Atmos. Chem. Phys. Discuss., 8, 13619–13632, 2008
www.atmos-chem-phys-discuss.net/8/13619/2008/
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Atmospheric Chemistry and Physics Discussions

Emission of sunscreen salicylic esters from desert vegetation and their contribution to aerosol formation

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Received: 21 May 2008 – Accepted: 24 June 2008 – Published: 16 July 2008

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Biogenic volatile organic compounds (BVOC) produced by plants are known to have an important role in atmospheric chemistry. However, our knowledge of the range of BVOCs produced by different plant processes is still expanding, and there remain poorly understood categories of BVOCs. In this study, emissions of a novel class of BVOC emissions were investigated in a desert region. Our study considered 8 species of common desert plants: blackbrush (*Coleogyne ramosissima*), desert willow (*Chilopsis linearis*), mesquite (*Prosopis glandulosa*), mondel pine (*Pinus eldarica*), pinyon pine (*Pinus monophylla*), cottonwood (*Populus deltoides*), saguaro cactus (*Carnegiea gigantea*) and yucca (*Yucca baccata*). The measurements focused on BVOCs with relatively high molecular weight ($>C_{15}$) and/or an oxygenated functional group. Significantly high emission rates of two salicylic esters were found for blackbrush, desert willow and mesquite with emission rates of 1.4, 2.1 and 0.46 μgC dwg^{-1} h^{-1}, respectively. The salicylic esters were identified as 2-ethylhexenyl salicylate (2-EHS) and 3,3,5-trimethylcyclohexenyl salicylate (homosalate) and are known as effective ultraviolet (UV) absorbers. We propose that the plants derive a protective benefit against UV radiation from the salicylic esters and that the emission process is driven by the physical evaporation of the salicylic esters due to the high ambient temperatures. In addition, the salicylic esters are predicted to be an effective precursor of secondary organic aerosol (SOA) because of their low vapor pressure due to a high number of carbon atoms (15 or 16) and the presence of three oxygen atoms. We estimated the contribution of the sunscreen esters themselves and their oxidation products on the SOA formation for the Las Vegas region using a BVOC emission model. The contribution was estimated to reach 90% of the biogenic SOA in the landscapes dominated by desert willow and mesquite and 25% in Las Vegas area.

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1 Introduction

Aerosol particles have a significant role for regional air quality and global climate change. In addition to their direct release into the atmosphere (primary aerosol), aerosol can also be formed by condensation of oxidation product of the atmospheric volatile organic compounds (VOCs) and is then classified as secondary organic aerosol (SOA). Because SOA is generated from molecules in the gas phase, it tends to be finer and has a longer residence time in the atmosphere than primary aerosols (Fuzzi et al., 2006). Terrestrial vegetation emits a significant amount of reactive VOCs into the atmosphere, known as biogenic VOCs (BVOCs). The most common BVOCs include isoprene (2-methyl-1,3-butadiene) and monoterpenes (C_{10} hydrocarbons). The global emission of BVOCs is an order of magnitude larger than that of VOCs from human activities (Guenther et al., 2006). In addition, BVOCs are generally very reactive and produce oxygenated and polar compounds via the degradation process (Atkinson and Arey, 1998). A portion of these products forms SOA in the atmosphere. For example, oxidation of monoterpenes leads to SOA formation in a forest (Kavouras et al., 1999), and the oxidation products of isoprene also contribute to the aerosol fraction (Matsunaga et al., 2003; Claeys et al., 2004; Matsunaga et al., 2005; van Donkelaar et al., 2007). Because of both SOA formation and gas phase photochemistry, BVOC emissions impact both regional air quality and the global climate.

However, it is likely that we know only a part of the total range of BVOC species being released into the atmosphere because of limitations of analytical technique and the lack of investigation. Particularly, scientists have inferred that more BVOCs exist than are routinely measured (Goldstein et al., 2004; Di Carlo et al., 2004) and compounds with a relatively high molecular weight (around C_{15}) have been targeted for study. One class of BVOCs that have received more recent attention are the sesquiterpenes (SQT), which are terpenoids, in most case, with a very high reactivity in the atmosphere (Helmig et al., 2006; Duhl et al., 2007; Matsunaga et al., 2008[1]). Because

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SQTs have 15 carbon atoms, the degradation process can result in multiple generations of products. Therefore, the entire atmospheric degradation time of SQTs can be longer than that of smaller VOC although lifetime of the original VOC is shorter. These products will be oxygenated, which lowers their vapor pressure and favors SOA formation.

