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Effect of VOC emissions from vegetation on air quality in Berlin during a heatwave

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Abstract

The potential of emissions from urban vegetation combined with anthropogenic emissions to produce ozone and particulate matter has long been recognized. This potential increases with rising temperatures and may lead to severe problems with air quality in densely populated areas during heat waves. Here, we investigate how heat waves affect emissions of volatile organic compounds from urban/suburban vegetation and corresponding ground-level ozone and particulate matter. We use the Weather Research and Forecasting Model with atmospheric chemistry (WRF-Chem) with emissions of volatile organic compounds (VOCs) from vegetation simulated with MEGAN to quantify some of these feedbacks in Berlin, Germany, during the heat wave in 2006. The model simulations indicate that emissions of isoprene from vegetation contribute ~ 12% on average to the ozone formation in summer. During the analyzed heat wave period this contribution increases to up to 60%. This contribution is expected to be even higher as the model underestimates isoprene concentrations over urban forests and parks by 0.6-1.4 ppbv. Our study demonstrates that biogenic VOCs can considerably contribute to enhanced air pollution during heat waves. We emphasize the dual role of vegetation for air quality and human health in cities during warm seasons, which is removal and lessening versus enhancement of air pollution. Radical reduction of anthropogenic sources of NOx, VOCs, and PM, e.g., reduction of motorized vehicle fleet, would have to accompany urban tree planting campaigns in order to make them really beneficial for urban dwellers.

1. Introduction

Programs to plant millions of trees in cities[1] aim at the reduction of summer temperatures (as trees increase evapotranspiration and provide shade), an increase of carbon storage, storm water control, provision of space for recreation as well as poverty alleviation[2]. Although these benefits speak for urban greening programs, the programs do not fully account for the interactions between urban vegetation and the urban environment. Green areas in cities are exposed to elevated temperatures[3] and high anthropogenic pollution of air[4], soil[4], and water[5]. Furthermore, urban soils are often compacted, which is unfavorable for water availability, and are exposed to additional stress such as de-icing substances[6], which is damaging for vegetation growing along streets. Urban and sub-urban vegetation responds to changes in abiotic conditions with modifications to its physiology and anatomy[7]. These changes affect not only the ability of vegetation to filter pollutants but also its gaseous emissions and, as a result, create a feedback mechanism to ambient conditions. The gaseous emissions from vegetation can react with air pollutants enhancing pollutants' concentrations. Neglecting these interactions may lead to unforeseen drawbacks of urban greening programs[8].

Plants emit volatile organic compounds (VOCs), some of which are, for example, odors we can smell. VOC emissions increase during warm seasons with high insolation and especially during the flowering periods[9], often exhibiting exponential temperature dependence[10]. Plants also increase their VOC emissions in response to drought conditions[9] and high concentrations of ground level ozone[11]. Moreover, insect outbreaks[12] or lawn mowing[13] trigger higher emissions of VOCs. VOC emissions scale with leaf area, which increases with higher CO_2 concentrations, although negative responses of VOC emissions to rising concentrations of CO_2 may compensate for this[14].

In areas with substantial levels of nitrogen oxides (NO_x=NO+NO_2) such as urban and sub-urban regions, VOCs can undergo chemical reactions leading to the formation of ozone and particulate matter (PM)[15]. Although plants release hundreds of different VOCs[16], only a few of them have a substantial effect on air quality. The most important reactive biogenic VOCs are isoprene, monoterpenes, and sesquiterpenes. Emissions of isoprene mostly contribute to the formation of ground level ozone[17], while monoterpenes and sesquiterpenes can lead to an increase in particle number and mass concentration[18]. While gaseous VOCs intensify ozone production, the transfer of VOCs between gas- and particle- phases can either slow down or enhance urban ozone formation. In case of high gas-phase concentrations of VOCs with more than five carbon atoms, semi-volatile compounds will transition to the particle phase and will be temporarily removed from the cycle of ozone production. Recent study suggests that this process may also take place in Berlin, Germany (Bonn et al., in prep.). If the organic PM concentration is high and temperatures increase, organic PM will partially evaporate and may then add to the ozone formation as supplementary VOCs.

Secondary organic aerosols (SOA) can contribute considerably to the mass of fine particles (particles smaller than 1 µm)[19] and also add to the mass of particles smaller than 10 µm (PM_{10}), which is typically dominated by large particles (> 1 µm). A large fraction of SOA mass can typically be attributed to emissions of biogenic VOCs[20]. Examples include studies by Tunved et al.[21, 22], who showed that over forested regions in Scandinavia the aerosol mass was proportional to the duration the air had been residing over the forest. Ghirardo et al.[23] showed that emissions of biogenic VOCs from trees significantly influenced ozone and particle formation in Beijing, China.

An increase in biogenic VOC emissions in response to air pollution or to climate change can influence SOA formation indirectly via enhanced concentrations and partitioning of precursors resulting in a charge of particle size distribution[24]. In a modeling study, Megaritis et al.[25] found that a temperature increase of 2.5°C led to a 20% increase in summertime biogenic SOA over the northern parts of Europe. The simulation of SOA formation with a numerical model is challenging, because of the large number of organic compounds relevant to the formation of organic aerosol particles[26] as well as the complex chemical pathways converting organic vapors into low-volatility compounds that can either partition onto existing organic particles (condensation) or form new particles (nucleation)[20].

Heat waves, which are defined here as five or more consecutive days during which the daily maximum temperature exceeds the average maximum temperature by 5°C or more, can enhance air pollution directly and indirectly. Directly, because high temperature and radiation intensify photochemistry[27] and formation of oxidized and thus less volatile organic compounds, and indirectly because anthropogenic emissions associated with enhanced use of air conditioning as well as biogenic emissions of VOCs tend to increase. In addition, stable atmospheric conditions typical for hot periods lead to increased pollutant concentrations near the surface[28]. Cities are more vulnerable than rural areas to heat waves, because they are warmer due to the urban heat island effect. Average annual temperatures in cities are usually higher than in surrounding areas by 1-3°C and this difference can go up to 10°C in summer nights[29] because of, for instance, heat energy stored during the day and emitted by buildings and paved surfaces at night, low evapotranspiration from limited green space, and various anthropogenic heat sources (e.g., heat released by industrial facilities, air conditionings, etc.). During heat waves cities experience a combination of the urban heat island effect and the heat wave itself[30]. For example, the heat wave in 2003 in Central Europe was accompanied by extremely high levels of ozone. In France, the highest hourly ozone value of 417 $\mu g/m^3$ (~210 ppb_V) was reached near Marseille[31]. In the UK, high levels of air pollution rather than the heat caused 21-38% of the estimated 2045 premature deaths[32] related to the heat wave in 2003. During hot periods vegetation tends to reduce stomatal openings leading to decreased ozone deposition. At the same time the high temperatures can substantially increase emissions of VOCs. Using results from a field campaign in August 2003 near London, Lee et al.[33] showed a rise in concentrations of isoprene from vegetation from 60 to 500 ppt_V, when air temperature increased from 20 to 30°C and related it to enhanced ozone concentrations (>110 ppb_V). Although poor urban air quality and high VOC emissions have been documented during excessively hot periods, the relative contribution of biogenic VOC emissions to the poor air quality episodes in mid-latitude cities have not been quantified.

