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Measuring Biogenic Volatile Organic Compounds from Leaves Exposed to Submicron Black Carbon Using Portable Sensor

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Abstract: Biogenic volatile organic compounds (BVOCs) are responsible for the formation of ozone and secondary organic aerosols (SOAs). Our knowledge about how black carbon particles influence BVOC emissions from terrestrial ecosystems is limited; terrestrial vegetation captures black carbon particles as a sink. In this research, the BVOC emissions from the leaves of four terrestrial plants were measured using an RAE PGM-7300 BVOC analyzer. Then, the leaves from four types of trees were exposed to submicron carbon black for 24 h and 48 h in an ambient environment, respectively. Comparisons between the BVOC emissions before and after exposure to submicron carbon black were performed. Our results indicated that the emissions of BVOC from the leaves of four types of trees varied from 90 to 270 μg g^{-1} h^{-1} and depended on the species. The exposure to submicron black carbon particles had negligible impacts on the BVOC emissions from the leaves of four types of trees.

Keywords: BVOC; black carbon particles; exposure; carbon capture

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1. Introduction

Terrestrial plants mitigate air pollution by acting as a sink for ambient particulate matter (PM) [1,2]. A previous study reported that trees in urban areas could capture 711,000 metric tons of air pollutants (O_3, PM_{10}, NO_2, SO_2, and CO) approximately every year in the United States [3]. A review conducted by Cai et al. [4] estimated that the mean deposition of PM on leaves was 1.71 ± 0.05 g m^{-2}·wk^{-1} after reviewing 150 studies derived from 15 countries. Black carbon aerosols are a major component of ambient PM, and they are released from the incomplete combustion of liquid and solid fuels [5–8]. Studies have demonstrated that using plants is an environmentally friendly strategy with a low cost to remove black carbon particles in anambient environment [4,7]. For example, a study conducted in Denton, Texas indicated that oak trees can accumulate ambient black carbon amounts ranging from 160 to 299 mg m^{-2} in a canopy per year [9]. Researchers found that the hexatriacontane wax of leaves could interact with ambient black carbon via hydrogen bonding [10]. Our study further explored how black carbon particles can pass through the mechanical barriers in *Platanus acerifolia* tree leaves, and then eventually relocate into the mesophyll system [7].

Although terrestrial plants can serve as environmental tools for reducing black carbon in the atmosphere, they can emit biogenic volatile organic compounds (BVOCs) [11,12]. BVOCs include isoprene, monoterpenes, and sesquiterpene, which play important parts in the formation of O_3 and SOA [13]. BVOC emissions are estimated to contribute to approximately 20% and 76% of O_3 and SOA formation globally, respectively [14,15]. In China, the BVOC emissions have been estimated to increase by ~55% over the past four decades because the increases in leaf biomass from forests and crops have increased to ~118% and ~316%, respectively [16,17]. Isoprene (C_5H_8) is found to contribute the most

