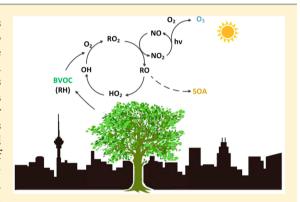


Role of Management Strategies and Environmental Factors in Determining the Emissions of Biogenic Volatile Organic Compounds from Urban Greenspaces

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Supporting Information

ABSTRACT: Biogenic volatile organic compound (BVOC) emissions from urban greenspace have recently become a global concern. To identify key factors affecting the dynamics of urban BVOC emissions, we built an estimation model and utilized the city of Hangzhou in southeastern China as an example. A series of single-factor scenarios were first developed, and then nine multifactor scenarios using a combination of different single-factor scenarios were built to quantify the effects of environmental changes and urban management strategies on urban BVOC emissions. Results of our model simulations showed that (1) annual total BVOC emissions from the metropolitan area of Hangzhou were 4.7×10^8 g of C in 2010 and were predicted to be 1.2–3.2 Gg of C (1 Gg = 10^9 g) in our various scenarios in 2050, (2) urban management played a more important role in determining future urban



BVOC emissions than environmental changes, and (3) a high ecosystem service value (e.g., lowest BVOC/leaf mass ratio) could be achieved through positive coping in confronting environmental changes and adopting proactive urban management strategies on a local scale, that is, to moderately increase tree density while restricting excessive greenspace expansion and optimizing the species composition of existing and newly planted trees.

INTRODUCTION

There is an increasing awareness of the influence that ambient fine particles, or PM2.5, have on the urban atmospheric environment and on human health worldwide. 1,2 Volatile organic compounds (VOCs) from biogenic (BVOCs) as well as anthropogenic (AVOCs) sources are believed to play critical roles in the serious problem of ambient fine particles found in many urban and suburban areas, especially in regions where PM2.5 are dominated by secondary organic aerosol (SOA).^{3,4} Moreover, VOCs can contribute significantly to the formation of tropospheric ozone (O₃) in the presence of sunlight and nitrogen oxides,⁵⁻⁷ which not only have a negative effect on human health but also cause significant damage to crops and vegetation.8-10

Surface ozone formation strongly depends on the ratio of VOCs to NO_x.6 Under "NO_x-limited" conditions, O₃ production is limited by the low concentration of NO_x. On the other hand, "VOC-limited conditions", in which the NO_X concentration is high and production of O₃ is limited by VOC availability, are often observed in urban areas. O₃ will be consumed by NO_X titration when NO_X concentrations reach a critical level. The optimal VOC/NO_X ratio for O_3 production is usually found in peri-urban areas. However, if urban VOC emissions continue to increase, the optimal ratio may be also reached in urban centers.⁶ To tackle ozone pollution, different urban areas require different control methods. In some situations, NO_X emission control strategies alone are sufficient to mitigate O_3 pollution. ^{13,14} In others, reductions in VOC emissions are necessary. In still others, both VOC and NO_X must be controlled. 11,14

BVOC fluxes far exceed that of the AVOC on a global scale. 11,18 In urbanized regions, the large amount of AVOC emissions from industrial and traffic sources leads to a BVOC proportion relatively lower than that in rural areas. However, concurrent with the measures to mitigate AVOC emission in urban areas, the contribution of BVOC to total VOC has risen significantly. 6,19,20 If emissions of BVOC are not taken into account, the success of the current measures for controlling AVOC to achieve the desired goals of air quality improvement will be compromised. ^{19,21} Moreover, although the BVOC emissions from greenspaces make up only a small proportion of

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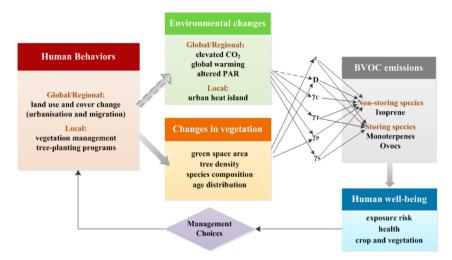


Figure 1. Conceptual framework of BVOC emissions from urban greenspaces.

the global BVOC emissions, their influence could be significant in urban areas having high population densities. The composition of BVOC is also important to air quality. Some trees have high emissions of isoprene that might enhance ozone formation,⁶ while oxidation products of monoterpenes and other VOCs have high yields for SOA, even if their emissions are lower than isoprene emissions.^{22,23}