Here, we investigate the effect of a heat wave on the emissions of VOCs from vegetation as well as on the ground level concentrations of ozone and particulate matter in the Berlin-Brandenburg metropolitan area, Germany, in 2006. This was the year of the latest well documented heat wave with significant increase in premature mortality in that area[34]. We compare modeled pollutant concentrations in summer 2006 with those in summer 2014, when meteorological conditions were more typical and test the sensitivity of the results to the emissions of VOC from vegetation.

Methods

Below we describe the study domain, VOC measurements used for model evaluation, model setup, evaluation of the model's ability to simulate biogenic VOCs, as well as the model experiments to estimate the contribution of biogenic VOCs to the concentrations of ozone and particulate matter in the Berlin-Brandenburg metropolitan area, Germany.

Study Domain

The Berlin-Brandenburg metropolitan area is located in the northeastern part of Germany (~52.52 degrees north, 13.4049 degrees east). Berlin is the largest city in the study area with a population of 3.35 million and covering 891.7 km^2 [35]. Forests (18%), parks (13%), and agriculture (4%) cover 35% of the Berlin area[36], making it one of the greenest European capitals. Berlin is surrounded by the Federal State of Brandenburg, the area of which is dominated by agriculture (50%) and forests (36%)[37].

Between July 10th and July 30th 2006, Berlin experienced a heat wave with average daily maximum temperatures well over 30°C. The highest temperature observed was 36.6°C. In contrast, the average daily maximum temperatures were between 26°C and 27°C in July 2014. The monthly mean temperature of July 2006 (23-24°C) was ~4°C higher than the climatological mean temperature of Berlin in July (19-20°C depending on the measurement station[38]). During the three weeks of the 2006 heat wave, the all-cause mortality was ~ 20% higher than the average number of deaths per day calculated over a period of 17 years (1990-2006)[34].

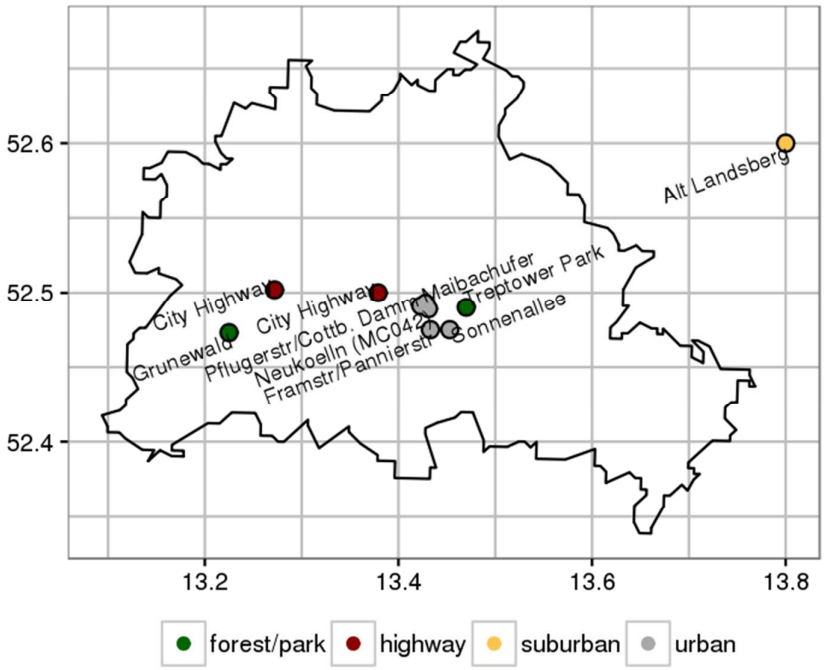

Figure 1. Locations of sites, where canister samples with VOCs have been collected during the BAERLIN field campaign[39] in summer 2014. The city limits of Berlin are shown with a black line.

VOC Observations

VOC concentrations were continuously measured during the BAERLIN field campaign in summer 2014 at a site located in a residential neighborhood of the Neukölln district in the center of Berlin (Figure 1). In addition, air samples have been taken with canisters in different locations of Berlin and one location in Brandenburg (Figure 1, Table 1)[39]. Continuous measurements were performed using a **P**roton **T**ransfer **R**eaction – **M**ass **S**pectrometry (PTR-MS) system from June 6th until August 29th, 2014 at the main Neukölln site (MC042)[40]. 68 different air constituents were continuously monitored with a five minute time step. Collection of canister samples took place at the sites representing urban background, urban forest and park, as well as city's highways. For these samples ambient air was flushed into pre-vacuumed canisters and diluted by synthetic air. Ozone was removed by a heated steel surface at the inlet line to prevent further oxidation of collected VOCs. The VOCs in these samples were analysed using a gas chromatography - mass spectrometry instrument[39]. This allowed detection of individual constituents and quantification of the spatial heterogeneity in VOCs concentrations across Berlin related to changing environmental conditions and VOC emission sources[39].

Table 1. Description of sites, where canister samples with VOCs have been collected during the BAERLIN field campaign in summer 2014 (if several coordinates are given, samples have been collected at different locations in the same area).

	Site Name	Lat. (°N)	Long. (°E)	Date	Time	Samples #	Site Type
1	Neukölln (MC042), Berlin	52.489	13.431	Aug 1, 2, 6, 12, 21-24	10:00-17:45	19	Urban background
2	Maibachufer, Berlin	52.493	13.428	Aug 6	10:00-11:00	2	Urban background
3	Framstrasse/Panierstrasse, Berlin	52.475	13.433	Aug 6	9:40	1	Urban background
4	Pflugerstr/Cottbuser Damm, Berlin	52.491	13.423	Aug 6	10:20	1	Urban background
5	Sonnenallee, Berlin	52.475	13.453	Aug 6	10:00	3	Urban background
6	Grunewald , Berlin	52.423 52.429	13.136 13.122	Aug 6	11:30-12:00	2	Urban forest
7	Treptower Park, Berlin	52.49	13.47	Aug 2	16:00-18:00	11	Park
8	Alt Landsberg, Brandenburg	52.6	13.8	Aug 2	13:00-14:30	10	Urban background (sub-urban)
9	City Highway, Berlin	52.5 52.502	13.379 13.272	Aug 4	12:40-14:10	11	Highway, Tunnel

PM observations

An analysis of organic carbon in PM_{10} was conducted using particle size classifiers for physical parameters and filters for chemical analysis. While the physical parameters were recorded continuously throughout the area of interest by a set of appropriate devices, 31 samples were collected for chemical analysis between 3rd of June and 3rd of September, 2014 at the main site in Neukölln[44] (MC042, Table 1, Site 1). Filter samples usually were collected continuously about two days to acquire sufficient particle mass and subsequently stored in refrigerated glass basins until the analysis. All filters were protected against direct loss of particle mass and ageing effects were minimized at a temperature of -20°C. The analysis included a classification of the fractions of elemental carbon (EC), i.e., soot, organic carbon (OC) in the three different volatility stages low, medium and high volatile and inorganic aerosol components[41, 42].

