MEASUREMENT OF VOLATILE ORGANIC COMPOUNDS EMITTED BY GREEN PLANTS: UNDERSTANDING PLANT CONTRIBUTIONS TO AIR QUALITY

A Research Report to the

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Abstract

To answer critical questions regarding the interactions between green plants and air quality, two three-year projects are underway to investigate emission of volatile organic compounds (VOC) from selected plant species. These biogenic VOC (BVOC) and oxides of nitrogen (NOx) can react in the lower atmosphere in the presence of sunlight to form ozone and secondary particulate matter, the principal air pollutants in California airsheds. This work will provide a better understanding of the role that citrus and other crops play in ozone destruction via surface deposition, stomatal uptake, and reactions in the crop canopy. Results will improve biogenic emission inventories and increase understanding of regional VOC levels, and therefore aid the California Air Research Board in improving air quality attainment strategies. For example, results may affect regulatory emphasis on other VOC sources (e.g. cars, trucks, pesticides) and NOx controls (e.g. emission controls on engines). Other possible implications regard chemical signaling between insects and plants. This work includes laboratory investigations at UC Berkeley and field studies in Tulare County. The Slosson endowment provided seed money for these projects.

1.0 EXECUTIVE SUMMARY

The Issue:

Green plants in gardens and landscapes play important direct roles in improving air quality through sequestration of carbon dioxide, emission of oxygen, and providing surfaces for deposition of airborne particles and gases. Plants also play significant indirect roles in reducing air pollution through providing shade and lowering air temperatures, thus reducing the need for energy consumption for cooling. Plants also play important roles in air quality through emission of volatile organic compounds (VOC), which may react with oxides of nitrogen (NOx) to produce ozone, which in the lower atmosphere is a pollutant affecting human health and reducing crop yields. Conversely, ozone may be destroyed by plants through stomatal uptake, surface deposition, and within-canopy chemical loss processes.

What has ANR done?

To answer critical questions regarding the interactions between green plants and air quality, two three-year projects are underway to investigate emission of VOC from selected plant species. We identified and quantified VOC produced (emitted and stored) by leaves of 22 woody and herbaceous plants found in California. We also measured ozone deposition rates to selected plant species.

The Payoff

- BVOC emission shows a typical daily pattern with maximum emissions around noon.
- Navel orange is the highest BVOC emitter of citrus measured in this study (0.45 $\mu gC\ g(DW)^{-1}\ h^{-1}$). However, that emission rate is much lower than emission rates measured for many plant species found in natural plant communities and urban landscapes.
- Ozone is removed by plants, and the removal rate also shows a typical daily pattern.

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2.0 PROJECT DESCRIPTION

2.1 INTRODUCTION AND BACKGROUND

Green plants in gardens, orchards, and landscapes play important direct roles in improving air quality through sequestration of carbon dioxide, emission of oxygen, and providing surfaces for deposition of airborne particles and gases. Plants also play significant indirect roles in reducing air pollution through providing shade and lowering air temperatures, thus reducing the need for energy consumption for cooling.

Plants also interact with the atmosphere in other ways. Frits Went postulated that organic molecules emitted from vegetation were responsible for the blue hazes found in heavily forested regions (Went, 1960). Isoprene, a five-carbon compound, was shown to be emitted by plants (Sanadze, 1969) as were compounds of larger molecular weights (Isidorov et al., 1985). However, more complete realization of the importance of such emissions came later when their magnitudes and atmospheric reactions became better understood (Chameides et al., 1988), and currently there is intense worldwide interest from several vantage points in the emission of VOC from plants. For example, an accurate estimate of the magnitude of these biogenic VOC (BVOC) contributions is important in formulating strategies to reduce concentrations of certain secondary pollutants, such as ozone, fine particles, and other compounds such as PAN, because an effective air quality attainment strategy must take into account the strength of total VOC emissions. Quantifying the nature of plant VOC emissions also aids in understanding the role of plants in the ecosystem. Although the addition of a few individual plants of any species has little effect on local air quality, massive planting programs may have significant impact, in which choice of low-emitting species vs. high-emitting species may result in a large difference in BVOC emissions. Emission rate information is being requested by landscape architects and urban planners, and could be an additional factor considered in species selection when large-scale planting programs are proposed for urban heat island mitigation and carbon sequestration. Emission rates for plants grown in large-acreage agricultural fields are also of interest to ag producers as well as those who model regional air quality.