Urban greenspace is purported to offset greenhouse gas (GHG) emissions, remove pollutants from air and water, cool the local climate, and improve human health. 24,25 To utilize these ecosystem services, urban planners and managers have focused efforts on designing and implementing large-scale ecosystem service-based tree planting programs in urban areas. 25,26 However, in most cases, they failed to recognize the wider ecosystem impacts such as BVOC emissions.⁴ Recently, field measurements and inventory work concerning BVOC emissions from urban greenspaces have been conducted in many cities. 8,27,28 Nevertheless, only a few measures were actually implemented to reduce BVOC emissions because of the lack of accurate forecasts of urban BVOC emissions, and uncertain guidance about what measures should be taken as well as incomplete knowledge of their corresponding effectiveness.²¹ To solve these problems, forecast models of urban BVOC emissions that integrate human management factors and natural environmental factors, based upon realworld cases, are urgently needed. These models will help in the systematic analysis of the relative importance of environmental changes and urban management strategies with regard to the temporal dynamics of urban BVOC emissions while providing policy makers with various options for achieving optimal regulation.

Hangzhou city $(29^{\circ}11'-30^{\circ}34' \text{ N}, 118^{\circ}20'-120^{\circ}37' \text{ E})$, located on the southeastern coast of China, with its rapid economic growth and urbanization, is one of the most developed cities in China. In recent years, the occurrence of hazy days in Hangzhou began to increase as a consequence of urban activities, increasing to ~160 days per year. Ozone pollution has also become a serious environmental problem in urban and suburban areas of Hangzhou, especially in the summer, during which the 8 h ozone concentration often exceeds $200 \,\mu\text{g/m}^3$ and has already become a threat to human health. In this study, we (i) develop a comprehensive estimation model of BVOC emissions from urban greenspaces, (ii) quantify the influence of urban management and/or

environmental changes on BVOC emissions and forecast BVOC emission dynamics in single-factor and multifactor scenarios, and (iii) determine realistic management strategies for urban managers and planners to maximize the ecosystem services.

■ METHODOLOGY

BVOC Algorithms. Only the BVOC emissions from tree leaves were taken into consideration in this study. ^{27,28} BVOCs were grouped into three categories: isoprene, monoterpenes, and other VOCs (OVOCs). The estimate of BVOC emissions is mainly based on algorithms presented by Guenther et al. ³⁰ and Guenther ³¹ and modified by the results of Staudt et al. ³² and Heald et al. ³³ The light intensity determines the emission rates of some BVOCs, which largely depends on the presence of storage compartments in leaves. The estimation model distinguished between synthesis emissions (depend on both light and temperature) and pool emissions (depend on temperature only). The synthesis emission rate (E) was quantified as

$$E = \varepsilon D \gamma_{\rm T} \gamma_{\rm p} \gamma_{\rm S} \gamma_{\rm C} \tag{1}$$

where ε is the basal emission rate (BER, micrograms of C per gram of leaf dry weight per hour) at 30 °C and 1000 μ mol m⁻² s⁻¹, D is the peak foliar mass (grams of leaf dry weight), and γ_T , γ_P , γ_C , and γ_S are environmental correction factors accounting for the influence of leaf temperature, light intensity, atmospheric CO₂ concentration, and seasonal variation on BVOC emissions, respectively. The pool emissions were quantified as

$$E = \varepsilon D \gamma_{\rm T} \gamma_{\rm S} \tag{2}$$

The details and calculations of D, γ_T , γ_P , γ_C , and γ_S are given in the Supporting Information.

It was assumed that all monoterpenes and OVOCs were pool emissions in this study because of the lack of information about the light dependency of monoterpene emissions. In addition, there are many other factors (e.g., canopy effect, soil moisture, photosynthesis response to CO_2 , and ozone concentration) that could influence the synthesis and emissions of BVOC, which were not considered in this study.

Model Description. The conceptual framework for the estimation of urban BVOC emissions is given in Figure 1. This

Table 1. Environmental Changes and Urban Management Scenarios since 2010 and Descriptions of Assumptions^a

