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

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

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

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

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

352 353 4.2 ^{31}P -NMR tests

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

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).

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

384 chromatography with mass spectrum (HPLC-MS) have been widely applied and have a
385 much lower detection limit, on the order of pg P mL^{-1} , but the target species to be
386 quantitatively analysed must be known. Proton-transfer-reaction-mass-spectrometry
387 (Ruuskanen et al., 2011) and silicone tubes (Ooki et al., 2008) are also common methods for
388 VOC analysis.

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

395 396 4.3 P in gaseous phase

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

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

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

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

426 Most gaseous P emission studies have focused on phosphine. Glindemann et al., 1996
427 found that the PH_3 concentration appeared higher at night than in the daytime, higher in the
428 lower terrestrial troposphere than at high altitudes, and higher in urban areas than in rural
429 areas, and the authors noted several observations of PH_3 around Germany in the range of
430 $0.04\text{--}157 \text{ ngPH}_3 \text{ m}^{-3}$. Liu et al., 1999 found that PH_3 appeared more in specific areas around
431 Beijing, China, such as reservoirs and landfills, and a maximum of $65 \text{ ngPH}_3 \text{ m}^{-3}$ in the

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

435 Other P compounds found in the gas phase were not included in the estimation of global
436 atmospheric P emissions. Wang et al., 2014 explained that the imbalance between global
437 atmospheric P emissions and deposition was caused by underestimation of combustion
438 sources. However, this estimation of combustion-related P emissions contains large
439 uncertainties ($0.5\text{--}4.4 \text{ TgP yr}^{-1}$ with a 90% confidence interval). Wang's method depended on
440 the P concentration in fuel and ash as well as the conditions of combustion; however, there
441 are studies that proposed gaseous P emission in flue gases from combustion (Beck et al.,
442 2005). Ahl et al., 1988 inferred that gaseous P consisted of soluble orthophosphate (H_3PO_4)
443 and tetraphosphine oxide (P_4O_{10}) and that these compounds condensed and mixed with other
444 particles in a short time given their unstable chemical properties at normal temperatures,
445 which resulted in concentrations of P in particles of small size that were much higher than
446 those in particles of larger size. There is a considerable concentration of phosphorus on
447 particulate matter smaller than $0.05 \mu\text{m}$ during coal combustion but it is difficult to correlate
448 this concentration to the concentration of fly ash PM. Raison et al., 1985 found that volatile P
449 was important during combustion and inferred the forms as P_4O_{10} and P_4O_6 . Volatile P
450 condensed and mixed with other particles in a short time due to its unstable chemical
451 properties at normal temperatures, which resulted in the concentration of phosphorus in
452 particles of a small size being much higher than that in large particles. This result indicated
453 that there could be large uncertainties when we estimated the P emissions by Wang's method
454 and that the emission estimation could be improved with respect to this sector.