non-methane hydrocarbon to BVOC, accounting for a global estimated emission of approximately 5000 Tg yr^{-1} [18]. In the atmosphere, isoprene can interact with oxidizing substances including nitrate radicals, ozone, and hydroxyl radicals [19]. Since isoprene exhibits high emissions and good reactivity with hydroxyl radicals, isoprene plays a dominant role in the occurrences of photochemistry under the atmospheric boundary layer [18–20]. It was observed that the oxidation of isoprene under sunlight could result in the generation of species with low volatility, which then coagulates to generate SOA [20]. The yield rate of SOA from the oxidation of isoprene is found to be as high as approximately 3% [18–20]. Based on this estimation, the generation of SOA from the oxidation of isoprene under sunlight is supposed to be approximately 13 Tg yr^{-1} [18–20]. The emission of isoprene from terrestrial plants is associated with the intensity of sunlight and increases with an increasing temperature [21]. In several field studies, the highest level of mixing ratio of isoprene was usually found in the early evening, with mixing ratios recorded as high as a couple of ppb [21–23]. When the sun sets, the mixing ratio of isoprene decreases dramatically. In the evening, nitrate radicals are observed to be the main oxidants for the decay of isoprene [21–23]. Usually, the mixing ratio of nitrate radicals varies from 10 to 100 ppt in continental air masses under the atmospheric boundary layer [23]. In some cases, high mixing ratios of nitrate radicals up to several hundred ppt were recorded in continental air masses over North America and Europe [23]. The reaction rate between isoprene and NO_3 radicals was found to be as high as 7×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, which suggests that NO_3 radicals dominate the reaction of isoprene during the nighttime [22,24]. Other than isoprene, BVOC emissions from terrestrial plants consist of monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$), as well as oxygenated compounds (e.g., methanol, 6-methyl-5-hepten-2-one, and 2-methyl3-buten-2-ol) [24]. Though the emissions of monoterpenes, sesquiterpenes, and oxygenated compounds were lower than that of isoprene in the atmosphere, these compounds also exhibit high aerosol formation potential because of their high reactivity with oxidizing substances, including nitrate radicals, ozone, and hydroxyl radicals [22,24]. For example, β-caryophyllene, serving as the most abundant sesquiterpene, is usually emitted by terrestrial plants including deciduous trees, conifers, and flowers [25]. β-caryophyllene in the atmosphere undergoes two oxidation steps with oxidizing substances under sunlight due to the presence of two double bonds in the molecule structure [26]. The constants of reaction rates for these two reactions are found to be 1.2×10^{-14} cm^3 $molecule^{-1}$ s^{-1} and 1.0×10^{-16} cm^3 $molecule^{-1}s^{-1}$, respectively [27]. The atmospheric lifetime of β-caryophyllene is observed to be 1.5 min when the mixing ratio of O_3 is 40 ppb [26]. In this case, it is estimated that the lifetime of the first formation of chemical products is estimated to be 2.5 h [26]. The products of β-caryophyllene react with oxidizing substances during the first- and second-reaction stepwhere oxidation products are condensed in the particle phase, including β-caryophyllonic acid, β-caryophyllinic acid, β-caryophyllon aldehyde, and β-nocaryophyllon aldehyde [27].

Plants can also release increased BVOC emissions after exposure to phytotoxic air pollutants like O_3 [11]. Ozone could lead to negative influences on the metabolic processes of plants, therefore resulting in decreases in the assimilation of carbon in plants, plant growth, and the control of stomata of the leaves in plants [28]. One of the consequences associated with exposure to ozone is the reduced efficiency of water use in plants [29]. The impacts of increased ozone exposure on BVOC emission in plants are highly associated with experimental parameters, including temperature, the concentration of O_3, the species of plants, the types of BVOC, and seasonality [11]. Carriero et al. [11] investigated the BVOC emissions of 3-year-old silver birch under different levels of O_3 and found that long-term O_3 exposure could simulate BVOC emissions of 3-year-old silver birch. This finding indicated that the uptake of excess O_3 into the stomata of leaves could lead to leaf damage and decrease photosynthesis by creating reactive oxygen species (ROS), which can result in cellular death through the oxidation of cell walls [30]. The exposure to O_3 pollution leads to a lower carbon uptake by vegetation, resulting in decreased crop and timber yields. The emissions of total BVOC could increase by a factor of 5–16 in *Pinus sylvestris* L. after

exposure to elevated O_3 levels [11,12]. This effect was observed to be stronger in summer than in spring [11,12]. The concentration of 50 ppb could increase the emission of BVOC from Norway spruce by a factor of 2 using an open-field experiment [31]. In addition, an increase of 1 °C in the ambient environment and a 1.5 times greater ambient concentration of O_3 can enhance the emissions of several types of BVOCs from Scots pine [32]. The above-mentioned studies used open-field experiments to compare the variations in BVOC emissions of terrestrial plants with and without exposure to O_3 to illustrate the role of O_3 in the BVOC emissions of terrestrial plants [11,12].

Ambient black carbon particles are found to induce cellular death through the generation of reactive oxygen species (ROS) in vivo [33]. Prior studies have demonstrated that ambient black carbon particles can become hydrophilic under visible light and O_3 and can enhance oxidative capacities [34]. Atmospheric wet deposition, including rain and snow, brings aged black carbon particles into terrestrial ecosystems [35,36]. So far, limited studies have been performed to investigate the impact of exposure to black carbon particles on the total BVOC emissions from different terrestrial plants using a methodology similar to prior studies [11,12]. The results are essential for the design of engineered control systems inspired by plants to reduce ambient black carbon pollution and minimize the total BVOC emissions of plants associated with exposure to ambient black carbon pollution.