Model Setup

In this study we use the Weather Research and Forecasting model version 3.7.1 coupled online with atmospheric chemistry[43, 44] as well as with the **M**odel of **E**missions of **G**ases and **A**erosols from **N**ature (MEGAN) 2.04 [45]. We refer to this model as WRF-Chem in this paper. MEGAN simulates emissions of 20 classes of volatile organic compounds from vegetation including isoprene, monoterpenes (trans-β-ocimene, 3-carene, myrcene, limonene, sabinene, α-pinene, β-pinene, and other monoterpenes), and sesquiterpenes (α-farnesene, β-caryophyllene, and other sesquiterpenes). The model setup includes the RADM2 chemical mechanism in the kinetic preprocessor (KPP) version and the MADE/SORGAM aerosol scheme. Monoterpenes and sesquiterpenes are not represented explicitly in RADM2, but described by the lumped mechanism species “OLI”. “OLI” represents all alkenes with an internal double bond, so that a range of VOC species is lumped into this generic chemical mechanism species.

We set up the WRF-Chem model in a one-way nested configuration centered on Berlin with a horizontal resolution of 15x15 km^2 for the outermost domain, a 3x3 km^2 for the first nested domain, and a 1x1 km^2 for the innermost domain. The model domains extend vertically up to 50 hPa and are divided into 35 vertical levels. The lowest level is centered at around 30 m, and there are 12 vertical levels below 700 hPa. We replaced the commonly used land use data from US Geological Survey (USGS) with the land use data from the Coordination of Information on the Environment (CORINE) project for Europe[46]. We mapped CORINE land use classes to the USGS land use classes and included three urban classes. We did not use MODIS land cover data available for WRF-Chem, because all urban areas are mapped into a single land use class in this data set.

The model set-up with the exact locations of model domains, the physical and chemical parameterizations applied, as well as mapping of CORINE to the USGS land use classes are described in detail in Kuik et al.[47]. Here, we use the model set-up referred to as “base run” in Kuik et al.[47] with the original, unmodified WRF-Chem parameterization of the dry deposition of gaseous species and the input data for MEGAN described below.

Modification of Inputs to MEGAN

MEGAN, which was originally developed as a stand-alone model[45], is called in WRF-Chem before the atmospheric chemistry module. MEGAN requires input data produced by an accompanying pre-processing tool. Input data for this include maps of vegetation type, leaf area index (LAI), and VOC

emission factors (emission rates per leaf biomass under defined meteorological conditions of radiation and temperature). The vegetation classification in MEGAN includes four vegetation types such as broadleaf trees, needleleaf trees, shrubs/brushes, and herbaceous/crops/pastures. Global maps of fractions of each vegetation type per pixel are stored in four data files corresponding to each vegetation type. These global maps have been created using data at three different spatial resolutions such as ~ 50 km (AVHRR, MODIS2, G95-P, HYDE, IMAGE, MAPPS), ~ 8 km (IBIS), and ~ 1 km (SPOT, AVHRR2, MODIS3, MEGAN-P)[45]. The source of the MEGAN vegetation data differs for various parts of the world. For Europe it is the "default" which is the University of Maryland GLCF derived from vegetation continuous fields based on AVHRR and MODIS satellite data (http://glcf.umd.edu/data/vcf/) (Alex Guenther, personal communication). These data do not provide information on urban areas and therefore values from the surrounding region were interpolated over these areas for MEGAN vegetation classification.

In the MEGAN input dataset, vegetation in Berlin is characterized primarily by grassland and shrublands with a maximum LAI of two. In reality, the dominant vegetation types in Berlin are broadleaf/needleleaf trees mixed with grasses and shrubs. We therefore used the CORINE land use dataset[46], which provides a state-of-the-art land cover classification for Europe, to adjust the MEGAN land cover datasets (1 km resolution) for urban areas. The original CORINE dataset includes 44 land use classes at spatial resolutions of 250 m and 100 m. Only pixels identified as "urban" in CORINE (with GRID ID 1-11, Table 2) have been adjusted in the respective input datasets for MEGAN. All other "non-urban" pixels retained their original properties. The adjusted input datasets for MEGAN include fractional vegetation cover (%) for needle leaf forests, broadleaf forests, shrublands/brushes, herbaceous/crop as well as the respective LAI. This approach allows a more realistic representation of dominant urban vegetation within each 1 km pixel of the model domain, but cannot represent the heterogeneity of vegetation types and other land use types within those pixels. Representation of the subgrid scale heterogeneity is beyond the scope of this study.

In a first step, the fractional vegetation cover of pixels corresponding to urban land use types in CORINE (Grid ID 1-11, except mineral extraction site, Grid ID 7) has been adjusted (Table 2) assuming that land use types such as discontinuous urban fabric, green urban areas, as well as sport and leisure facilities have a high vegetated fraction (80%) and low sealed fraction (20%). All other urban land use types are assumed to have a high sealed fraction (80%) and low vegetated fraction (20%). For consistency, the assumptions about sealed/unsealed fractions are based on the definitions of urban classes suggested for the WRF model by Tewari et al.[48] and corresponding to the land use classes of CORINE[46]. Thereafter, the vegetated fraction of each pixel was assumed to be equally covered by four vegetation types represented in MEGAN, e.g., urban pixels with 80% vegetation had 20% of broadleaf trees, 20% of needle leaf trees, 20% of shrub/brush, and 20% of herbaceous/crop. A more precise quantification of vegetation fractions and vegetation types in urban areas requires datasets with high spatial resolution, which are not yet available for Europe.

Table 2. Fractions of the four plant functional type categories (broadleaf/needleleaf trees, shrubs/brush, herbaceous/crop) assigned to each of the CORINE urban land use types. Mineral extraction sites with Grid ID 7 are excluded, because these are not representative for urban areas.