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

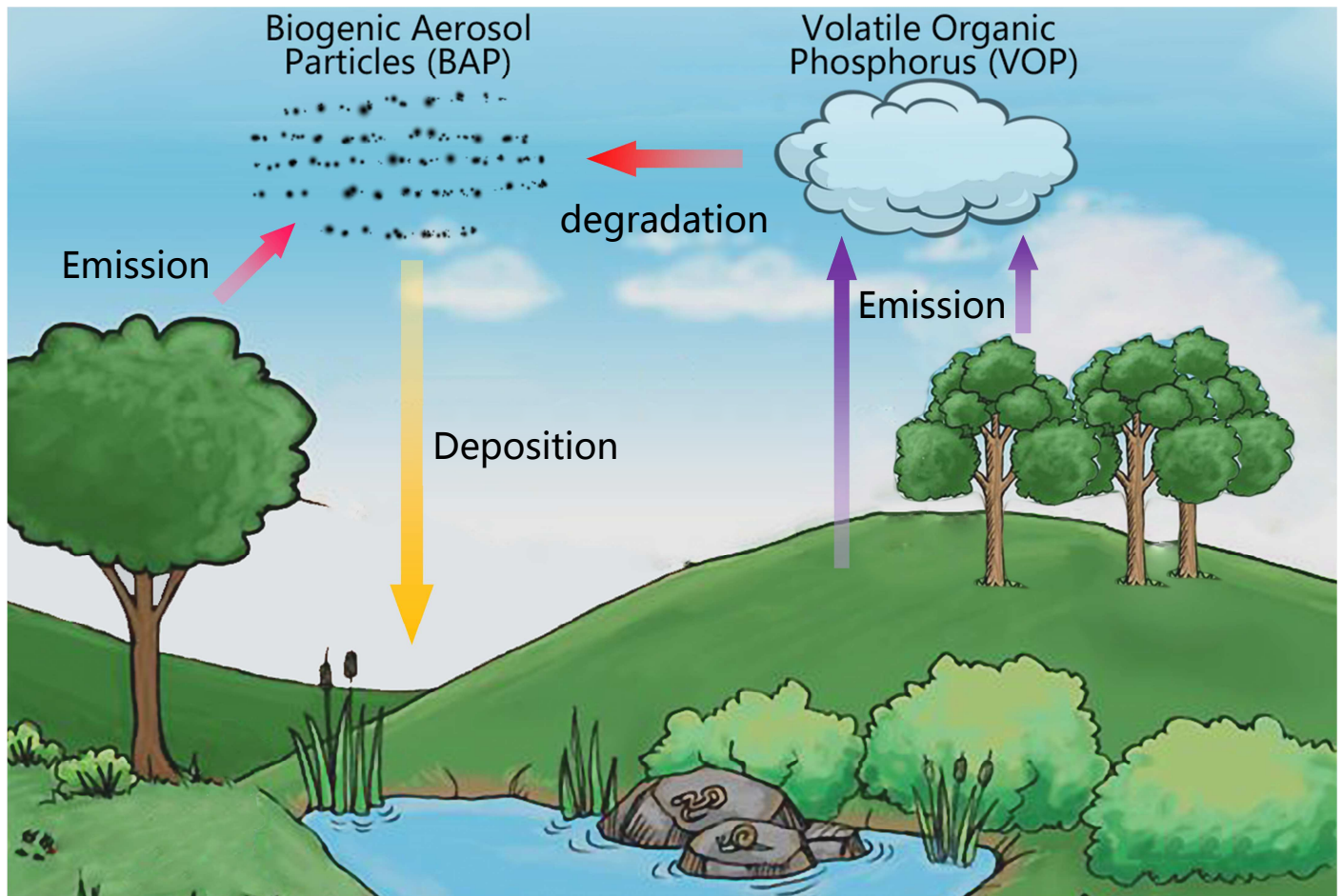
456 inventory because of the small amount of emissions and the complexity of human activity.
457 For example, organophosphate pesticides (Degrendele et al., 2015, Coscollà et al., 2011)
458 appeared at a 12 pgm^{-3} concentration in agricultural land. Gaseous organophosphate
459 ester-flame retardants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

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

470 5. Conclusions

471 In this work, we found a contribution of atmospheric P emitted by plants in an OP form.
472 ^{31}P -NMR testing showed that the main composition provided by plants is phosphate
473 monoesters. The P in the gas phase was measured directly and appeared to be 1 - 2 orders of
474 magnitude lower than the TP concentration in PM but was higher during plant growing
475 seasons. According to the bag-sampling and GC-MS tests, we inferred that the atmospheric P
476 emitted by plants was in the form of triethyl phosphate. Due to the instability of this
477 substance, triethyl phosphate might rapidly transfer onto PM and then be counted as PBAP
478 in aerosol studies. More research into the mechanisms and measurements of atmospheric P
479 emissions should be conducted without neglecting this biogenic source.

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494 Cited from website: <http://acamrmicheal.weebly.com/ecology---abiotic--biotic.html>

497 Table 1. A summary result of the ^{31}P -NMR test.

498
499 Figure 1. The sampling condition used in the greenhouse experiment.