There are potentially many other BVOCs with high molecular weights that also could be involved in SOA production; the esters 2-ethylhexenyl salicylate (2-EHS) and 3,3,5-trimethylcyclohexenyl salicylate (homosalate) are two candidates. These compounds are used as an active ingredient in sunscreen due to their UV absorption. In a similar manner to how plants employ flavonoid compounds to protect their DNA from UV radiation damage (Stapleton and Walbot, 1994), desert plants may employ these sunscreen esters as a protective mechanism. Because 2-EHS and homosalate are C_{15} and C_{16} salicylic esters, respectively, they will evaporate only at high ambient temperatures but may be released into the atmosphere in warm environments. Analogous to SQTs, these sunscreen esters are expected to degrade and form semi-volatile products. Because of oxygenation during these degradation steps, the entire SOA yield can be more than unity. These sunscreen esters represent a previously unknown source of SOA, and here we report for the first time the emission rates of the sunscreen esters from desert plants and a model estimate of the contribution of these esters to SOA production.

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2 Experiment

2.1 Sample collection and treatment

Plant enclosure sampling was performed between 1 July and 6 July 2006 from typical urban and wild land desert shrubs and trees at four sites located in the Las Vegas, NV, USA area: a desert shrubland, a golf course, the campus of the Desert Research Institute and at a city public park. The SQT samples were collected from 8 species of typical plant in those area. Leaves or small branches were enclosed in a 1-liter glass cuvette with temperature control (Fig. 1). The internal temperature of the enclosure was set to approximately ambient air temperature (25–35°C). Air, purified with a coconut charcoal trap (Orbo tube , Supelco, Bellefonte, PA, USA), flowed continuously through the glass enclosure at a rate of 720 ml min^{-1}. While CO_2 concentration may be changed by the charcoal trap, the resulting CO_2 concentrations remained close to ambient levels. CO_2 and water vapor concentrations of the air entering the cuvette was analyzed with a Li-COR 6400 (Li-COR Biosciences, Lincoln NE, USA). The Li-COR 6400 also had a second trap (Restek Hydrocarbon Trap, Restek, Bellefonte PA, U.S.A.) on its air inlet to remove ambient hydrocarbons and ozone. Air for VOC analysis was withdrawn from the enclosure at a rate of 220 ml min^{-1}, and sampling times ranged from 1.5 to 4 h.

Another portion of air exiting the cuvette was collected onto 30 mg of Super Q adsorbent (Alltech, Columbia MD, USA) in a 6.3 mm diameter glass tube (Volatile Collection Trap, Analytical Research Systems, Inc., Gainesville FL, USA). Collected compounds were extracted from the adsorbent immediately after sampling with approximately 2 ml of dichloromethane. After extraction from the collection trap, the samples were placed into 2 ml glass vials, sealed with a plastic cap with PTFE liner and stored in a freezer (approximately −15°C) prior to being shipped back to the NCAR (Boulder, CO, USA) laboratory for analysis. Although they were covered with coolants, the samples may have been exposed to above-freezing temperatures (0–10°C) during shipping. The extracts were concentrated in the laboratory by evaporating the solvent with a gentle argon flow to less than approximately 2–3 μl, and then 30 μl of hexane was added to

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the vial to adjust the volume. These final solutions were stored in the freezer until analysis.

2.2 Analysis

A gas chromatograph (GC, HP5890GC, Agilent Technologies, USA) with a flame ionization detector (FID) was used for separation and quantification of the compounds. The esters were identified using a gas chromatograph mass spectrometer (GC/MS, Saturn 2000, Varian, USA.), and their GC retention times were compared with those of the authentic standards (see Fig. 2 for mass spectra). The GC is equipped with a cold on-column injector and fused silica capillary column (HP-5, 0.32 mm i.d., 0.5 μm film thickness, 60 m) and uses helium as carrier gas. A 2 μl aliquot of the final solution of the sample was injected into the GC. Compounds were identified by comparison of retention time with authentic standards and were quantified by comparison of peak area with a standard solution of the authentic standards which were gravimetrically quantified. Calibrations using a standard solution were performed every day and used to determine the amount of the compounds in samples injected within the same day. Control (blank) samples were also collected directly from zero air flow. Obtained peak areas from the sample analysis were corrected based on a "loss factor" which characterizes the fraction of the esters that remains in the final vial after the concentration process. The loss factor was 0.45 for both 2-EHS and homosalate. The loss factor was obtained by a comparison of peak area of compounds in Ar concentrated solution and in a solution with a diluted solution based on gravimetrically determined concentration without any concentration process. In addition, the uncertainty due to the concentration process could be standard deviation of 10–15%. The emission rates of the esters discussed in this report are adjusted using the loss factor.