CORINE				**MEGAN**			
Land Use Types	Grid	Vegetated	Sealed	Broad	Needle	Shrub/	Herbaceous/

	ID	%	%	leaf tree %	leaf tree %	Brush %	Crop %
Continuous urban fabric	1	20	80	*5*	*5*	*5*	*5*
Discontinuous urban fabric	2	80	20	*20*	*20*	*20*	*20*
Industrial or commercial units	3	20	80	*5*	*5*	*5*	*5*
Road and rail networks and associated land	4	20	80	*5*	*5*	*5*	*5*
Port areas	5	20	80	*5*	*5*	*5*	*5*
Airports	6	20	80	*5*	*5*	*5*	*5*
Dump sites	8	20	80	*5*	*5*	*5*	*5*
Construction sites	9	20	80	*5*	*5*	*5*	*5*
Green urban areas	10	80	20	*20*	*20*	*20*	*20*
Sport and leisure facilities	11	80	20	*20*	*20*	*20*	*20*

In a second step, the LAI of pixels corresponding to the land use categories 1-11 in CORINE has been modified: the LAI map of each month has been merged with the fractional vegetation maps. A subset with LAI values for pixels with 20% of broadleaf/needleleaf trees, 20% shrub/brush, and 20% herbaceous/crop have been extracted for each month of the year using the original MEGAN input datasets. Thereafter the maximum, minimum, and mean LAI values for each month have been calculated using the values provided in Table S1. The same procedure was used to calculate maximum and minimum LAI values for grid cells with a low vegetated fraction (Table S2). Only LAI values for summer months were used in model simulations in this study.

Model Simulations

In order to investigate the contribution of biogenic emissions to the formation of ozone and particulate matter during the 2006 heat wave period, simulations with different combinations of anthropogenic and biogenic emissions have been performed (Table 5). Simulations were performed with anthropogenic emissions only (ANTH), with both anthropogenic and biogenic VOC emissions using original MEGAN input data (ANTH+BIO), and with both anthropogenic and biogenic VOC emissions using modified MEGAN input data (ANTH+BIOm). The modified MEGAN input data include changes to the four fractional vegetation types and LAI of urban areas as described in the previous section. The model simulations have been performed for the time periods June-August 2006 and June-August 2014.

Table 5. List of model simulations.

Abbreviation of Model Simulation	Anthropogenic Emissions	Biogenic Emissions	Land Cover Input Data
ANTH	included	none	-
ANTH+BIO	included	included	original
ANTH+BIOm	included	included	modified

The Impact of Biogenic VOCs on Air Quality

To estimate the impact of VOCs from plants on ozone ($Impact_{ozone}$) we calculate the difference in ozone values between model simulations with ($OZONE_{ANTH+BIO}$) and without ($OZONE_{ANTH}$) emissions of

biogenic VOCs normalized by the modeled ozone values obtained with anthropogenic VOC emissions only ($OZONE_{ANTH}$):

$$Impact_{ozone} = \frac{\mathrm{OZONE_{ANTH+BIO}} - \mathrm{OZONE_{ANTH}}}{\mathrm{OZONE_{ANTH}}} * 100\% \quad (1)$$

Ozone values ($OZONE_{ANTH+BIO}$ and $OZONE_{ANTH}$) represent the 8-hour daily maximum values, which were calculated as follows. Running 8-hour averages were calculated for each hour of the day. The highest 8-hour average for each day was then recorded as the 8-hour daily maximum and used to estimate the impact of VOCs from vegetation on ozone.

To assess the impact of changes in VOCs from vegetation on particulate matter we investigate their effect on the simulated SOA concentration. SOA formation is very closely linked to the biogenic emissions of VOCs and we expected a substantial contribution to SOA during the periods with high VOC emissions from vegetation. SOA anomalies for 2006 were calculated relative to the SOA average over the summer (i.e., positive values indicate that SOA concentrations are higher than the average, negative values indicate SOA concentrations smaller than the average, Figure S3). Because of the poor signal to noise ratio in SOA, the effect of changes in biogenic SOA emissions on the total mass concentration of PM1 or PM2.5 is not investigated here.

Model Evaluation

The ability of WRF-Chem with the abovementioned setup to simulate various meteorological and chemical variables in the Berlin-Brandenburg metropolitan area was evaluated in-depth using observational data for the summer of 2014 by Kuik et al.[47].

Here, we test the model's ability to simulate realistic concentrations of biogenic VOCs and their sensitivity to the prescribed input data, i.e., vegetation fraction and type. We extracted the simulated isoprene concentrations averaged over the 1x1 km^2 grid cells of the innermost model domain corresponding to the location of observational sites (Table 1). Some measurements were taken relatively close to each other and were within the same model grid cell (Table 1, sites 1-4). These measurements were then compared to the same simulated values. The remaining five sampling sites (Table 1, sites 5-9) were located in different grid cells of the model and were compared to corresponding simulated concentrations of isoprene. Observed values represent point measurements of isoprene concentrations averaged over one hour at the observational sites (Table 1). Simulated and observed isoprene values below 0.05 ppbV were excluded from the analysis of the correlation between observed and modeled isoprene concentrations, because the corresponding observed data are close to or below the detection limit. We compare the simulated response of ozone to biogenic VOCs for grid cells, where measurements of isoprene were available, as explained above.

We compare isoprene emission factors in the MEGAN model to the ones calculated based on the species composition within the vegetation types typical for Berlin. For this we compared isoprene emission factors for grid cells with the highest fractions (> 60%) of four vegetation types such as deciduous broadleaf forest, evergreen needleleaf forest, shrublands, and herbaceous/croplands. To calculate isoprene emissions factors typical for Berlin vegetation we used the inventory of Berlin street trees[49] for deciduous broadleaf forests and data provided by the Umweltatlas of Berlin[50] for evergreen needleleaf forests. This includes a 31% fraction of deciduous trees including 13% oaks.

The emission factors were taken from various literature sources (see Supplementary Materials, Table S3 and S4 for details) and the units were transformed using the foliage density values[51] and the canopy correction factor[45].

Results and Discussion

Effect of Biogenic VOCs on Air Quality

Results of the model simulations show that the VOCs of biogenic origin contribute substantially (~12%) to the ground level ozone formation in Berlin in summer (Figure 1a and 1b). The mean contributions of biogenic VOCs in the ANTH+BIO simulation is slightly higher in summer 2006 (~13±11%) than in summer 2014 (~12±14%). The mean contribution of biogenic VOCs to ozone concentrations did not change substantially in response to changes in land cover and LAI (ANTH+BIOm) with contributions of around 12% (±7% for max LAI and ±14% for min LAI) in 2006 and ~11% (±13% for max LAI and ±12% for min LAI) in 2014.

The differences between the modeled ozone responses at various urban sites are small under default conditions (ANTH vs. ANTH+BIO). The maximum temporal standard deviation of modeled ozone response to biogenic VOCs at different sites increased from ~6% in the ANTH+BIO simulation to ~10% in the ANTH+BIOm simulation in 2006. This is not surprising, because the modified land cover has more patchy vegetation in comparison to the homogeneous vegetation cover of Berlin prescribed in the original MEGAN input dataset. The modified land cover had large differences between vegetation fractions in grid cells classified as discontinuous urban fabric, green urban areas, and sport/leisure facilities (80% of area covered with vegetation) and other land use types, e.g., continuous urban fabric, roads, etc. with 20% of area covered with vegetation. In the original land cover data, however, these contrasts between different grid cells within city do not exist.