500 Figure 2. Construction of the bag-sampling device.

501 Figure 3. The results of the greenhouse experiment.

502 Figure 4. The results of the ^{31}P -NMR test of the three PM samples and one soil sample.

503 Figure 5. The results of the GC-MS test of one bag-sampling analysis in the shed Tree.

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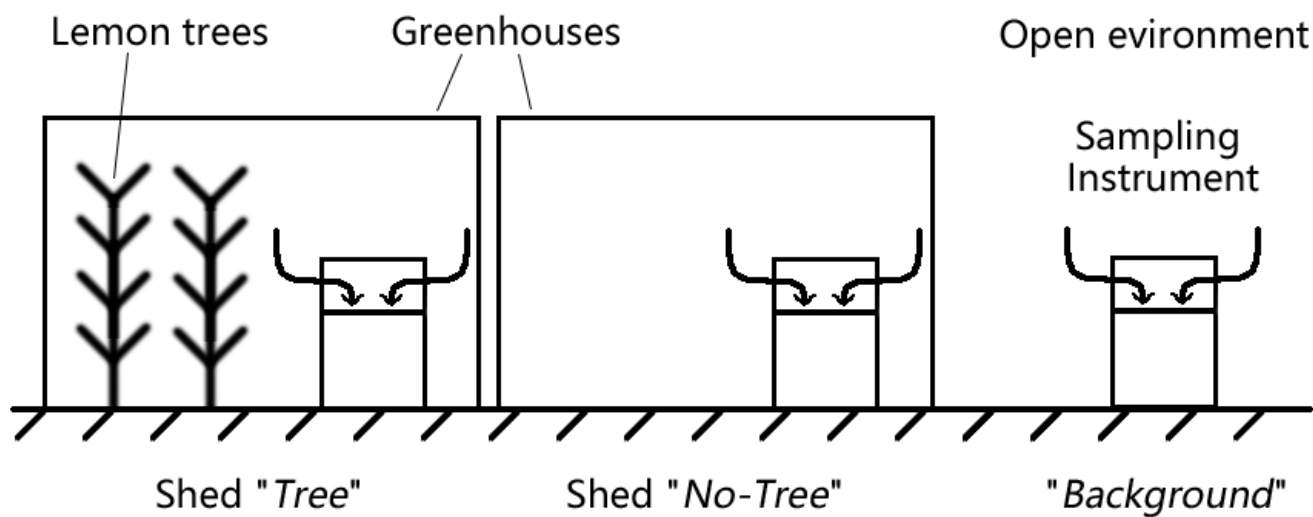
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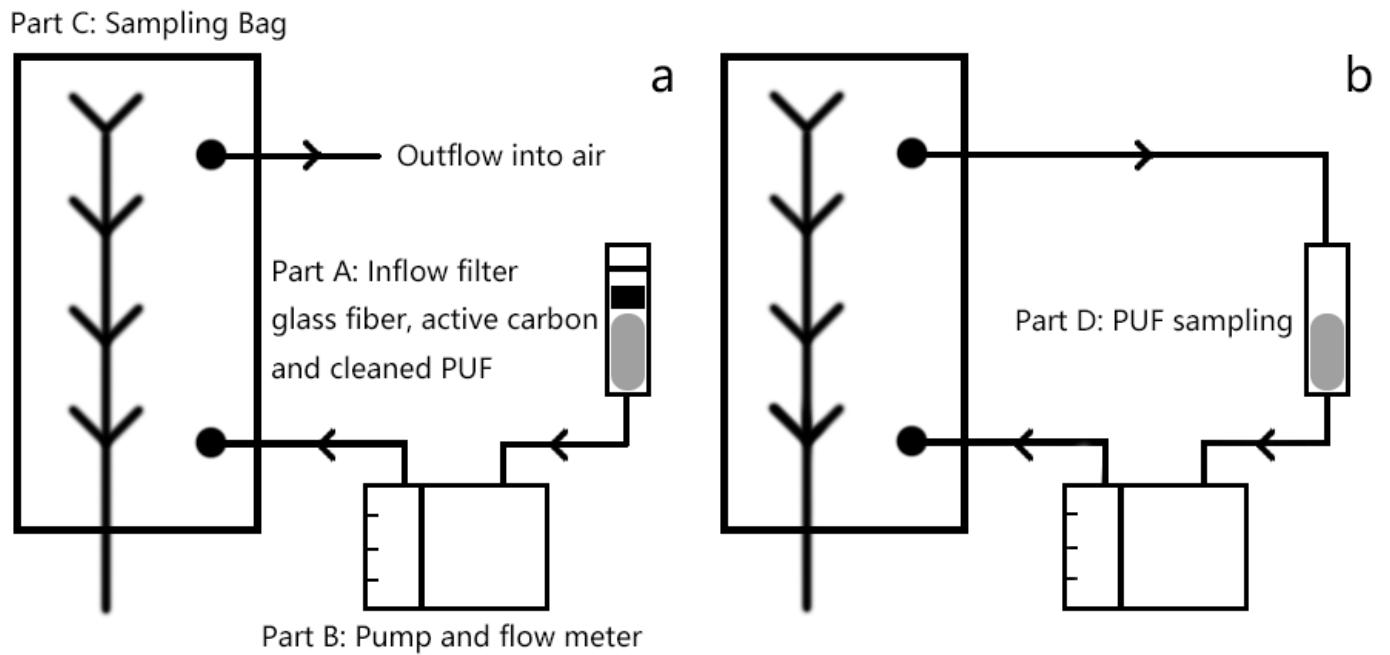
507 Table 1. A summary result of the ^{31}P -NMR test. It shows the normalized area ratio of five
508 signal peaks in every sample. Names of each sample are given in the first column. Tree
509 represents the sample from the shed under lemon cultivation. No-Tree represents the sample
510 from the shed without plants. Soil is one soil sample collected from the Tree shed. PKU is
511 the long-term observation. Mark a ~ e are 5 symbol signal peaks, representing
512 orthophosphate, phosphate monoesters, phospholipid, nucleic acid and pyrophosphate,
513 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%

