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EMISSIONS OF NON-METHANE ORGANIC COMPOUNDS FROM A GRASSLAND SITE

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Abstract. A mixture of oxygenated hydrocarbons (OxHCs), isoprene, and monoterpenes was detected in the emissions from a grassland site in the midwestern United States. A plot dominated by crown vetch (*Coronilla varia*) and bluegrass (*Poa spp.*), exhibited a constant decrease in emissions of total non-methane organic compounds (NMOCs) from $580 \mu\text{g m}^{-2} \text{hr}^{-1}$ in June 1992 to $150 \mu\text{g m}^{-2} \text{hr}^{-1}$ in October 1992, except for a slight increase in August. Oxygenated hydrocarbons (methanol, acetaldehyde, and acetone) and terpenes (isoprene, limonene, myrcene, α -pinene, and β -pinene) composed about 90% and 10% of the identified NMOC emissions, respectively. Isoprene represented about 10% of the terpene emissions. Total NMOC emission rates based on vegetative biomass averaged $2.3 \mu\text{g g}^{-1} \text{hr}^{-1}$, with 10% of the identified NMOCs attributed to monoterpenes and the remainder mainly OxHCs. Over the course of the investigation, the relationship between the monoterpene emission rate and the temperature for a single plot was logarithmic and similar to the one between compound vapor pressure and temperature. However, emission rates normalized to temperature decreased throughout the summer and fall, indicating that parameterizations of emission rates from herbaceous plants must include a factor to compensate for environmental conditions such as soil moisture and nutrient deposition, which affect plant phenology and the seasonal pattern of species dominance.

Introduction

Non-methane organic compounds (NMOCs) play an important role in the photochemical production of ozone in both urban and rural atmospheres [Lurman et al., 1983; Trainer et al., 1987; Chameides et al., 1988; Cardelino and Chameides, 1990; Fehsenfeld et al., 1992]. Biogenic sources account for about 90% of the global emissions of NMOCs,

with the major fraction derived from terrestrial vegetation [Zimmerman et al., 1978]. Emissions from deciduous and coniferous trees and agricultural crops have been investigated in both laboratory and field studies [Tingey, 1981; Isidorov et al., 1985; Lamb et al., 1985; Juuti et al., 1990; Guenther et al., 1991; Winer et al., 1992]. A compilation of data by Lamb et al. [1987] indicates that emission rates from deciduous and coniferous trees are greater by an order of magnitude than those for other types of vegetation. However, very little information exists on the identity and quantity of emissions from grassland vegetation.

The objective of this investigation was to determine the seasonal variation of NMOC emissions from a grassland ecosystem [Fukui, 1994]. Emissions were measured via an enclosure technique and collected in Summa[®] passivated stainless steel canisters. The samples were analyzed by cryogenic preconcentration/high-resolution gas chromatography for several classes of organic compounds including alkanes, alkenes, aromatics, terpenes, alcohols, aldehydes, and ketones. Seasonal variations in the type of NMOCs emitted from a grassland site and a quantitative assessment of the emission rates are presented.

Sampling and Analysis

The site of the investigation was the Argonne meteorological monitoring site in the southwest corner of Argonne National Laboratory, Argonne, Illinois. The study area contained a mixture of short, wild grasses and broadleaf plants about 10-40 cm high. Species common to the site included bluegrass (*Poa spp.*), yellow foxtail (*Setaria lutescens*), quackgrass (*Agropyron repens*), horse nettle (*Solanum carolinense*), and crown vetch (*Coronilla varia*).

Samples were collected via a closed-chamber technique with a rigid, semi-transparent polycarbonate chamber (United States Plastic Corp., Lima, OH). About 80% of the visible light energy from a cloudless sky was transmitted through the chamber. The internal dimensions of the chamber were 60 cm (L) x 40 cm (W) x 37.5 cm (H). The sides were slightly tapered, so that the internal volume was 84.5 L. A rectangular polymethyl

methacrylate frame (64 cm x 44 cm) with a trough 5 cm (W) x 3.5 cm (D) was made to fit the chamber. The inner edge of the frame was 12.5 cm deep. Two weeks before sampling, a rectangle was cut into the ground, and the frame was inserted and backfilled with dirt to minimize the flow of ambient air into the chamber (Figure 1). The air within the chamber was isolated from the ambient air by placing the chamber in a trough filled with water. For sites where biomass-based emission rates were determined, all vegetation covered by the chamber was clipped at a height of about 1 cm above the ground, sorted by species, dried at 65°C to constant weight, and weighed. The frame was then moved to another site. To observe temporal variations of the emission rate from a single site, another frame was permanently installed on the ground, and the vegetation within it remained undisturbed for the duration of the investigation.