2.3 Emission model

Salicylic ester emission factors determined from this study and the SQT temperature dependence reported by Helmig et al. (2007) were incorporated into the MEGAN biogenic emission model (Model of Emissions of Gases and Aerosols from Nature, Guenther et al., 2006). MEGAN includes methods for characterizing and processing land cover type and density, improved simulation of canopy environment including leaf energy balance calculations, light penetration through varying canopy types, and detailed chemical speciation. MEGAN is a global model but has a 1 km spatial resolution and so can be used for regional modeling. The landcover inputs used to drive MEGAN were based on remote sensing and ground measurements conducted by Maria Papiez (Desert Research Institute).

3 Results and discussion

3.1 Emission rates of the sunscreen esters

The emission rates of 2-EHS and homosalate varied from 0.01 and 0.03 μgC dwg^{-1} h^{-1} to 1.1 and 1.7 μgC dwg^{-1} h^{-1}, respectively (see Table 1). The emission of the salicylic esters was assumed to be temperature dependent because the emission process is most likely evaporation from the plant surface. This assumption is reinforced by our conclusion that these esters function as a UV absorbent–there is no obvious benefit to specifically emitting these compounds. We used an empirical equation to describe temperature dependent emission which was developed for monoterpenes (Guenther et al., 1993) and modified to work for sesquiterpenes (Helmig et al., 2006).

$$E_s = E/\exp[0.17(T - 303)] \quad (1)$$

T is leaf temperature, E is the measured emissions and E_s presents VOC emission rate at 30°C. Using this equation, observed temperature can be converted into the rate

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at the standard temperature (30°C). Table 1 also shows the emission factor E_s for each plant species calculated using (1). The emission rates vary by orders of magnitude for different species. Desert willow (*Chilopsis linearis*), blackbrush (*Coleogyne ramosissima*) and mesquite (*Prosopis glandulosa*) show much higher emission rates compared to the other species.

3.2 Impact of the sunscreen salicylate on biogenic SOA formation

Figure 2 illustrates estimated sunscreen compound contributions to total biogenic SOA formation. This value was obtained by applying an average SOA yield to the July average emission. The emissions were calculated using the MEGAN model and the SOA yields were based on Sakulyanontvittaya et al. (2008), assuming that the salicylic esters have an SOA yield similar to SQT. The salicylic esters often contributed at least 25% of the estimated total and were responsible for 90% in landscapes dominated by the high emitting desert willow and mesquite. Additional surveys are needed to determine if there are high emitting species in more landscapes.

4 Conclusions

Two salicylic esters, which have the capacity to absorb UV radiation, have been identified as being significantly emitted by plants living in a desert environment. Assuming an aerosol yield of 1 for these sunscreen esters, they are found to have a remarkable contribution to biogenic secondary organic aerosol (SOA) formation in the Las Vegas region. The contribution was estimated to be 25% for many areas; however, it exceeded 90% in some areas dominated by desert willow and mesquite. This study is the first report that salicylic esters are being emitted into the atmosphere from desert plants and that they can be a significant factor for SOA formation.

Acknowledgements. This study was supported by the Advanced Study Program in National Center for Atmospheric Research which is sponsored by the National Science Foundation and

was also supported by the Clark County Division of Air Quality and Environmental Management.

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Table 1. Observed emission rate and emission factor of the salicylic esters from desert plants.