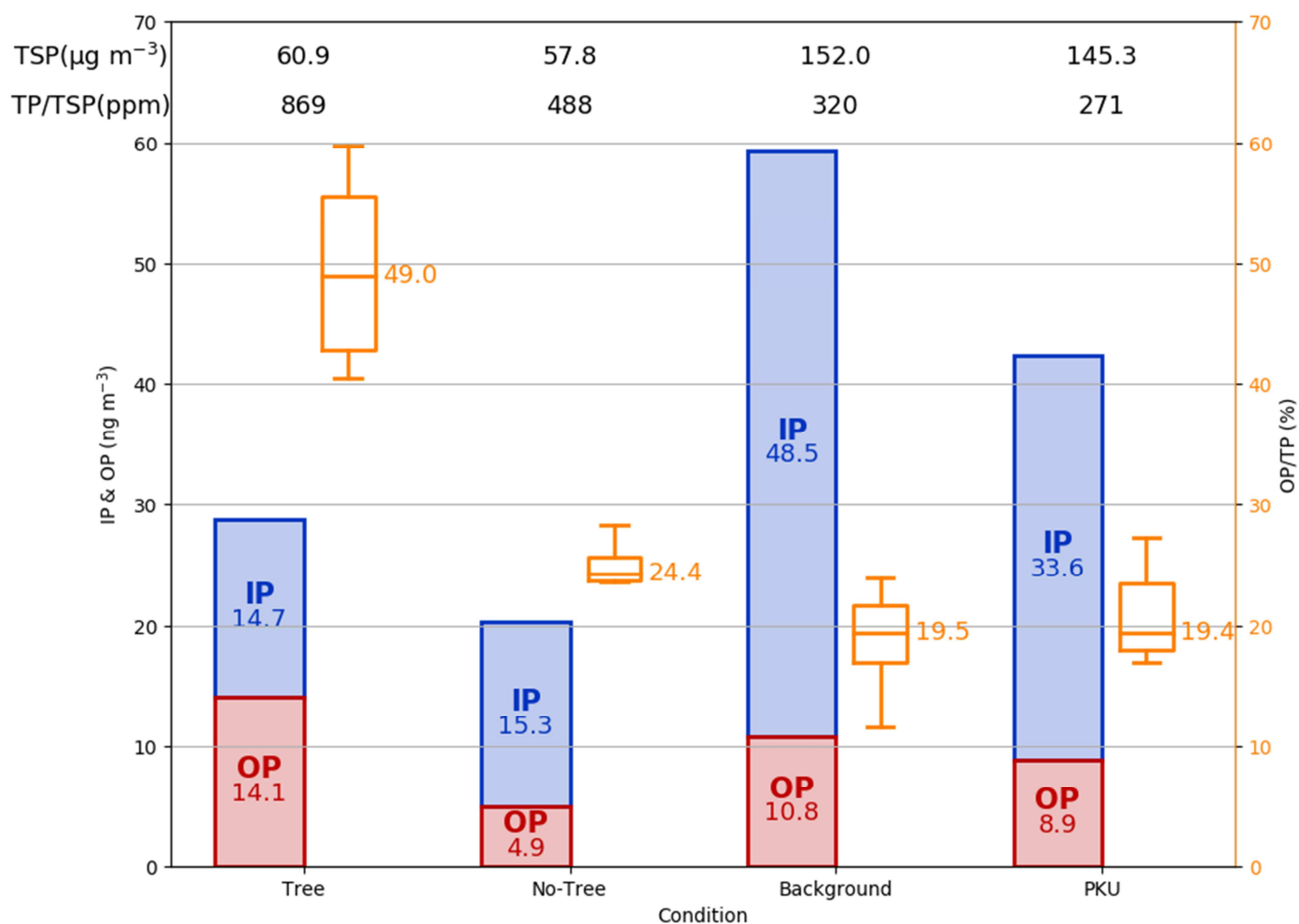
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515 Figure 1. The sampling condition used in the greenhouse experiment. The first shed of the
 516 greenhouse is used for lemon cultivation (shed Tree), while the other shed contained the
 517 same soil but no plants (shed No-Tree). One PM collector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