In the 2006 simulation, the ozone response to VOC emissions from plants reached a maximum of 60% during the heat wave in July (Figure 1b). The peak in this response corresponds with high concentrations of isoprene resulting in high ozone concentrations during that period (July 20-30th, Figure 2). The exponential response of isoprene emissions to temperature is well documented[10] and is reproduced by the model. In the 2014 simulation, the response of the ozone concentrations to biogenic VOC emissions was smaller and did not exceed 42% reached in June (Figure 1b). With the improved land cover and LAI data the ozone peaks were slightly smaller during the heat wave of 2006, because land cover dataset vegetation did change in the locations with high NO_X values.

Our results for the heat wave period (Figure 1) are consistent with the observation-based results of Duane et al.[52] for the North Italian city of Insubria. There, the isoprene emissions from broad-leaf deciduous trees were estimated to contribute 50–75% to local ozone formation in summer[52]. Based on the results of a box model incorporating the Regional Atmospheric Chemistry Mechanism (RACM), Papiez et al.[53] suggested that modest VOC emissions from palm trees and ashes can substantially degrade air quality in a suburban location downwind of Las Vegas, Nevada, U.S. The emissions of biogenic terpenes increased time-dependent ozone production rates by a factor of 50 under conditions of high NO_x and low anthropogenic VOC concentrations.

Although our results along with many studies covering Asia[4, 54-56], Europe[52, 57], and North America[53, 58] suggest that urban trees may exacerbate air pollution through VOC emissions, other studies of the same phenomenon complicate the picture. Ozone can get captured inside the leaves (e.g., diffusion through leaves' stomata) and on the leaves' surface as well as other surfaces such as soils and tree stems[9]. Ozone reacts with NO as well as VOCs such as monoterpenes and sesquiterpenes in particular[59-61]. Based on a long time series of observations from Europe and the USA, Paoletti et al.[62]

found similar rates of ozone increase in urban and rural settings, although ozone was traditionally lower in urban centers[63]. The role of vegetation in this trend, however, remains unclear.

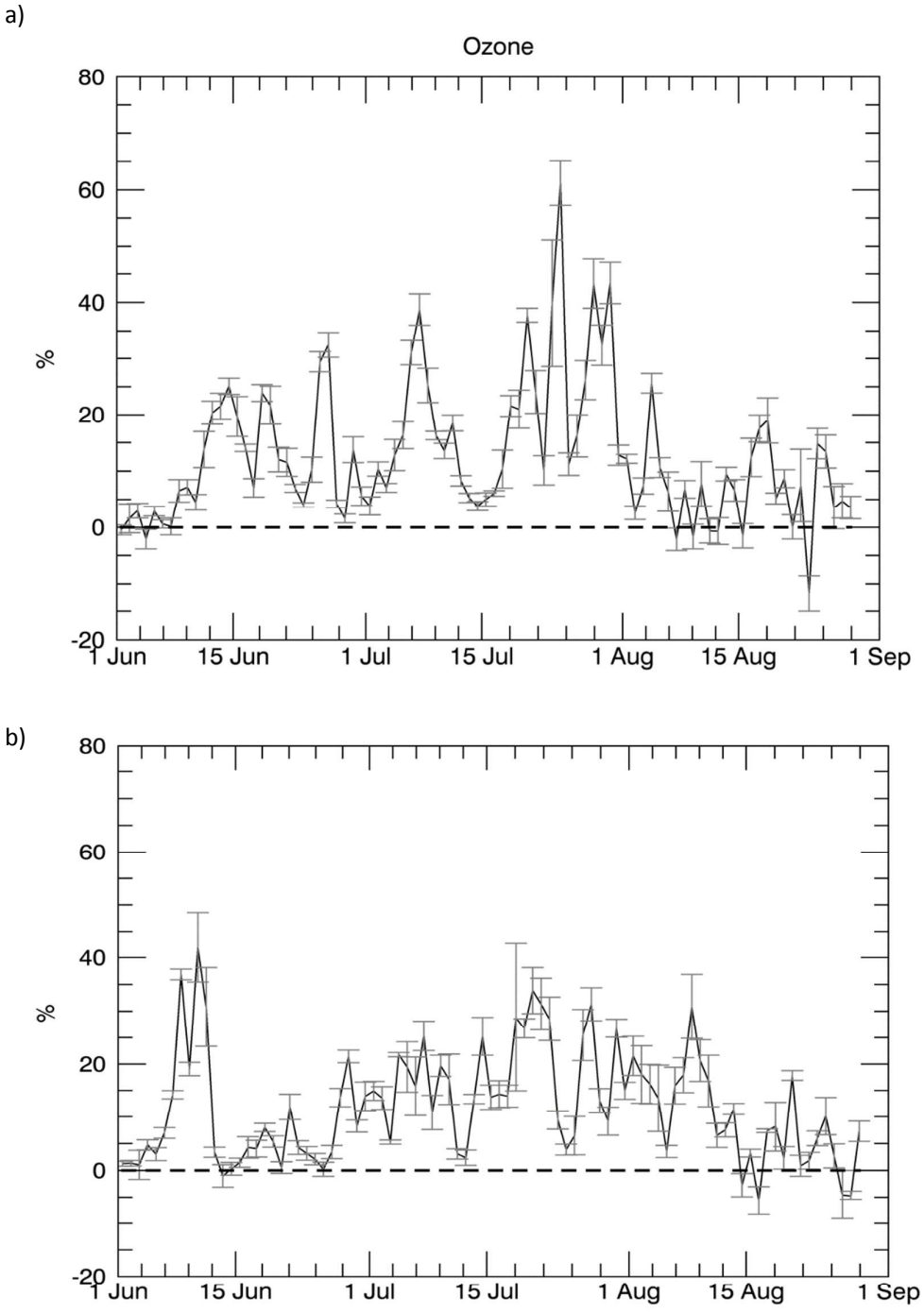

Figure 1. Contribution of VOC emissions from vegetation (Eq. 1) to the 8-hour daily maximum concentrations of ground level ozone in 2006 (upper panel) and 2014 (lower panel) from the ANTH+BIO simulation. The mean impact averaged over six grid cells with measurements is plotted as solid black line. The error bars show the standard deviation of the 8-hour values for each day.

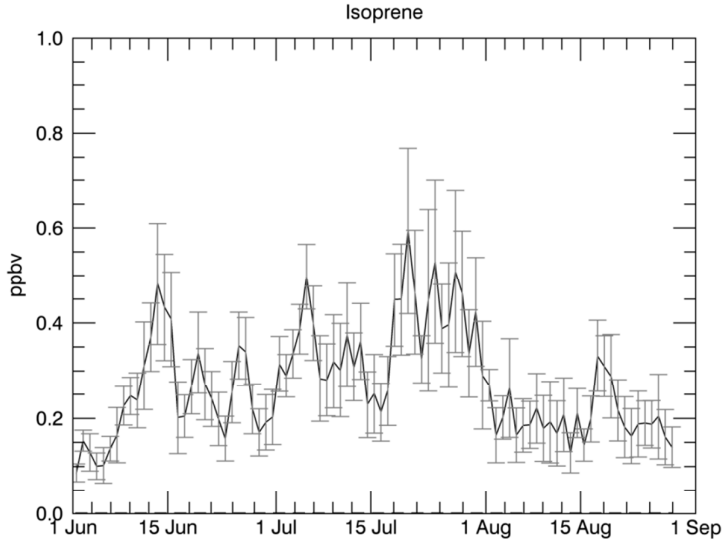

Figure 2. The 8-hour daily maximum concentrations of isoprene in 2006 from the ANTH+BIO simulation. The mean impact averaged over six grid cells with measurements is plotted with a solid black line. The error bars show the standard deviation of the 8-hour values for each day.