Air within the chamber was sampled from an upper corner through gas chromatographic grade stainless steel tubing (40 cm x 0.635 cm i.d.) as shown in Figure 1. Samples were collected in 6-L Summa[®] passivated stainless steel canisters (Scientific Instrumentation Specialists, Moscow, ID). Temperatures of the ambient and chamber air were monitored during sample collection. Emission rates were calculated from the concentrations of NMOCs in ambient air and the chamber air for separate covering periods of 10 sec, 1 min, 3 min, and 5 min by using linear regression analysis. Between emission measurements, the chamber was removed, and the surface was allowed to equilibrate for 5 min so that the temperature returned to ambient levels. Emission rates were based on either the covered surface area or the harvested plant biomass. Samples were collected every 2-3 weeks at noon and were analyzed immediately.

The canister cleaning and analysis techniques have been described elsewhere [Doskey et al., 1991]. Briefly, the samples were analyzed with a Chemical Data Systems model 330 (CDS 330) sample concentrator (Autoclave Inc., Oxford, PA), which was interfaced to a Hewlett Packard (HP) 5890A high-resolution gas chromatograph (HRGC) with flame ionization detector (FID). We typically preconcentrated sample volumes of 250 mL or less for

analysis because water in larger samples extinguished the flame in the FID. NMOCs were quantified with National Institute of Standards and Technology (NIST) standard SRM 1665b, containing 2.87 ± 0.03 ppm propane in air. The hydrocarbons were identified by comparing retention times of standards prepared in static dilution bottles with samples injected under identical chromatographic conditions. To derive the total NMOC concentration, the FID response of the identified oxygenated hydrocarbons (OxHCs) was subtracted from the total FID response. Except for the C₂ non-methane hydrocarbons (NMHCs) ethene, acetylene, and ethane, which were not quantified because they could not be resolved from methane, this difference was operationally defined as the total NMHCs. The total NMHC concentration, calculated by using the response of the propane standard, was converted from ppbC to ppb by assuming that the average molecular weight and number of carbon atoms were 100 g mole⁻¹ and 6, respectively. The OxHC responses were corrected by using effective carbon numbers as suggested by Jorgensen et al. [1990] and Scanlon and Willis [1985] to compensate for their diminished response in the FID. The total NMOC concentration was operationally defined as the sum of the identified OxHCs and the total NMHCs. The combined analytical error for concentration measurements via this technique is about $\pm 5\%$ for NMHCs and about $\pm 10\%$ for OxHCs. Average correlation coefficients and standard errors (in parentheses) for the measurements of the alkane, aromatic, OxHC, terpene, and total NMOC emission rates were 0.41 ($>\pm 100\%$), 0.64 ($\pm 40\%$), 0.82 ($\pm 20\%$), 0.82 ($\pm 25\%$), and 0.84 ($\pm 30\%$), respectively.

Results and Discussion

The NMOCs in the chamber air included a mixture of OxHCs, isoprene, monoterpenes, alkanes, and aromatics. OxHCs such as methanol, ethanol, acetaldehyde, and acetone were present in the highest concentrations. Isoprene and the monoterpenes limonene, myrcene, and α - and β -pinene were present in lower concentrations than the oxygenates. Lesser amounts of alkanes (propane, 2-methylpropane, n-butane, 2-methylbutane, and n-pentane) and aromatics (benzene, toluene) were found. The mixture of hydrocarbons observed at our grassland site

was similar to the mixture found in forested regions of the southeastern United States [Fehsenfeld et al., 1992].

We determined the covering period during which the NMOC emission rate would be constant by measuring the concentrations of hydrocarbons in the chamber for several different covering periods in full sunlight. The temperature inside the chamber typically increased at a rate of approximately $1\text{--}2^{\circ}\text{C min}^{-1}$, and water vapor generated during plant transpiration condensed on the chamber walls within about 1-3 min, depending on the amount of covered biomass. The emission rates for methanol, isoprene, and myrcene on 22 June 1992 for covering periods up to 1 min in length were 26, 2.5, and $5.4 \text{ ppbC min}^{-1}$, respectively. Emissions then decreased but remained constant at rates of 7.8, 0.12, and $1.5 \text{ ppbC min}^{-1}$ for covering periods up to 7 min long (Figure 2). The declining emission rates were apparently caused by stresses imposed on the plants by the enclosure or, for the more soluble oxygenates, by absorption in the condensed water on the chamber walls. For measurements in which the emission rate declined for covering periods greater than 1 min, we used the concentrations of the NMOCs in the ambient air and in the chamber air during the 10-sec and 1-min covering periods to derive the emission rate. Measurements of monoterpene emissions from various species of plants have indicated that the emission rate can be modeled after the logarithmic relationship between temperature and compound vapor pressure [Tingey et al., 1991; Guenther et al., 1993]. We were concerned that the increase in monoterpene concentration we observed was related solely to the increase in temperature of the chamber air. However, the increase in monoterpene concentration was linear and not logarithmic.