In this research, we aimed to test the hypothesis that exposure to black carbon particles during the atmospheric wet deposition process could lead to changes in the total BVOC emissions of different plants in the terrestrial ecosystem. We measured the BVOC emissions from the leaves of four terrestrial plants. Then, submicron carbon black was selected as the model compound in the exposure experiments. We compared the BVOC emissions of leaves from four types of terrestrial plants before and after exposure to model compounds of black carbon particles. The findings from this study provide valuable insights for designing environmentally friendly control technologies using leaves to remove black carbon particles from air and wet or dry deposition.

2. Methods

2.1. Black Carbon Particles

Carbon black at a diameter size of 5 nm was purchased from Sigma-Aldrich (Merck Cooperation, Darmstadt, Germany) and was selected as the model chemical for black carbon particles in a submicron size [10]. Briefly, we used a 30 mL glass flask to mix 5 nm of carbon black concentrated at 0.25 mg mL^{-1} with 2 mL of 25% ethanol solution. Then, the solution was mixed uniformly at 25 °C for 1 h. Then, the mixed solution was filtered using a syringe filter with a 0.22 μm pore. Finally, nanoscale carbon black was obtained.

2.2. Measurements of BVOC Emission

Leaves from four types of trees, including *Populus tomentosa*, *Salix babylonica*, *Broussonetia papyrifera*, and *Platanus orientalis*, were selected for the open-field measurements of BVOC because these four types of trees are typical street trees in Nanjing. The sampled leaves were placed in a cylindrical chamber made of polytetrafluoroethylene material and equipped with one port. The cylindrical chamber had a volume of 10.8 L with a diameter of 200 mm and a height of 250 mm. The BVOC concentration was measured by placing the probe of the RAE PGM-7300 BVOC analyzer (MiniRAE Lite, RAM Systems, Honeywell International Inc., San Mateo, CA, USA) in the lower part of the cylindrical chamber. A PGM-7300 BVOC analyzer equipped with a photoionization detector could measure the total emissions of isoprene and pinene ranging from 0 to 999 μg m^{-3} with a resolution of 0.1 μg m^{-3} in the atmosphere [37,38]. Before each measurement, a series of isobutene gas at the levels of 10, 20, 50, 100, and 500 μg m^{-3} were used for the in-house validation of the PGM-7300 BVOC analyzer. The levels of BVOC in the cylindrical chamber without the sampled leaves, which were used as blank samples, were measured using an RAE PGM-7300 BVOC analyzer. Then, the leaves of four types of trees including *Populus tomentosa*, *Salix babylonica*, *Broussonetia papyrifera*, and *Platanus orientalis* were weighed and put into the

cylindrical chamber. For each measurement, the experiment proceeded for 2 h at a temperature and humidity in the ranges of 18–20 °C and 40–50%, respectively. The BVOC emission rates from the leaves were estimated using the differences between the levels of BVOC in the cylindrical chamber with sampled leaves and without sampled leaves per leaf mass in one hour. To validate the BVOC results measured usingan RAE PGM-7300, solid adsorbent cartridges (Tenax TA, PerkinElmer, Waltham, MA, USA) equipped with automatic samplers at a flow rate of 200 mL min^{-1} were used for comparison while using the same sampling method. Then, the samples on the cartridges were shipped into the laboratory and analyzed by gas chromatography–mass spectrometry. A QP2010Ultragas chromatography–mass spectrometry tool (GC-MS QP2010Ultra, Shimadzu, Kyoto, Japan) was employed in this study, which included a DB-EUPAH capillary column and an electron-impact (EI) ion source with an electron energy of 70 eV in selected ion monitoring (SIM) mode.