scenario	assumptions			
Environmental Change				
S1 (leaf temperature)				
S1.1 (1 °C increase)	considering together global warming and the urban heat island, the leaf temperature will increase 1–3 $^{\circ}\text{C}$			
S1.2 (3 °C increase)				
S2 (CO ₂ concentration)				
S2.1 (500 ppm)	climbing up to 500 and 700 ppm due to human activities			
S2.2 (700 ppm)				
S3 (PAR)				
S3.1 (decrease by 20%)	the increasing cloud cover causes a 20% decrease in PAR; the increasing diffuse light reaching the leaf surface causes a 20% increase in			
S3.2 (increase by 20%)	PAR			
Urban Management				
S4 (tree density)				
S4.1 (increase by 20%)	tree planting programs will be conducted to achieve 20 and 50% increases in tree density			
S4.2 (increase by 50%)				
S5 [greenspace ratio (GSR)]				
S5.1 (increase by 20%)	tree planting programs will be conducted to achieve 20 and 50% increases in greenspace ratio			
S5.2 (increase by 50%)				
S6 (urban sprawl)				
S6.1 (50% HES are replaced by LES)	50% existing HES are replaced by LES (no urban sprawl); built-up area increase 200 km ⁻² , 50% decrease and 50% increase in the proportions HES when planting new trees			
S6.2 (HES decrease 50%)				
S6.3 (HES increase 50%)				
^a HES, high-emitting species; LES, low-emitting species.				

framework summarizes the drivers and processes influencing BVOC emissions from urban greenspaces. Urban managers and planners can directly influence BVOC emissions by adjusting the areal extent of the greenspaces, the tree density, the species composition, and the tree age distribution. The emissions will also be influenced by environmental changes caused by human activities on multiple scales.

We developed the estimation model for urban BVOC emissions based on the STELLA graphic programming system (High Performance Systems, Inc., version 9.1.2) (Figure S2 of the Supporting Information). The basic (static) structure of the model includes two parts (Figure S1 of the Supporting Information). Part 1 is used to simulate urban sprawl, the tree planting/replacement process, and tree growth with temporal resolution of one year. The outputs of part 1 are the leaf biomass of each species and a single LAI value for all species in each year. Part 2 is based on the BVOC algorithms outlined above and uses species-specific basal emission rates, meteorological [hourly temperature and photosynthetically active radiation (PAR) data and phenological data, and the outputs of part 1 as inputs. The modeling results are hourly emissions of the three kinds of BVOC for each tree species. The details of the estimation model are discussed in the Supporting Information, and further details of the input data used are given in Data Collection.

Data Collection. The species composition, tree density, and stem diameter at breast height (DBH) were collected from an urban vegetation survey of metropolitan Hangzhou conducted from 2010 to 2012.²⁷ A stratified random selection method was applied and a total of 252 plots (400 m²), and 6157 individual trees were recorded. Leaf and ring cores of primary tree species were also sampled during this survey.

Leaf area and dry mass were measured to calculate the specific leaf area (SLA) (Table S6 of the Supporting Information). The widths of the five newest tree rings were recorded to calculate an average annual increment of DBH

(Table S4 of the Supporting Information). Allometric models relating to DBH and leaf biomass (Table S5 of the Supporting Information) were collected and applied to estimate the changes in leaf mass during tree growth.

Isoprene emission rates of 15 dominant tree species and monoterpene emission rates of five tree species were measured (Tables S2 and S3 of the Supporting Information). An enclosure method was employed for gas sampling. The VOC constituents in the collected samples were then identified and quantified with a gas chromatograph/mass spectrometer (GC/ MS) (QP5050A, Shimadzu) equipped with a thermal desorption system (Turbo matrix ATD, PerkinElmer Instruments). Details are presented elsewhere.²⁷ The BERs of isoprene and total monoterpenes were assigned to all tree species in Hangzhou based on these measured values or from literature values using a taxonomic approach.⁸ For the emission rates of OVOCs, a recommended value of 1.5 μ g of C g⁻¹ h⁻¹ was assigned to all tree species.^{8,35} In this study, if the sum of a species' basal emission rates of isoprene and monoterpenes exceeds 10 μ g of C g⁻¹ h⁻¹, it is defined as a high-emitting species (HES), and if the sum is less than 1 μ g of C g⁻¹ h⁻¹, the species is defined as a low-emitting species (LES); otherwise, the species is a middle-emitting species (MES). In 2010, HES individuals accounted for 19% of the tree population in Hangzhou, MES individuals 61%, and LES 20%.

The PAR, air temperature, and CO_2 concentration data of 2010 were provided by the Environmental Monitoring Central Station of Hangzhou. Historical monthly temperature data were collected from the China Statistical Yearbook. Air temperature was used instead of leaf temperature as the latter was not available. Annual CO_2 concentration data from the Waliguan Baseline Observatory were used. Hourly PAR values were assumed to be the same as those in 2010 because of a lack of reliable data. Relevant historical data for Hangzhou (1980–2010) are summarized in Table S1 of the Supporting Information.