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



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

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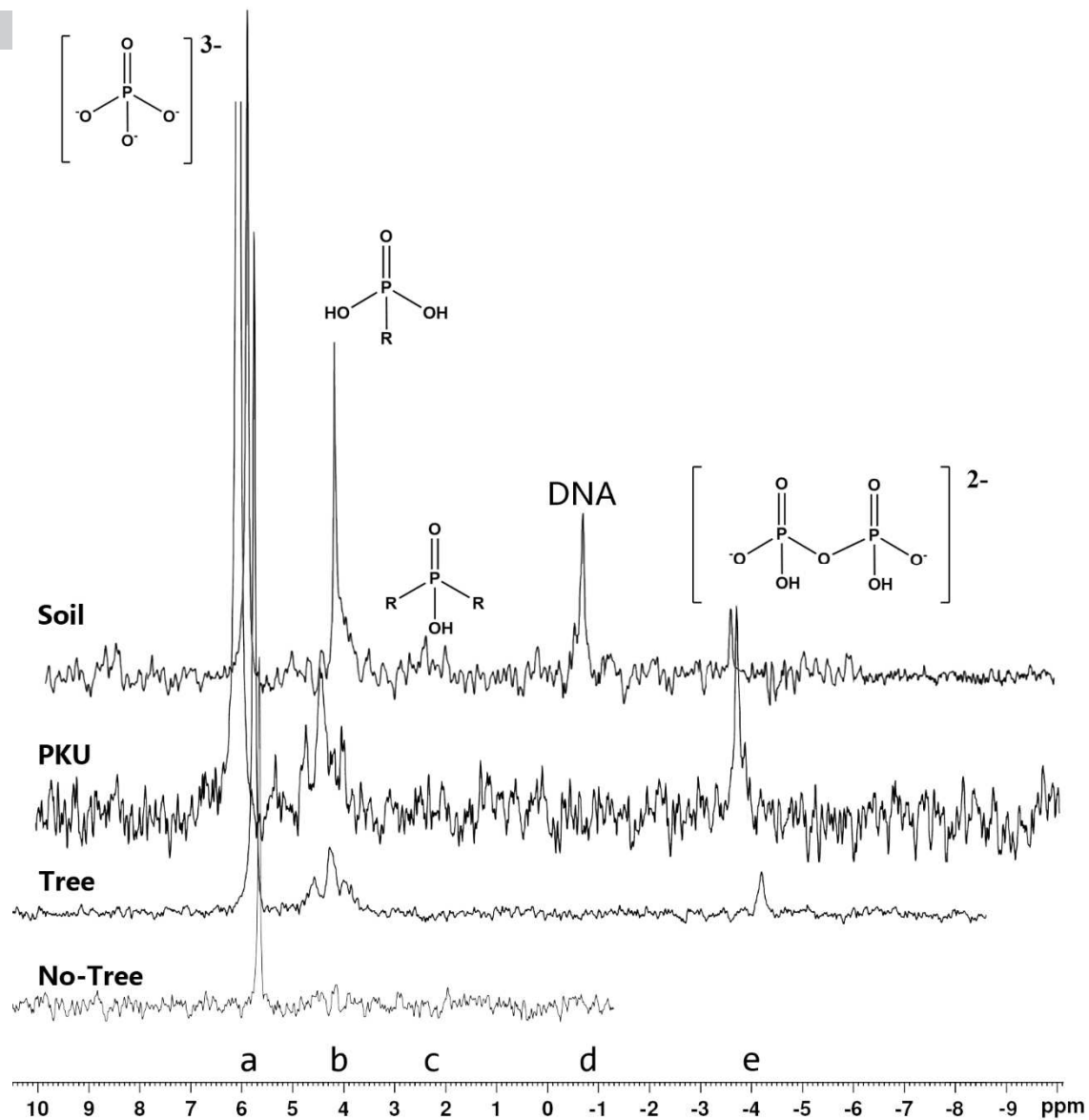