2.3. Exposure Experiments

An exposure experiment was carried out using mature trees with heights of 3–5 m and trunk diameters of 30–50 cm. The studied trees were located in Nanjing, Jiangsu Province, China. The measurement diagram for the emission rates of BVOC from leaves in four species (*Populus tomentosa*, *Salix babylonica*, *Broussonetia papyrifera*, and *Platanus orientalis*) under the exposure of black carbon is shown in Figure 1. Prior to the experiment, the leaves were washed three times using de-ionized water. After that, a series of known levels (2, 10, and 50 μg mL^{-1}) of carbon black in submicron size were sprinkled onto four leaves with normal growth once a day. We performed a control experiment using the same procedure with the use of de-ionized water on four replicated leaves of similar ages and leaf areas with normal growth. After conditioning exposure, we used a polytetrafluoroethylene chamber to place the leaves in the exposure and control groups to prevent the influences of ambient factors during the whole exposure. The whole experiment was preceded at a temperature ranging from 18 to 20 °C and humidity ranging from 40 to 50% within two days. During the study, the leaves were not plucked from the trees. On the second day, the emissions of BVOC from leaves were measured using an RAE PGM-7300 BVOC analyzer with the same procedure described above (Methods Section 2.2).

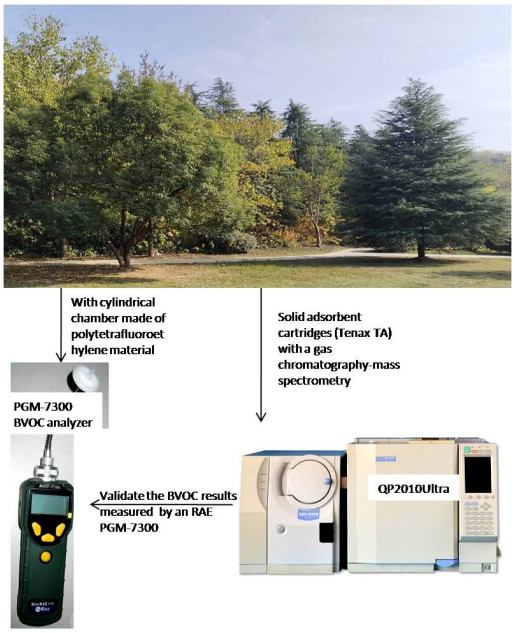

Figure 1. The measurement diagram for the emission rates of BVOCs from the leaves of four species (*Populus tomentosa*, *Salix babylonica*, *Broussonetia papyrifera*, and *Platanus orientalis*).

2.4. Statistical Analysis

The levels of BVOCs are presented in the form of the average level and standard deviation. The results were estimated from the results derived from at least three parallel experiments. We used the Wilcoxon rank-sum test to check the differences in the average concentrations of BVOCs between the experiment and control groups. The Wilcoxon rank-sum test was selected in this study because the dataset falls in a non-normal distribution according to the Shapiro–Wilk test. A post hoc test with the Bonferroni methodology was carried out to adjust the *p*-values. The significant differences were seen with an adjusted *p*-value lower than 0.05. The above data analyses were performed with SPSSV26.0.

3. Results and Discussion

3.1. BVOC Emission across Species

The linear ranges and limits of detection (LODs) are presented in Table 1. The limits of detection (LODs) refer to the sensitivity of the instruments, which was estimated three times using the standard deviation of the background noise divided by the calibration curve slope. In the measurements of BVOCs using Tenax with GC-MS, the linear range varied from 0.2 to 50 μg m^{-3}, and the coefficient of correlation was found to be higher than 0.99. The linear range of BVOCs using the PGM-7300 analyzer ranged from 10 to 500 μg m^{-3}, and the correlation coefficient was found to be higher than 0.98. Under five parallel determinations, the relative standard deviations for GC-MS and the PGM-7300 analyzer were lower than 5%. Using the two methods, the BVOC results in the plant leaves were comparable, indicating that the quality of the established method using the PGM-7300 analyzer meets the acceptance criteria of the quality control procedures for BVOC emissions from plants. Isoprene is the most abundant compound of BVOC in terrestrial plants, while some other compounds of BVOC including monoterpene are released from terrestrial plants [39–41]. The determination of individual compounds (e.g., terpenoids) at trace levels could be achieved by gas chromatography (GC) coupled with mass spectrometry (MS) [38]. The measurements of individual BVOCs for existing terrestrial plants using GC-MS in the laboratory should be carried out after the sampling of BVOCs on-site. In comparison, the portable BVOC analyzer (RAE PGM-7300, Honeywell International Inc., San Mateo, CA, USA) could measure the total BVOC from the leaves of existing terrestrial plants, which could avoid uncertainties associated with the shipment and pretreatment for the GC-MS measurements.