Preparation of Scenarios. We first conducted a baseline scenario and a series of single-factor scenarios to analyze the sensitivity of the estimation model to different driving factors. The reference year was 2010, and the target year was 2050. In the baseline scenario, only tree growth was considered; environmental factors and management strategies were assumed to be constant over time since 2010 (initial values are listed in Table S1 of the Supporting Information). The single-factor scenarios are based on the amplitudes of variation of different factors (summarized in Table 1). The single-factor scenario analysis was conducted by changing one variable when running the model while keeping all other variables constant. Scenarios S1 ("temperature"), S2 ("CO2"), and S3 ("PAR") are the environmental change scenarios. According to most forecasts, both temperature and CO2 concentration will continue to increase. The magnitude and direction of future changes in PAR are not as clear as changes in temperature or CO₂ concentration, so both a decrease (S3.1) and an increase (S3.2) in the future PAR were assumed. Scenarios S4-S6 are urban management scenarios. In scenarios S4 and S5, we assume that new trees will be planted from 2010 to 2020, but in two ways: increasing tree density and increasing greenspace ratio. Different ways may result in different light conditions caused by the canopy. Scenario S6 is about urban sprawl. Scenario S6.1 assumes no urban sprawl, while 50% of the HES will be replaced by combinations of LES of the same age. It was then assumed that the urban metropolitan area in Hangzhou will likely continue to expand at a high rate (20 km²/year was assumed on the basis of the increased rate of Hangzhou over the past 10 years) in the next 10 years in scenarios S6.2 and S6.3, and new greenspaces will be built to maintain a constant greenspace ratio to meet human needs. The proportion of HES in the newly planted trees can be reduced consciously (S6.2) or increased unintentionally (S6.3).

To improve our understanding of the roles of environmental change and urban management strategies in determining future urban BVOC emissions, we developed nine synthetic scenarios combining different single-factor scenarios listed in Table 1. These multifactor scenarios are constructed along two main dimensions: (A) attitude to confront environmental changes and (B) local environmental policies related to BVOC emissions (Table 2). In the first dimension (A), three distinct

Table 2. Comprehensive Scenarios Combining Attitude to Confront Global Environmental Changes and Local Environmental Policies

	positive coping (A1)	moderate control (A2)	negative coping (A3)
proactive (B1)	baseline + \$4.2 + \$6.1 + \$6.2	baseline + S1.1 + S2.1 + S4.2 + S6.1 + S6.2	baseline + S1.2 + S2.2 + S4.2 + S6.1 + S6.2
reckless	baseline + S5.2	baseline + S1.1 +	baseline + S1.2 +
(B2)	+ S6.3	S2.1 + S5.2 + S6.3	S2.2 + S5.2 + S6.3
reactive	baseline	S1.2 + S2.2 + S3.1 +	S1.3 + S2.3 + S3.1 +
(B3)		S4.1 + S5.1	S4.1 + S5.1

attitudes were identified. "Positive coping" (A1) means there is cooperation of responsible and involved stakeholders to keep the temperature and CO_2 concentration constant by means of reducing GHG emissions or enhancing the capacity of carbon sinks. "Moderate control" (A2) emphasizes local solutions for mitigating global warming and GHG emissions. The temperature will increase 1 $^{\circ}C$ (S1.1), and the CO_2 concentration will

increase to 500 ppm (S2.1) by 2050. "Negative coping" (A3) means environmental changes occur without control. The temperature and CO_2 concentration will obviously rise (S1.2 and S2.2) in this case. PAR was not included in the multifactor scenarios. In the second dimension (B), environmental policies are defined as "proactive" (B1), "reckless" (B2), or "reactive" (B3), depending on their potential to increase leaf mass and to control BVOC emission, on the basis of the results of our single-factor scenarios (Figure 2). Proactive local environmental policies are the combinations of a moderate increase in tree density (S4.2), a restriction of excessive greenspace

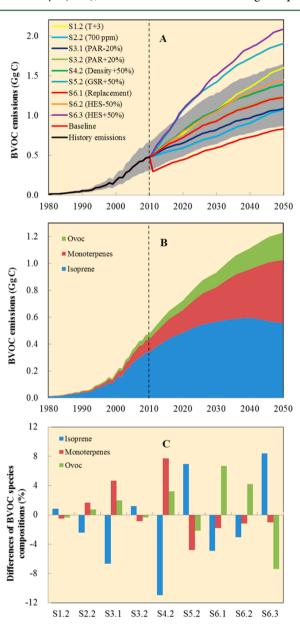


Figure 2. Time series of annual urban BVOC emissions and results of a single-factor scenario analysis. (A) The calculated historical total BVOC emissions (medians) from 1980 to 2010 and the single-factor scenario analysis results from 2011 to 2050. Shaded areas denote the 95% confidence interval on the calculated uncertainties of historical BVOC emissions and emissions in the baseline scenario. (B) Annual isoprene, monoterpene, and OVOC emissions in the baseline scenario. (C) Differences between the BVOC species composition in 2050 in various single-factor scenarios and that in the baseline scenario.