Common Name Species	Mondel Pine Pinus eldarica	Black Blush Coleogyne ramosissima	Pinyon Pine Pinus monophylla	Yucca Yucca baccata	Mesquite Prosopis glandulosa	Populus Populus deltoides	Desert Willow Chilopsis linearis	Saguaro Cactus Carnegiea gigantea
Leaf Temp	35.1	34.2	29.4	31.2	36.8	24.9	35.2	35.4
Emission Rate, E (μgC dwg^{-1} h^{-1})								μgC cm^{-2} h^{-1}
2-EHS	0.015	1.1	0.026	0.011	0.20	0.007	0.44	5.0E-04
Homosalate	0.054	0.27	0.028	0.015	0.26	0.017	1.7	1.6E-03
Total	0.070	1.4	0.054	0.026	0.46	0.024	2.1	0.002
Emission Factor, E_s								
2-EHS	0.006	0.550	0.029	0.009	0.063	0.017	0.18	2.0E-04
Homosalate	0.023	0.13	0.031	0.012	0.083	0.040	0.70	6.6E-04
Total	0.029	0.682	0.060	0.021	0.15	0.058	0.88	0.001

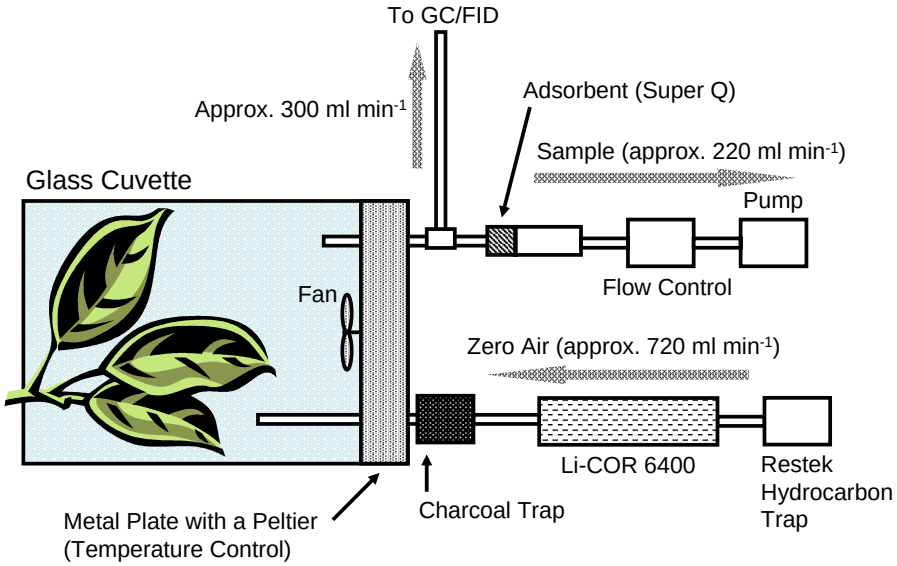

Fig. 1. A schematic of the plant enclosure.