We also expected to see a response of the SOA concentration (mass) to the emissions of VOCs from vegetation in the model simulations and an amplification of this response during the heat wave. High temperatures and stable atmospheric conditions during heat wave periods result in an accumulation of SOA in the boundary layer, aging of VOCs (getting less volatile by oxidizing), and atmospheric residence times of up to 10 days. Measurements in the Berlin-Brandenburg metropolitan area conducted within the framework of the BAERLIN campaign indicated that VOCs play an important role in particle formation in that area[39]. Calculated contributions of both anthropogenic and biogenic VOCs to particulate matter formation (PM_{10}) in summer 2014 were on average 38.2±9.4%[40] as compared to, for instance, diesel soot contribution of 13.2±6.2%. PM_{10} loading was 17.9±3.9 $\mu g/m^3$ of which 6.8±1.9% was organic carbon. The organic carbon consists of two groups, i.e., pre-existing organic carbon that has been transported from elsewhere to the site of interest and organic carbon which is formed onsite. The first group may partially contain aged SOA with a lot of functionalities and lower volatility. In order to separate the organic from elemental carbon, all OC was assumed to be completely volatile at a temperature of 760°C. If OC was not regained as gas at this temperature it was assumed to be elemental carbon[42]. The analysis was made as lower estimate of organic carbon. The majority was high and medium volatile organic carbon with contributions of 35% and 43.2% respectively. Based on a box model study (Bonn et al., in prep.) the contribution of anthropogenic VOC sources to SOA formation is minor, particularly to be very small away from the emission source. Close to the highways, however, this contribution is likely to be higher.

Because of the large variability of SOA in the model simulations and the rather short simulation periods, statistically significant results for the contribution of biogenic VOC emissions to the simulated particulate matter in the study area could not be obtained. The analysis of the SOA anomalies calculated for several sites in the study area showed a poor signal to noise ratio (see Figure S2 in the supplementary material) consequently we did not proceed with the analysis of PM_1

and $PM_{2.5}$. Furthermore, the chosen SOA mechanism in the applied configuration of WRF-Chem (SORGAM[64]) is known to underestimate the formation of SOA[65] impacting also SOA related aerosol dynamics and deposition. The model deficits can be partially explained by a simplified treatment of the biogenic VOCs in the RADM2 chemical mechanism of WRF-Chem used here, because eight different groups of monoterpenes and three classes of sesquiterpenes simulated by MEGAN are lumped together into one chemical species (OLI). Individual treatments of the VOC groups implemented in the RADM2 model may alleviate these problems as diverse VOC groups contribute differently to particle formation. Furthermore, RADM2 does not include the oxidation of biogenic monoterpenes and has a limited treatment of anthropogenic VOC oxidation[66].

How reasonable were the simulated responses?

Kuik et al.[47] demonstrated that the WRF-Chem model setup similar to the one in this study simulated summer temperatures at the 2 m height for Berlin and Potsdam reasonably well at a 1kmx1km horizontal model resolution (bias mostly positive, smaller than +1.5°C at all 15 stations with observations). The model did not reproduce the highest observed temperatures. The diurnal cycle of the planetary boundary layer height was reproduced reasonably well by the model, as compared to observations derived from a radiosonde and a ceilometer. The comparisons suggested that the nighttime planetary boundary layer height was underestimated in the model. Although main wind directions were modeled reasonably well, wind speed was overestimated by 0.5-1.3 m/s in the simulation with a 1kmx1km horizontal resolution. NO_x concentrations were simulated satisfactory on average, but overestimated at night, which is probably at least partly related to the underestimated boundary layer height. Maximum daily 8-hour means of the ozone concentration were slightly underestimated with a bias of up to ~-13 mg m^{-3} depending on the station. Concentrations of particulate matter were underestimated with larger biases. PM_{10} was underestimated by ~50%, while $PM_{2.5}$ was underestimated by ~20-35%. An adjustment of the chemical mechanism would be most likely required for better skill in reproducing observed concentrations of particulate matter.

Observations of isoprene

Measurements of isoprene mixing ratios obtained during the BAERLIN campaign in 2014 show a gradient from high values in urban forests and parks to low values at urban background stations and very low or zero concentrations at city highways (Figure 3). The differences between urban and sub-urban sites could be explained by different vegetation fractions. Low values of isoprene mixing ratios observed at the city highways could be related to relatively long distance to emission sources, i.e., VOC emitting plants, and/or to available isoprene immediately entering reactions with NO_x emitted in substantial quantities from motorized vehicles on the highway. Large number of deciduous trees with high emissions of isoprene in urban forest sites is most likely responsible for the high mixing ratios of isoprene characteristic for urban forest.

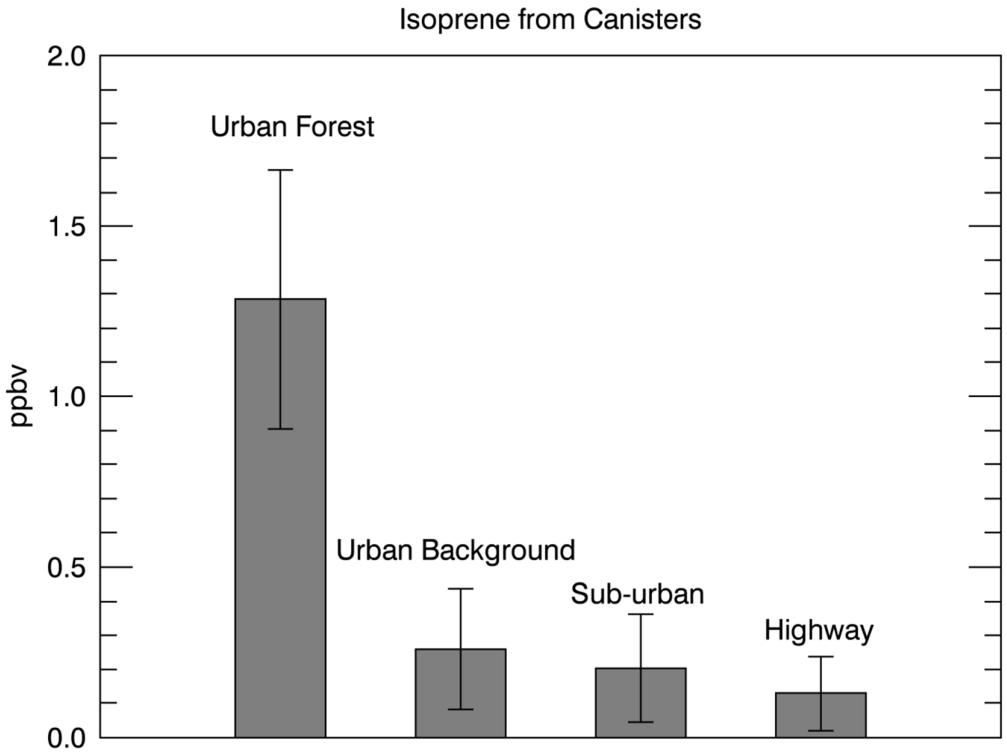

Figure 3. Variability of observed isoprene concentrations over different urban land use types. The bar height indicates the mean hourly concentration calculated from all samples collected at each land use type. The standard deviation is shown as error bars.