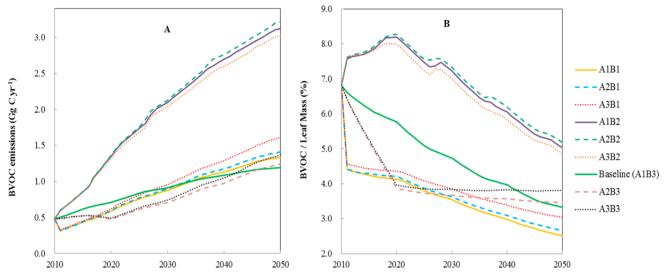


Figure 3. Projected total BVOC emissions (A) and BVOC/leaf mass ratios (B) in various comprehensive scenarios from 2011 to 2050.

expansion, and optimization of the species composition of existing (S6.1) and "newly planted" trees (S6.2). Reckless environmental policies include the unmanaged expansion of urban greenspace (S5.2) and an inappropriate species selection when planting new trees. Reactive policies mean no urban expansion and no new tree planting. In reality, none of the nine scenarios represent a "best" or "worst" path. Instead, they illustrate different choices that may be made and highlight some of the trade-offs that will be faced.

Uncertainty Analysis. In this study, we conducted a Monte Carlo simulation (10000 runs) to characterize the uncertainties associated with our urban BVOC estimates. Input variables related to emission factors, leaf biomass, meteorological data, and some model parameters have been assumed to vary and have been randomly sampled. The medians and 95% confidence intervals represent the uncertainties associated with our BVOC emissions estimates. The probability distribution functions, sampling method, and uncertainty values assumed for the 20 model parameters and data input variables are summarized in Table S7 of the Supporting Information.

■ RESULTS

BVOC Emissions in Single-Factor Scenarios. The annual BVOC emission from urban greenspaces in 2010 was 4.7×10^8 g of C (3.1-6.7 \times 10⁸ g of C); isoprene, monoterpenes, and OVOCs contributed 71.5, 20.2, and 8.3%, respectively. The total BVOC emissions of all scenarios showed rapidly rising trends (Figure 2A). In the baseline scenario, the growth rate gradually slows from 2010 and reaches 1.2 $(0.9-1.6) \times 10^9$ g of C in 2050 (Figure 2A), increasing by ~150%. Annual isoprene emissions increase from 3.4×10^8 to 6.0×10^8 g of C in 2040 initially and then slowly decline to 5.5 $(3.9-7.4) \times 10^8$ g of C in 2050 because of light limitations. As monoterpene and OVOC emissions were assumed to be light-independent, both of their emissions continued increasing year by year, from $9.5 \times$ 10^7 and 3.9×10^7 g of C km⁻² to $4.7 (2.6-5.9) \times 10^8$ and 2.0 $(1.8-2.5) \times 10^8$ g of C km⁻² in 2050, respectively (Figure 2B). In 2050, the combined emissions of monoterpenes (38.5%) and OVOCs (16.5%) exceed those of isoprene (45.0%).

Temperature increases considered here enhanced the emissions of all BVOC species. A 1 $^{\circ}$ C increase (S1.1) and a 3 $^{\circ}$ C increase (S1.2) in leaf temperature result in the total

emissions being 8.9 and 31.0% higher, respectively, than the baseline emissions in 2050. When the $\rm CO_2$ concentration gradually increases to 500 ppm (S2.1) and 700 ppm (S2.2) in 2050, annual emissions are 5.3 and 12.4%, respectively, lower than those in the baseline scenario (Figure 2A), because of inhibition of isoprene emissions. A 20% increase and a 20% decrease in PAR result in total BVOC emissions that are 6.4% higher and 11.8% lower, respectively, than those in the baseline scenario.