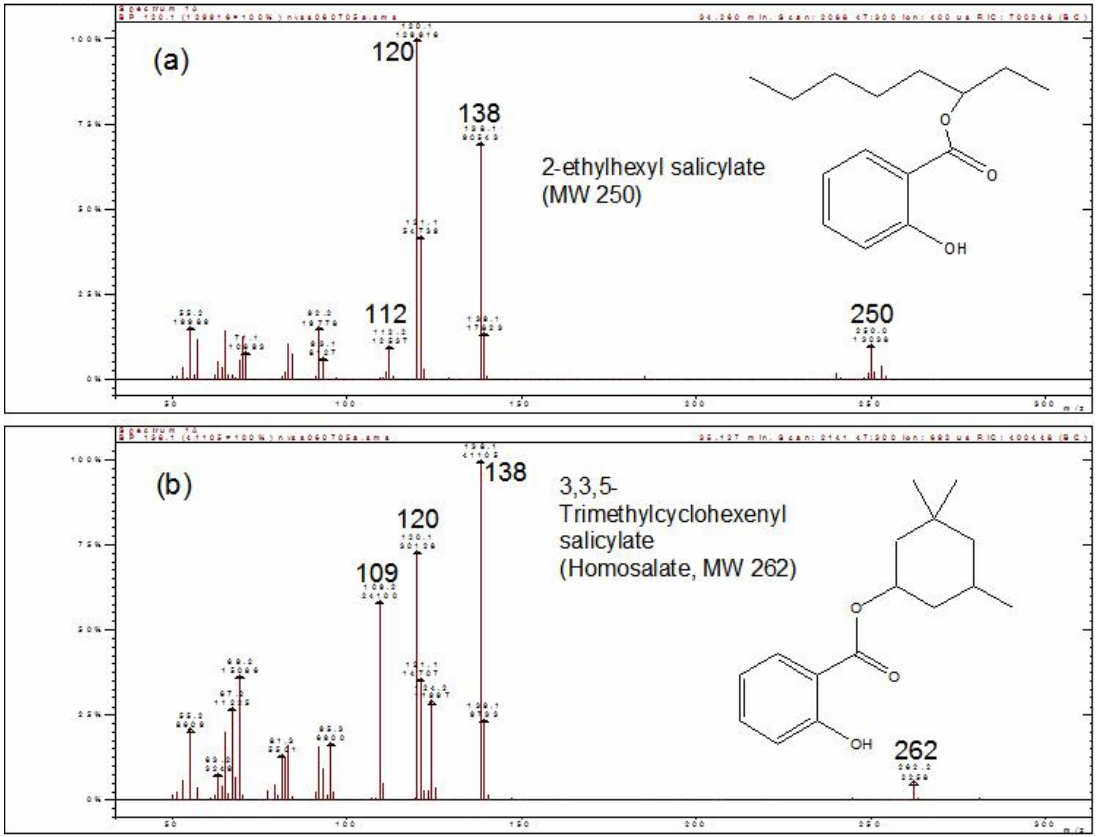

Fig. 2. Chemical structure and ion trap mass spectrums of **(a)** 2-ethylhexyl salicylate and **(b)** 3,3,5-trimethylcyclohexenyl salicylate.

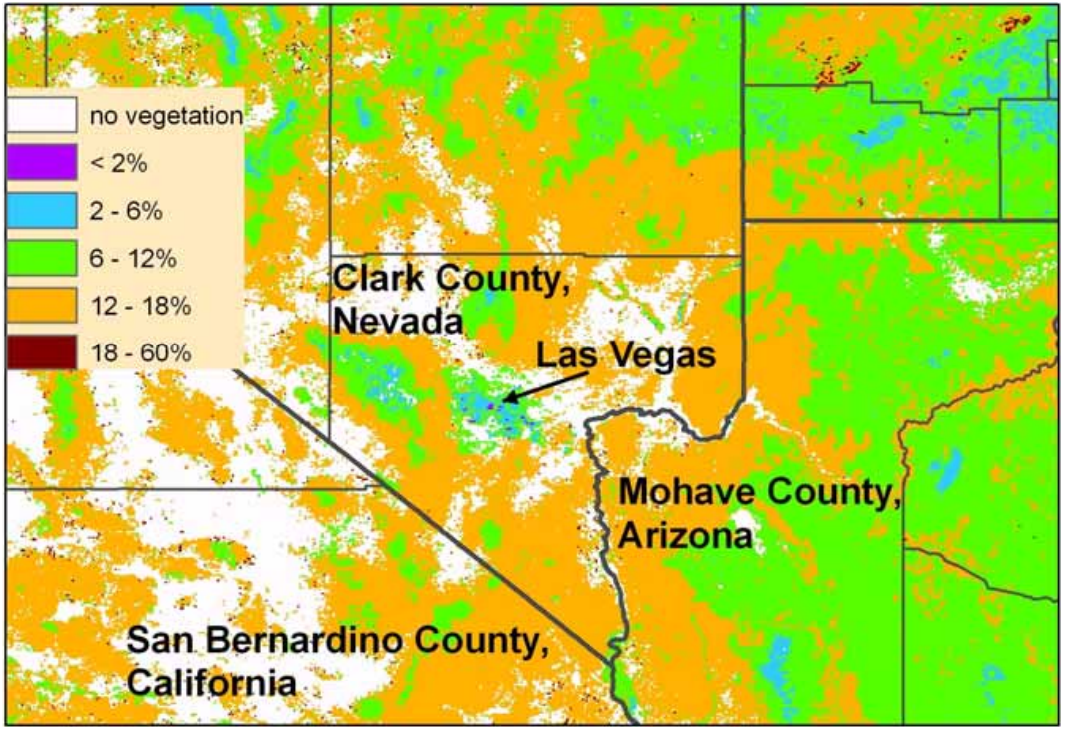

Fig. 3. Contribution of 2-ethylhexenyl salicylate and 3,3,5-methylcyclohexenyl salicylate on total biogenic secondary organic aerosol formation under the assumption of an aerosol yield of 1 estimated by an emission model.

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