Figure 4. The results of the ^{31}P -NMR test of the three PM samples and one soil sample. The X-axis is the chemical shift of the signals. Tree and No-Tree represent two sampling conditions in the experimental plants. There was no obvious peak showing in the high field of the No-Tree sample, and it 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.

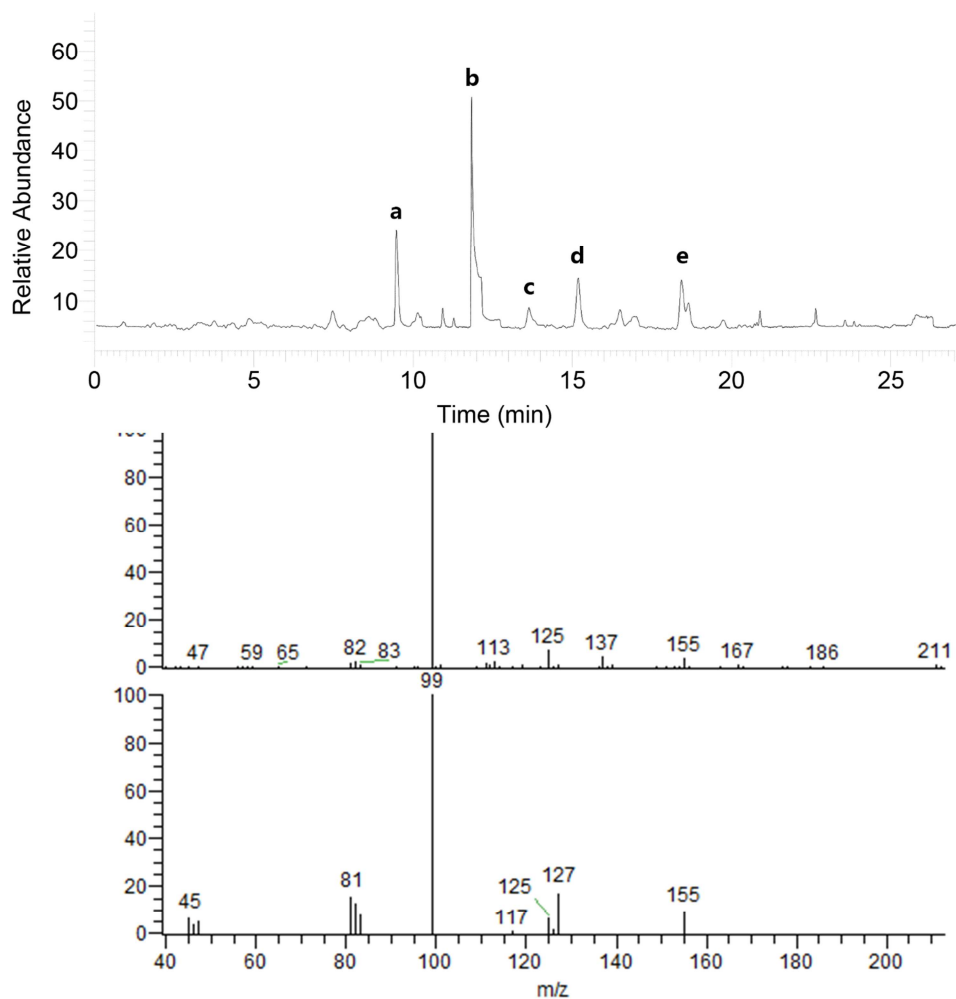


Figure 5. The results of the GC-MS test of one bag-sampling analysis in the shed Tree. The upper subplot is the GC result, in which the X-axis is the retention time in GC and the Y-axis is the relative abundance of the signal. The 5 peaks represent compounds, while we ignored the other compounds, such 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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744

- 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.

Journal Pre-proof

There is no conflict of interest in this study.

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

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Laurent Li: Writing - Review & Editing

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Tianya, Yin: Writing - Review & Editing

Xinyue Li: Writing - Review & Editing

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