The BVOC emissions in scenario S5.2 ("GSR + 50%") (1.9 Gg) are 37% higher than in scenario S4.2 ("density + 50%") (1.4 Gg), though the same numbers of trees are planted in the same years with the same species composition. Tree species selection has a significant influence on the change in annual emissions when the urban area continues to expand (S6). The optimal solution in scenario S6.2 ("GSR - 50%") increases the number of individual urban trees by 50%, while increasing BVOC emissions by only 18% relative to that in the baseline scenario. However, selection of HES trees (S6.3) will cause much higher emissions in 2050, ~70% higher than that in the baseline scenario (Figure 2A). Our results suggest that if urban expansion were to cease, tree species replacement would be the fastest way to reduce BVOC emissions, although it is a more intense practice. Transforming 50% of HES to a combination of LES $(S\overline{6}.1)$ will cause a 32.2% reduction in 2050 compared to the baseline scenario without a loss of urban greening quantity.

Our results indicate that, an increase in CO_2 concentration (S2.2), decreased PAR (S3.1) and HES (S6.2), an increased tree density (S4.2), and tree replacement (S6.1) could drastically lower the proportion of isoprene compared to that in the baseline scenario. Increases in greenspace ratio (S5.2) and HES (S6.3) were ways to increase the proportion of isoprene. In addition, an increase in temperature (S1.2) and an increase in PAR (S6.2) seemed to have little effect on the proportions of the three kinds of BVOC (Figure 2C).

BVOC Emissions in Multifactor Scenarios. It was estimated that urban BVOC emissions in Hangzhou could be 1.2–3.2 Gg/year in 2050 in various scenarios (Figure 3). The lowest and highest annual BVOC emissions were found with scenarios A1B3 (baseline scenario) and A2B2, respectively. The settings of the baseline scenario are the same as those in the single-factor scenario analysis, discussed above. Scenario A2B2

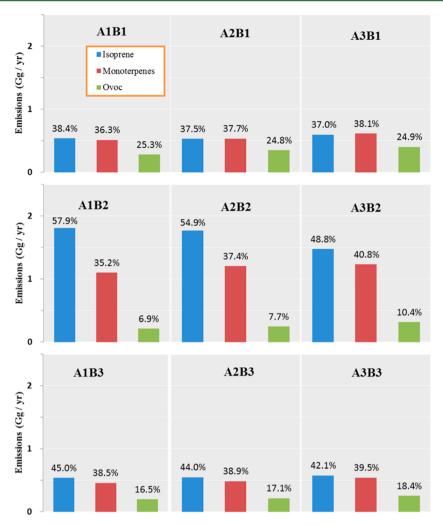


Figure 4. Allocation of BVOC emissions in different scenarios in 2050.

represents moderate environmental changes and reckless urban development on a local scale. Scenarios A1B2 (3.1 Gg/year) and A3B2 (3.0 Gg/year) also produced relatively high BVOC emissions that were ~2.5 times those in the baseline scenario. The three scenarios (B1) adopting proactive development patterns resulted in medium levels of BVOC emissions, which are much lower than those found in the B2 (reckless) scenarios and slightly higher than those found in the B3 (reactive) scenarios. Our results suggest that local intervention can mitigate the impacts of global decisions or actions. The three B3 scenarios produced the lowest emissions, but they are the most unlikely to occur, especially in developing countries experiencing rapid urbanization.

As different BVOC species may have different ozone and SOA formation potentials, identification of the species composition of BVOC emissions is also a crucial issue for air quality control strategies. The proportions of isoprene, monoterpenes, and OVOCs in 2050 were quite different among the various scenarios (Figure 4). In the three B1 (proactive) scenarios, isoprene accounted for only 37.0–38.4% of BVOC emissions and was no longer the dominant BVOC species. This is mainly due to the decrease in the proportion of HES (most of which are high-isoprene emitters) caused by tree replacement and tree species selection. Scenarios A1B2, A2B2, and A3B2 produced higher proportions of isoprene than the

baseline scenario, while scenarios A2B3 and A3B3 yielded almost the same isoprene proportions as the baseline scenario.

DISCUSSION

Comparison with Other Studies. Our future estimates of BVOC emissions (1.2–3.2 Gg/year) from urban greenspaces in various scenarios show proportional increases (151–575%) larger than those in previous studies on regional (mainly natural vegetation) BVOC projections (Table S8 of the Supporting Information), even though the time period of this study is the shortest. However, different factors affecting BVOC emissions were considered among these studies. Lathière et al.³⁸ investigated the combined effects of foliar expansion, climate change, and ecosystem redistribution on total BVOC emissions. Sanderson et al.,³⁹ Wiedinmyer et al.,⁴⁰ and Makkonen et al.⁴¹ meanwhile focused on modeling the future emissions of the two most important BVOC species, isoprene and monoterpenes, and further refined vegetation changes into climateand CO₂-driven and anthropogenic land use-driven scenarios. In recent years, the CO₂ inhibition of isoprene emissions has been taken into consideration, making the predicted isoprene and total BVOC emissions much smaller than previous estimates. ^{33,42,43}