Although simulated isoprene values at the urban background sites agree reasonably well (gray and black filled circles in Figure 4), the gradient in isoprene concentration from low values near the highway to the high values in urban forests could not be reproduced by the model. In particular, the model overestimates isoprene concentrations at the suburban site and does not capture the high values of isoprene concentrations characteristic for locations with a high fraction of vegetation (green filled circles in Figure 4) with a model bias in the order of 1-1.4 ppb_v. The underestimation can be attributed to several reasons including spatial resolution (high dilution), emission factors for biogenic VOCs used in the model, poor representation of urban vegetation in the MEGAN input data, as well as the simple chemical mechanism of WRF-Chem used in this study (too fast degradation). In this study we tested how a more refined representation of the vegetation in MEGAN can improve simulations of isoprene.

Modification of fractional vegetation types and LAI improves only marginally the isoprene concentrations at the study sites (see Supplement, Figure S4). The improvement was noticeable for a suburban site in Alt Landsberg, where the model originally overestimated concentrations of isoprene (yellow filled circles in Figures 4 and S4) and the urban forest site in Grunewald (green filled circles in Figures 4 and S3), where isoprene values were greatly underestimated in the model simulation with the default MEGAN input data (ANTH+BIO). The modifications of the MEGAN input data resulted in a

lower LAI (from 2.9 to 2.1/1.7 in July) in Alt Landsberg, which lowered simulated emissions of isoprene at that site, and in higher LAI (from 2.5 to 5.4/1.5 in July) in Grunewald, which increased modeled isoprene values at that site. While for Alt Landsberg this modification resulted in good agreement between modeled and measured isoprene concentration, for Grunewald and other densely vegetated sites the model still underestimates the isoprene by ~ 0.6 -1.4 ppb_v (max LAI simulation). This suggests that also the emission factors of biogenic VOCs would have to be adjusted for urban vegetation, or the LAI would need to be further refined, e.g., based on high resolution remote sensing data products.

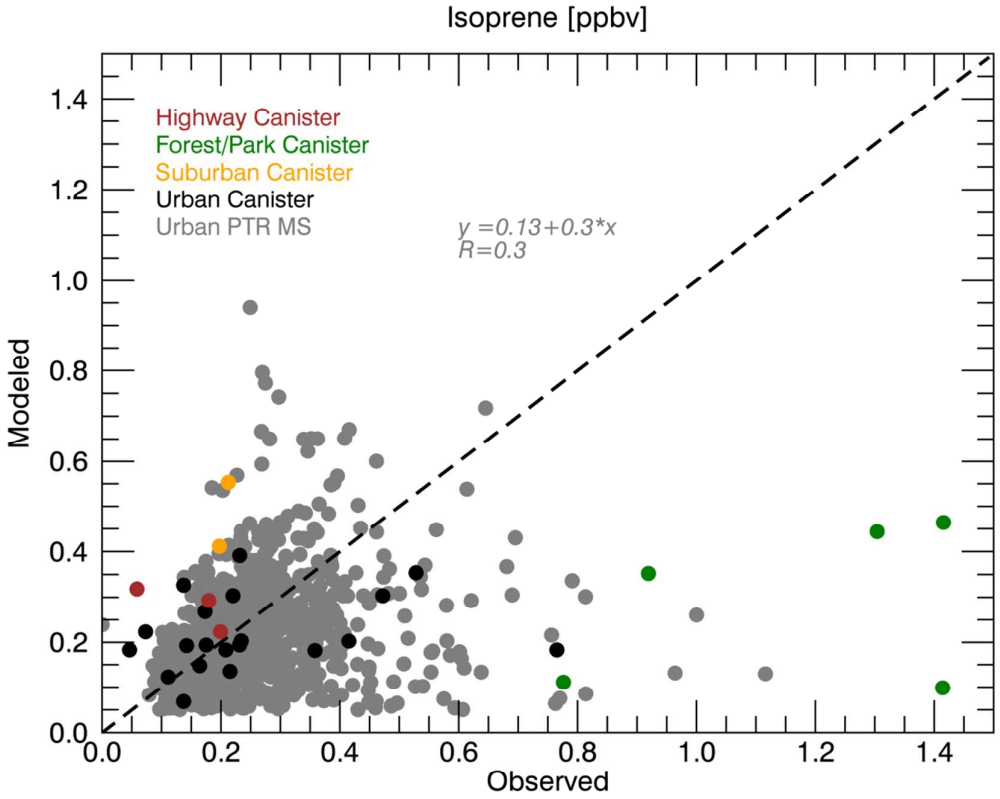

Figure 4. Comparison of modeled and observed concentrations of isoprene measured with PTR-MS and canisters (Table 1) in Berlin in summer 2014. Modeled values represent instantaneous hourly isoprene concentrations calculated for the 1x1 km^2 grid cells closest to the measurement sites. Observed values represent point measurement of the isoprene volume mixing ratio averaged over one hour. Modeled and observed values below 0.05 ppb_V have been excluded from this comparison, because such concentrations are below or close to the detection limit of the PTR-MS.

The isoprene emission factors used in the model likely result in an underestimation of isoprene emissions from vegetation over Berlin, which possibly leads to a correspondingly smaller concentrations of isoprene over green areas (Figure 4) and the ground level ozone, especially during ozone peaks. To investigate this further, we calculated the emission factors for the Berlin vegetation, considering the species distribution within the different urban green types (Table 6). This shows that emission factors used in the model are too low for broadleaved forest. In Berlin, high isoprene

emitting species such as oaks, plane trees, and locusts constitute almost 20% of broadleaf trees. The typical coniferous forests in Berlin are dominated by the low isoprene emitting pines, which may be however, compensated by an addition of 13% of oaks. Since these are not evenly distributed, local emission factors of conifer forests might be higher than the calculated average.

Table 6. Comparison of isoprene emission factors used in MEGAN and calculated from literature for Berlin vegetation. Emission factors were extracted for grid cells with maximum vegetation coverage (>60%) in the study area (innermost domain of the model simularions).