In general, broadleaved plants, such as oaks and eucalyptus, have as their largest BVOC emission the five-carbon compound isoprene. The influence of light and temperature on emission rates for isoprene from woody plant families and genera has become relatively well understood (Guenther et al., 1993). Quantitative isoprene emission rate measurements of plants found in California landscapes were made for more than 60 plant species important in California, including many landscape and garden ornamentals (Karlik and Winer, 2001). Additional semiquantitative measurements of total VOC emission by plants have helped to describe BVOC emissions for an additional 200 plant species (Winer and Karlik, 2001; Karlik et al., 2002). The data have also been used to test the taxonomic method proposed by Benjamin et al. (1996) for assigning BVOC emission rates for isoprene and monoterpenes to ornamental species in California airsheds.

Less is known about emission of oxygenated compounds. Fortunately, a new analytical technique of proton transfer mass spectroscopy (PTR-MS) was developed by Werner Lindinger of the University of Innsbruck which is now being used to measure these compounds with high precision and accuracy. PTR-MS allows air sample analysis without sample preconcentration with cryogenics. It can measure speciated BVOC to lower part per trillion levels, and is also capable of real-time analysis of BVOC concentrations in sampled air, thus allowing rapid measurements to be made.

2.2 STATEMENT OF THE PROBLEM

Although many plant species have been characterized regarding climatic adaptations, pest susceptibilities, and other horticultural characteristics, benchmark data for emission of aerosol precursors and oxygenated BVOC for many genera and species are lacking. These data are needed to understand the role of green plants in mitigating air quality problems, for formulating effective air quality policy, and for more informed selection of plant species for large-scale planting programs. Also, data acquired by advanced instruments are needed to validate results for plants comprising extensive areas of land cover (Winer et al., 1992).

2.3 RESEARCH PROGRESS

In two funded projects, twenty-two plant species have been measured using an dual enclosure system constructed of Teflon sheeting suspended within a PVC frame and supported by a stand. A photo and diagram of the experimental apparatus are shown as Figures 1 and 2. Air containing a known concentration of CO_2 entered the enclosures at a known flow rate. The downstream air was directed to GC/MS and PTR-MS for compound identification and quantification. We also compared BVOC produced (emitted and stored) by leaves. Emitted BVOC were collected by passing air from the cuvette enclosing the branch through a glass tube packed with carbon based adsorbents. The adsorbents were later liquid extracted and concentrated in the laboratory. BVOCs stored in the plant tissues were extracted with an organic solvent, after plant grinding. Both BVOC emitted and BVOC stored were identified and quantified using the same GC-MS equipment. Most identified leaf emissions and stored compounds were terpenoids, but BVOC from other biosynthetic classes (benzenoids and fatty acid derivates) were not negligible. Differences between herbaceous and woody crops, and a variety of foliar secretory structures (e.g. secretory cavities, secretory ducts, glandular trichomes, and glands) were evaluated in terms of BVOC content and emissions to the atmosphere.

Plants may contribute to cleaning the air when the ozone is deposited on the canopies through stomatal and non-stomatal mechanisms, but ozone is also known to oxidize leaf tissues after entering stomata, resulting in a decrease of carbon assimilation and crop yield. To characterize ozone deposition for lemon (*Citrus limon*), mandarin (*Citrus reticulata*), and orange (*Citrus sinensis*), the branch enclosures allowed direct measurement of ozone uptake under different physiological conditions obtained in a greenhouse-controlled environment. A second aim of this part of the study was to measure VOC emissions from *Citrus* species which may play a key role in removing ozone through gas-phase chemical reactions in the intercellular spaces and outside the plant. Ozone uptake was quantified to be in the range of 2-11 nmol $m^{-2}s^{-1}$ under the highest conditions of physiological activity. Under high levels of ozone concentration, measured ozone deposition was lower than modeled ozone deposition based on the level of stomatal aperture, and this slope was even lower when correcting for the additional non-stomatal ozone sink represented by BVOC reacting with ozone in the gas phase. Our study highlighted the occurrence of two processes which in turn increase or decrease ozone deposition to citrus plants. First, BVOC contribute to increase of ozone deposition and fluxes by removing ozone through reactions in the gas-phase, and second, especially under high atmospheric ozone concentration, ozone accumulation in the intercellular spaces leads to a decrease of ozone fluxes.

2.4 SELECTED OUTCOMES

Selected outcomes include the following:

- BVOC emission shows a typical daily pattern with maximum emissions around noon.
- Navel orange is the highest BVOC emitter of citrus measured in this study (0.45 $\mu gC\ g(DW)^{-1}\ h^{-1}$). However, that emission rate is much lower than emission rates measured for many plant species found in natural plant communities and urban landscapes.
- Ozone is removed by plants, and the removal rate also shows a typical daily pattern.

Abstracts from this work have been presented at the national American Geophysical Union meeting as noted in the references (Fares et al., 2009; Park et al., 2008; Ormeno et al., 2008; 2009). Also, a poster describing this work was presented at the UC ANR conference held May, 2009, in Sacramento, in which Slosson funding was specifically acknowledged. The first two papers from the study have been submitted to *Environmental Science and Technology* and *Atmospheric Environment*. Additional manuscripts are in preparation.