The largest disparity between our results and those of previous studies was the differences caused by vegetation dynamics. When only tree growth of existing urban trees is

considered (baseline scenario), our projected BVOC emissions in 2050 are 151% higher than present emission in 2010 (Table S8 of the Supporting Information). This could be explained by the fact most urban trees are relatively young and have a large potential for growth. Moreover, the specific urban environment (e.g., higher temperature and CO₂ fertilization) and gardening activities may help individual trees grow faster and retain more foliar mass than trees in rural forests, 44 although, in some scenarios (B1 and B2 scenarios), we highlighted the important role of urban management strategies in determining future vegetation characteristics. Given that the rapid urbanization and greenspace expansion are unlikely to slow, anthropogenically driven vegetation changes in urban areas will always enhance urban BVOC emissions. That is quite different from some regional projections, in which anthropogenic land use change could lower BVOC emissions by converting forested areas to croplands, urban areas, and pastures. 40,43 Furthermore, the differing spatial and temporal resolution of the data used to drive the models used in these studies can also affect estimates of BVOC emissions. 45,46 These comparisons suggest that future urban BVOC emissions may be influenced by factors specific to urban areas and would tend to increase emissions more than in natural systems.

Roles of Greenspace Management Strategies and Environmental Factors. The intention of this paper was not to predict the exact BVOC emissions from urban greenspaces. Instead, we are trying to illustrate the roles of environmental changes and/or urban management strategies in altering BVOC emissions. On the basis of the results of the single-factor scenarios and multifactor scenarios presented here, the following conclusions are drawn.

- (1) In general, urban management strategies could directly change vegetation characteristics (e.g., leaf mass and species composition) and play a more important role than environmental change in determining future BVOC emissions from urban greenspaces (Figures 3 and 4). However, the diurnal and seasonal variations of BVOC emissions are primarily determined by the short-term (temperature and PAR) and long-term (phenology) impact of the environmental factors, which was found to be similar to those described in other studies.^{8,19}
- (2) When the same number of trees were planted, adopting proactive greenspace management strategies (i.e., increasing greenspace area and the proportion of LES when planting new trees) could reduce BVOC emissions effectively compared to reckless management (i.e., increasing both the areal extent of greenspace and the proportion of HES when planting new trees). In China, only the areal extent of greenspace is currently recorded and used as a major achievement for the local government, while the quality of the vegetation (e.g., tree density) is seldom considered. The continued expansion of urban greenspaces will always result in higher BVOC emissions in urban areas. In addition, the foliage of most urban trees is exposed to high PAR.⁴⁷ A modest increase in tree density will slow the rate of increase of light-dependent BVOC emissions from urban trees.
- (3) Greenspace management strategies have a time-lag effect on BVOC emissions, meaning that the difference in BVOC emissions between different strategies is small for the first few years but increases over time (Figure 3). During the lag phase, local governments need to maintain the continuity of proactive environmental policies and improve efforts to make people understand the benefits.

Trade-off between BVOC Emissions and Ecosystem Services. Decision making should be based on a trade-off between the ecosystem service costs and benefits of urban greenspaces. Most of the time, plants in urban environments are selected for their ornamental characteristics and ability to thrive under urban conditions. In recent years, researchers are taking BVOC emissions from urban trees into consideration. Donovan et al. developed an urban tree air quality score (UTAQS) to rank trees in order of their combined effects of pollutant removal and BVOC emission. Simpson and McPherson used a tree BVOC index (TBI) as a tool for the implementation and monitoring of a tree program designed to reduce BVOC emissions. Guo et al. Calculated the BVOC/NPP ratios of primary tree species in metropolitan Ningbo and suggested that tree species with a low ratio should be chosen for future urban greening.