Table 1. The performances in the measurements of BVOCs using two methods.

Methods	Linear Range (μg m^{-3})	Correlation Coefficients (R^2)	Limits of Detection	Relative Standard Deviations	Sample 1 (n = 3, μg m^{-3})	Sample 2 (n = 3, μg m^{-3})
GC-MS	0.2–50	0.99	0.05	3.2	34 ± 2	15 ± 1
PGM-7300 analyzer	10–500	0.98	5	4.8	39 ± 5	20 ± 4

The average levels of BVOC emissions from the leaves of four tree types varied greatly across species, ranging from 90 to 270 μg g^{-1} h^{-1}. The highest average level was observed in *Populus tomentosa* (270 μg g^{-1} h^{-1}), followed by *Platanus orientalis* (138 μg g^{-1} h^{-1}), *Salix babylonica* (135 μg g^{-1} h^{-1}), and *Broussonetia papyrifera* (90 μg g^{-1} h^{-1}) (Table 2). The average levels of BVOCs in trees (*Populus tomentosa*, *Salix babylonica*, *Broussonetia papyrifera*, and *Platanus orientalis*) were consistent with several prior studies [39,42–44]. Table S1 summarizes the BVOC emission rates of typical tree species across some areas of China [43]. Notably, the BVOC emission rates from typical tree species were influenced by many factors including humidity, light, temperature, insects, human disturbance, herbivore feeding, CO_2 concentration, and ozone concentration [43]. Furthermore, the measurements of BVOC emission rates from typical tree species were affected by the instruments' stability, like GC-MS and internal standards [43,44]. Therefore, the emission rates of the same tree may

differ across different studies due to different environmental factors and measurement conditions. Our study aims to assess the impacts of black carbon particle exposure on terrestrial plants, and not to quantify the BVOC emission rates of terrestrial plants to acquire the source profiles of specific trees [43]. We carried out the measurements of BVOC emissions from the leaves of four types of terrestrial plants under the same environmental factors and measurement conditions before and after exposure to the soot particles.

Table 2. Emission rates of BVOCs from leaves of four types of terrestrial plants before and after 24 h of exposure to submicron black carbon at 2, 5, and 10 μg mL^{-1}, respectively.

Species	BVOC Emissions (μg g^{-1} h^{-1})	2 μg mL^{-1}	*p*-Value	5 μg mL^{-1}	*p*-Value	10 μg mL^{-1}	*p*-Value
Populus tomentosa	270 ± 10	285 ± 13	0.08	280 ± 15	0.09	287 ± 9	0.07
Salix babylonica	135 ± 4	143 ± 2	0.10	145 ± 2	0.11	138 ± 4	0.12
Broussonetia papyrifera	90 ± 2	92 ± 3	0.07	94 ± 2	0.08	95 ± 2	0.09
Platanus orientalis	138 ± 2	140 ± 2	0.18	142 ± 2	0.11	144 ± 3	0.17

3.2. The Impacts of Submicron Black Carbon

We used a series of known concentrations of carbon black (2–10 μg mL^{-1}) with particle sizes less than 30 nm to investigate the relationships between concentrations of carbon black and levels of BVOC emission in the leaves of four types of trees. As shown in Table 2, the levels of BVOC emissions in the leaves with and without exposure to submicron black carbon varied slightly. The level of carbon black at 2 μg mL^{-1} with particle sizes lower than 0.1 μm is equivalent to the ambient air concentration (<5 μg m^{-3}) if it is supposed that the submicron particles contributed about ~30% to the leaves in the form of the total deposited particles [3,7,35]. It is noteworthy that the levels of BVOC emission in the leaves from the four trees were not dependent on the exposure levels of submicron black carbon. With the increase in the levels of carbon black, the BVOC emissions in the leaves from four types of trees were not found to change. This result could be attributed to the wax of the leaves capturing carbon black through physisorption [7]. It is supposed that limited amounts of submicron carbon black could be inhaled into the leaf stomata, resulting in changes in the BVOC emissions in leaves.