Modeled vegetation types	Maximum pixel area covered in MEGAN [%]	Emission factors assumed in MEGAN [mol km^{-2} hr^{-1}]	Emission factors from literature weighted by species composition [mol km^{-2} hr^{-1}]
Deciduous broadleaf forest	64	78-84	102
Evergreen needleleaf forest	76	8-37	26
Shrublands	73	76-91	84
Herbaceous	95	6-54	15

Model simulations suggest that vegetation can have a pronounced effect on ground level ozone in Berlin, Germany. The mean contribution of biogenic VOCs to maximum 8-hour ozone levels in Berlin in summer 2014 is found to be ~12%. The contribution increased up to 60% during the heat wave in July 2006, because vegetation emitted more VOCs with rising temperatures. This modeled contribution is likely to be on a low side as WRF-Chem underestimate biogenic VOC concentrations of vegetated urban areas. Observations of VOCs suggest that isoprene mixing ratios could reach 1.4 ppb_v (corresponding modeled values 0.05-0.8 ppb_v) over urban broadleaf forests and parks of Berlin, which may become potential hot spots for ozone in summer. Previous studies showed that NO_x concentrations in Berlin remained high over the years and were thought to be responsible for elevated ozone levels in the presence of sufficient VOCs. Reducing car traffic in the city, which is the major source of NO_x and of anthropogenic VOCs, remains a top priority here.

Our modeling study revealed shortcomings of WRF-Chem for simulations over urban areas. First, WRF-Chem as set up in this study has a limited ability to simulate SOA, PM and associated effects of biogenic VOCs on PM formation in urban areas. Refined treatment of biogenic VOCs and representation of SOA in WRF-Chem are needed to assess the effects of biogenic VOCs on particle formation in urban areas. Explicit representation of monoterpenes and sesquiterpenes in chemical mechanism of WRF-Chem would be recommended. Second, WRF-Chem has a limited ability to simulate isoprene mixing ratios over urban forests because of a rather poor representation of urban vegetation in MEGAN (location, leaf area index, VOC emission factors). It should be kept in mind that an evaluation of modeled isoprene concentrations with point measurements is challenging because of the rather coarse spatial model resolution (1x1 km).

The heat wave in 2006 resulted in an increased premature mortality in Berlin, which was primarily attributed to high air temperatures. Here, we argue that the increased air pollution during that heat wave may have contributed to the amplified mortality as well. Previous studies report enhanced levels of ozone and particulate matter also indoors, where people spend most of their time and consequently breath in air pollutants during the heat wave in Europe in summer 2003[67]. Implications

of high temperature combined with high air pollution concentrations for human mortality are still not that clear. Air pollutants may have confounding and/or synergistic effects on the temperature-mortality relation[68]. Our study demonstrates that biogenic VOCs can contribute considerably to enhanced air pollution during heat waves. Therefore, we emphasize the dual role of vegetation for air quality and human health in cities during warm seasons, which is removal (through leaf stomata uptake and plant surface deposition) and lessening (through reduction of heat island effect) versus enhancement of air pollution. Radical reduction of anthropogenic sources of NO_x, VOCs, and PM through e.g., city traffic reduction, would have to accompany urban tree planting campaigns in order to make them fully beneficial for urban dwellers.

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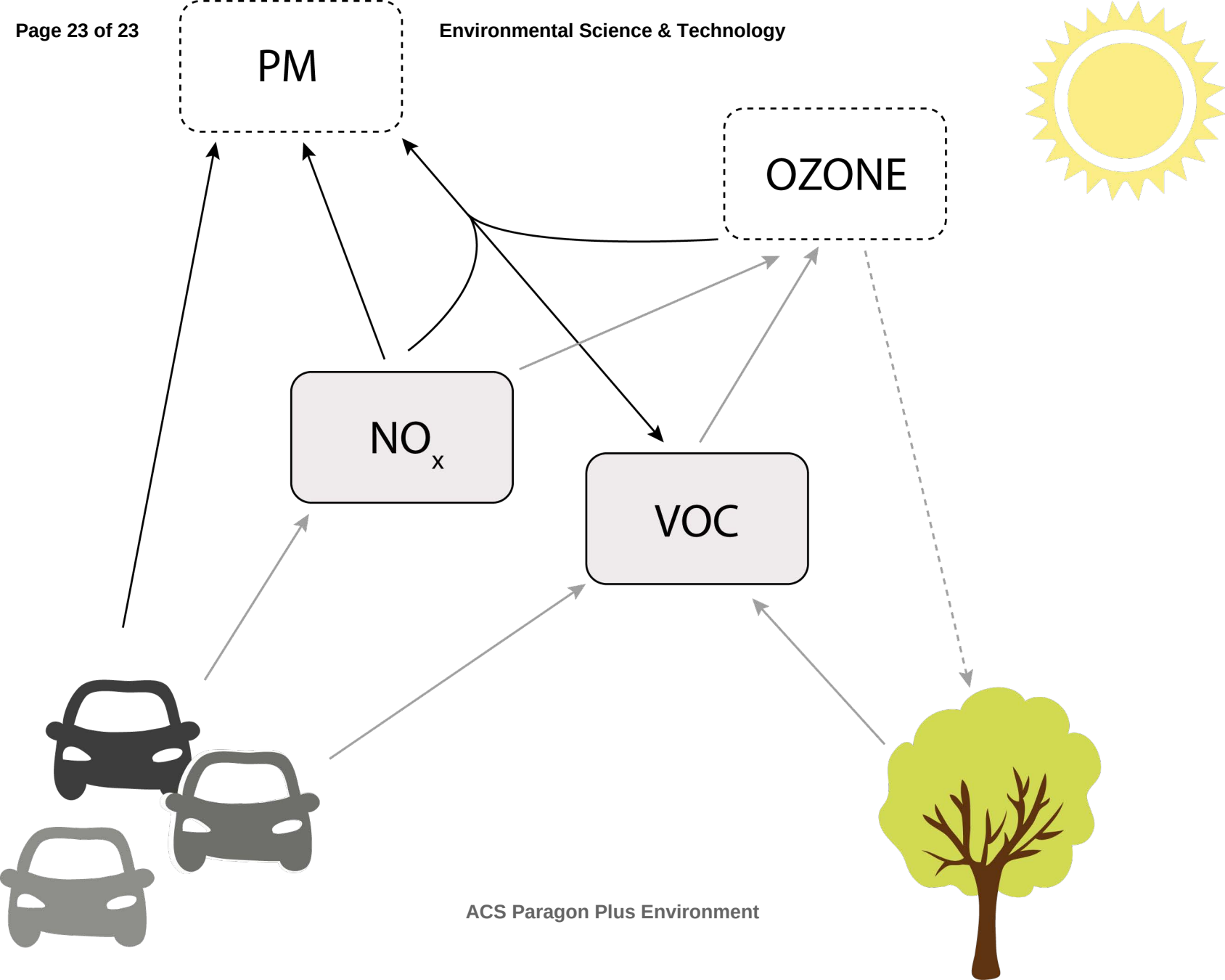
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