To incorporate BVOC emissions into urban design and management, we choose the BVOC/leaf mass ratio to roughly represent the benefit to urban ecosystem services in various scenarios. A low ratio gives a high ecosystem service value. Results are shown in Figure 3B. In the baseline scenario, the BVOC/leaf mass ratio showed a sustained downward trend from 6.8% in 2010 to 3.2% in 2050. The ratios of the three B2 (reckless) scenarios increased initially, reaching peak values around 2020 and then decreasing with the approach of 2050, but they still have BVOC/leaf mass ratios higher than those of the other scenarios in 2050, of which scenario A2B2 (5.2%) is the highest. Values of scenarios A2B3 and A3B3 decrease initially prior to 2020 and then remain relative constant because of the opposing effects of rising temperature and CO2 concentrations. The three B1 (proactive) scenarios appear to be the best choices, as the ratios decrease quickly after 2011 when the tree placement is being conducted and then continue to decline. Scenario A1B1 had the lowest BVOC/leaf mass ratio (2.5%), suggesting that the highest ecosystem service value could be achieved by taking a positive attitude to confront environmental changes and adopting proactive local environmental policies.

Uncertainties. Besides the uncertainty sources considered in the Monte Carlo analysis, there are still some factors that may affect our BVOC estimates. Given the growing body of evidence of direct emissions of many monoterpenes and oxygenated VOCs, ^{18,19} the assumption that all monoterpene and OVOC emissions are light-independent may increase the uncertainties of BVOC estimates. If 50% of monoterpene emissions were assumed to be both light- and temperature-dependent, the flux estimates of BVOC of Hangzhou in 2010 would be underestimated by 5% versus the estimates assuming all monoterpenes were pool emissions.²⁷

Light varies dramatically within a tree canopy, resulting in much lower light-dependent BVOC emissions. ¹⁸ The canopy effect was not considered in our estimation model because the assumption of horizontal homogeneity on which most canopy models are based may not apply in the spatially heterogeneous urban environment. ²¹ Canopy models developed for urban trees are urgently needed. In this study, air temperature was used in the equations instead of leaf temperature because of the lack of data. BVOC emissions would be underestimated as leaf temperatures of urban trees are higher than air temperatures most of time. ⁵¹

The decrease in isoprene emissions caused by elevated CO_2 concentrations could be offset by increases in BVOC emissions as a result of the CO_2 fertilization effect on tree productivity.⁷

In this study, the latter effect has not been considered, leading to an underestimation of BVOC emissions. Other important issues omitted are the effects of soil moisture and $\rm O_3$ concentrations on BVOC emissions. A more in-depth discussion of the uncertainties associated with these assumptions and omissions is given in the Supporting Information.

Implications. With the unprecedented urban transitions worldwide and the growing number of tree planting programs conducted in many countries, urban greenspaces will become increasingly large sources of BVOC emissions. These emissions should be fully accounted for when conducting global and regional BVOC estimations.

These emissions could be controlled by a positive response to environmental change and effective urban management. Environmental change will tend to enhance urban BVOC emissions, but actions are being taken worldwide to limit the magnitude and/or rate of long-term environmental change. For urban managers and planners, mitigation can be achieved. Optimization of tree species composition of existing and newly planted trees, and a modest increase in tree density, results in the greatest BVOC reduction and highest ecosystem service value. However, bridging the gap between the present reality and the ideal situation requires improvements to urban management strategies.

The BVOC/leaf mass ratio is a useful aid for decision makers for incorporating BVOC emissions into urban design and management. In reality, many trade-offs (costs and benefits and ecosystem services and disservices) may occur when designing and managing greenspace to achieve local environmental goals.²⁵ Ideally, all effects of trees on air quality and human quality of life should be included in tree selection to maximize net benefits. We recommend that a more comprehensive index, which integrates the primary ecosystem services and negative impacts, be developed to guide future decision making. In addition, environmental changes and urban planting schemes will not only alter BVOC emissions but also affect other atmospheric processes that interact to govern the concentrations of both the primary emission species and their oxidation products. Recent work has demonstrated clearly that taking all of the processes involved in the reactive carbon cycle into consideration substantially affected projections of the impact of land use and land cover change on surface ozone and aerosol concentrations. 52,53 To consider changes in BVOC emissions alone precludes an accurate assessment of the impacts of future change on air quality and other ecosystem services. This is a limitation of this study that should be addressed by future research.

ASSOCIATED CONTENT

S Supporting Information

Detailed descriptions of the data, methods, and model used for calculating the BVOC emissions and related uncertainties; historical information about Hangzhou (Table S1); data sources and main parameters (Tables S2–S4 and S6); leaf biomass equations (Table S5); uncertainty values used in the Monte Carlo method (Table S7); comparison to other regional BVOC emission projections (Table S8); emissions in different temperature scenarios (Table S9); structure of the BVOC estimation model (Figures S1–S3); comparison between the calculated areal extent of greenspace and statistical data (Figure S4); seasonal and diurnal variations in BVOC emissions (Figure S5); and diurnal variations of the leaf-to-air temper-

ature difference (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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