2.5 BUDGETARY NOTE

The Slosson funding was intended to provide seed money, since the budget proposed and funded by Slosson ($7850) was known to be a fraction of what BVOC studies cost. The principal difference in expectation and outcome was in timing, because the projects to measure VOC began in 2007, a few years later than anticipated. These three-year projects are still ongoing at this writing. Also, the focus was shifted to mostly measure VOC from fruit and vegetable plants, many of which are grown in home gardens as well as agricultural fields, due to the interests of the principal funding sources.

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Figure 1: Branch cuvettes used for measuring gas exchange and VOC emission from green plants.

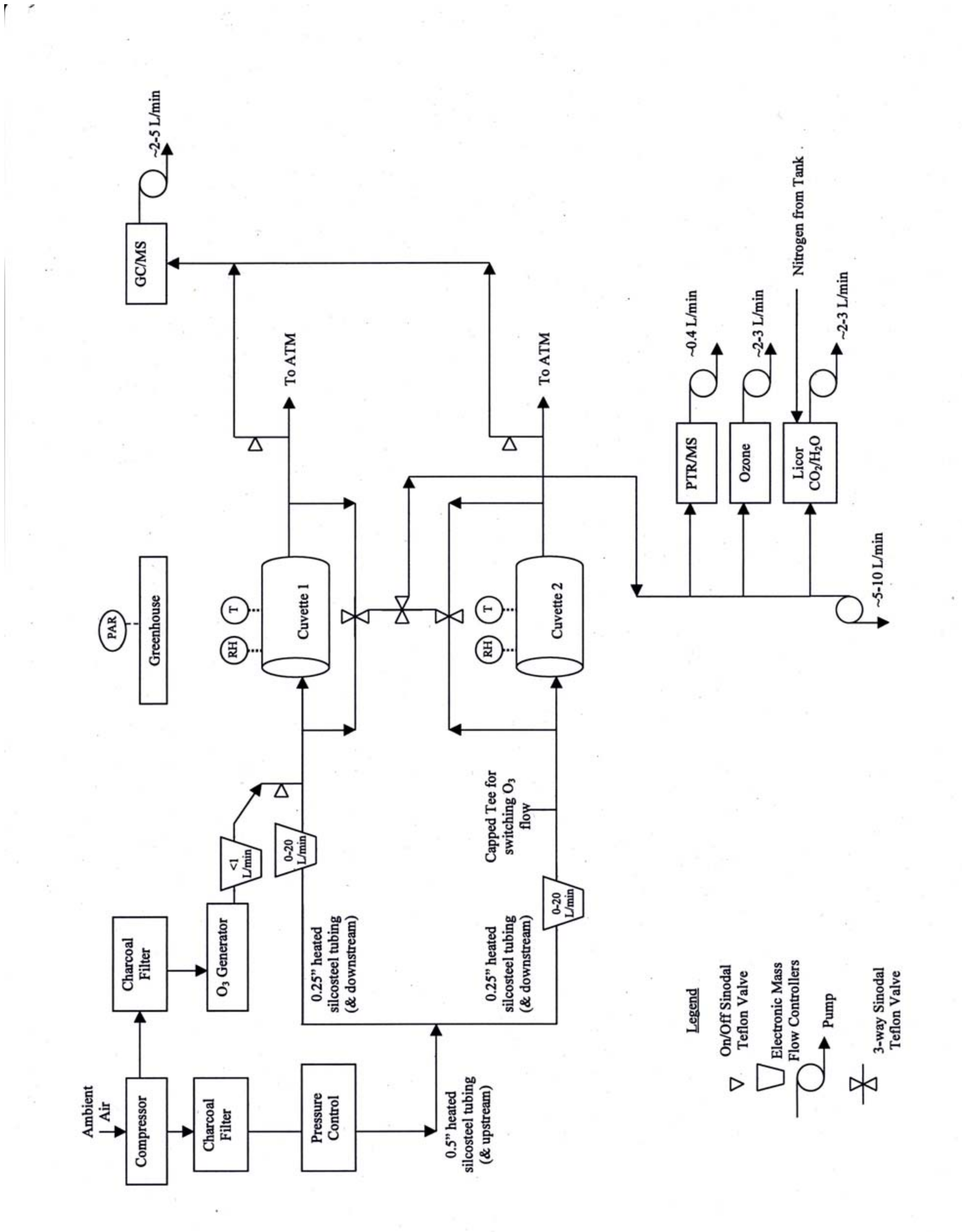

Figure 2. Experimental setup for measuring ozone uptake and BVOC emission with enclosures, showing air flows and analytical equipment.