With exposure to carbon black at 2 μg mL^{-1} for 24 h and 48 h, the average levels of BVOC emissions from the leaves of the four tree types did not change significantly (Figure 2). Enhanced emissions of BVOC from plants occur in response to plant injury and a decrease in plant growth [11,12,36]. The variations in the physiological and biochemical conditions of leaves (e.g., inhibition of photosynthesis) resulting from the entry of phytotoxic air pollutants (e.g., O_3) through the stomata could lead to a consequent effect on plant growth [30]. Although prior studies have illustrated that wax on leaves can capture black carbon particles (e.g., carbon black) through physisorption [10], these physical processes do not result in variations in the physiological and biochemical conditions of leaves. Therefore, no significant changes in the BVOC levels were observed in the leaves of four tree types before and after exposure to carbon black.

Our study has several limitations, including the portable BVOC analyzer, which has a high detection limit for the total VOC and the inability to measure individual VOC species. It is noteworthy that the responses to total VOC under the exposures to submicron carbon black may also depend on the concentrations of carbon black, the particle size, and the types of trees [11,12,43]. The exposure to the increases in the concentrations of carbon black and decreases in particle size may lead to variations in the total VOC in these four types of terrestrial plants. It is deduced that the variations in total VOC under the exposure to submicron carbon black in other types of trees may differ from the findings in this study [39]. This study selects these four types of terrestrial plants because they are typical street trees in Nanjing. Future studies may strive to explore the relationships between the levels of total VOC in other types of terrestrial plants under enhanced levels of carbon black

and smaller particle sizes. Nevertheless, the findings in this research indicate that exposure to ambient black carbon particles does not enhance BVOC emissions from terrestrial plants, which also provides cost-effective control strategies for reducing air pollution.

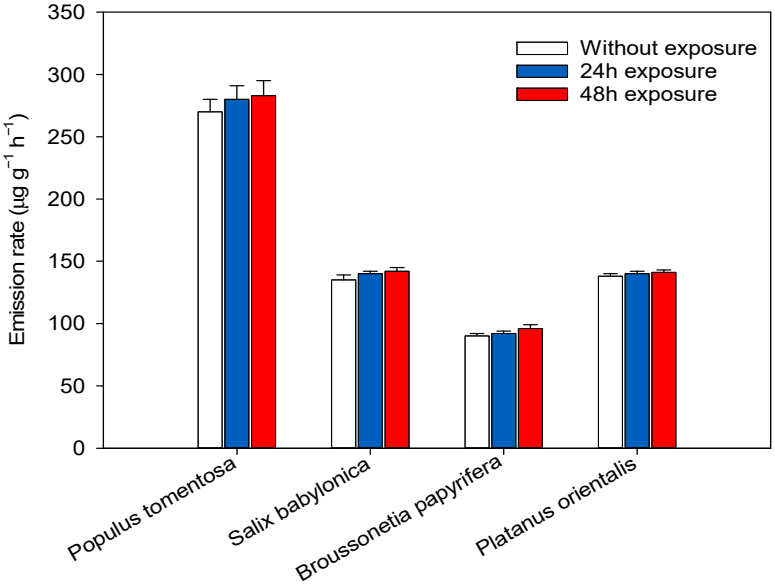

Figure 2. The emission rates of BVOCs from the leaves of four types of terrestrial plants before as well as after 24 h and 48 h of exposure to submicron black carbon at 2 μg mL^{-1}.

4. Conclusions

In this research, the BVOC emissions of the leaves of four types of existing trees on-site were determined using a portable instrument, and it was found that the BVOC emissions varied from 90 to 270 μg g^{-1} h^{-1} across species. After exposure to black carbon particles in wet deposition simulation experiments, the BVOC emissions from the four types of trees exhibited little variation compared with those without exposure. Our results demonstrate that exposure to ambient black carbon aerosols might have a negligible impact on BVOC emissions from terrestrial plants. This study provides direct evidence that terrestrial trees could remove ambient black carbon particles and release limited amounts of BVOC associated with the exposure of black carbon particles. The eco-friendly mitigation way to reduce ambient black carbon aerosols using trees could not lead to the enhanced emissions of BVOC, which regulate the formation of ozone and SOA in an ambient environment. The results of our research suggest the considerable roles of terrestrial trees in the regulation of air pollution.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pollutants4020012/s1.

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