We were also concerned with the effect of light on emission measurements. Vegetation exposed to a variably cloudy sky exhibited rates of methanol, isoprene, and myrcene emissions that decreased from 100, 3.8 and $19 \mu\text{g m}^{-2} \text{ hr}^{-1}$, respectively, under a clear sky to 49, 0.94, and $10 \mu\text{g m}^{-2} \text{ hr}^{-1}$, respectively, when a cloud came overhead. The temperature of the chamber air increased by 6.5°C under clear skies within the 3-min measurement period but only by 0.5°C when the cloud was overhead. MacDonald and Fall [1993] found a direct

correlation between methanol emissions from plants and stomatal conductance. Light is also necessary for the emission of isoprene from vegetation, and algorithms describing its influence have been reported [Guenther et al., 1993]. Light has an insignificant effect on monoterpene emissions in comparison to temperature, but light indirectly affects emissions through its control of the monoterpene pool size [Tingey et al., 1991]. We decided to limit our measurements to clear-sky conditions because changes in the flux of radiation created temperature fluctuations in the chamber, and the effect of light on NMOC emissions from the plant species in our investigation was unclear.

We measured the emissions of NMOCs for an undisturbed plot containing predominantly crown vetch and bluegrass from 22 June 1992 through 22 October 1992 (Table 1). Data were collected when radiation levels were greater than 500 W m^{-2} . The total NMOC emissions decreased almost linearly from $580 \mu\text{g m}^{-2} \text{ h}^{-1}$ at the onset of summer to about $150 \mu\text{g m}^{-2} \text{ h}^{-1}$ during fall, except for a slight increase in the emission rates during August. The majority of the emissions were OxHCs.

Trends in the seasonal emission profiles of the aromatics and alkanes were different from those of isoprene, the monoterpenes, and OxHCs (Table 1). Aromatic hydrocarbons were sorbed by the surface during all measurement periods. Similar results were obtained during a preliminary investigation at a different site in 1991. At that time our experiments demonstrated that declining concentrations of aromatics in the chamber air were not due to sorption by the polycarbonate chamber or the polymethyl methacrylate frame. Our results indicated that the atmosphere may be the source of the aromatic hydrocarbons observed in uncontaminated soil [Simonart and Batistic, 1966].

The emission profiles of the alkanes were dissimilar from those of the aromatics (Table 1). Some sampling periods had slight emissions of alkanes, while during others they were being deposited. However, the uncertainties in the alkane emission rates are large, as indicated by the very large standard errors ($>\pm 100\%$). The large uncertainties are caused by the similarity of the concentrations of n-alkanes in the ambient and chamber air. Results from

investigations cited by Graedel [1979] indicated that light alkanes are emitted from grass. Kimmerer and Kozlowski [1982] found that ethane is emitted from plants under stress. The dissimilarity of the alkane and terpene emission profiles would argue against a vegetation source. Smith and Restall [1971] found that *n*- and *i*-butane are produced in soils. Isidorov [1990] reported that C₁-C₄ alkanes are among the final products of metabolism of anaerobic soil bacteria. Our data indicate that the flux of these compounds can also be into the soil. However, these nonpolar hydrocarbons are unlikely to be sorbed by the soil. Therefore, the exchange of these gases may be related to changes in pressure within the chamber during sampling, like the effects observed during measurements of the N₂O flux from soils [Denmead, 1979]. These changes in pressure may also be responsible for the large uncertainties.

The bulk of emissions at our site were composed of OxHCs (Table 1). The similarity of the methanol and terpene emission profiles may indicate a common source. MacDonald and Fall [1993] identified methanol as an NMOC emission from several species of plants. Another source may be the microbial degradation of organic matter in soils. For example, methanophiles produce methanol during the aerobic oxidation of methane [Stainer et al., 1986]. Ethanol was also observed in our samples, but it could not be routinely separated from 2-methylbutane. Acetaldehyde emissions exhibited three maxima during our investigation, the most prominent during August. Maxima in acetone emissions preceded the largest acetaldehyde emissions, except for a period during June when the maxima coincided. Ethanol is produced during the fermentation of organic matter and could originate from either microbial activity in the soil or anaerobic respiration in vegetation. Fermented toxic products like ethanol and acetaldehyde are formed in roots of flooded plants, transported to aboveground portions of the plant, and removed in the transpiration stream [Chirkova, 1978]. Ethanol use in roots is known to form acetaldehyde initially and ultimately to produce acetone [Cossins, 1978]. Kimmerer and Kozlowski [1982] found enhanced emissions of ethanol and acetaldehyde from plants exposed to oxidizing pollutants (e.g., SO₂, O₃), water deficit, and freezing. Thus,

these oxygenated hydrocarbons can apparently be emitted from plants in both flooded and dry soils.

Isoprene and monoterpene emissions were lower than those of the OxHCs (Table 1). The monoterpenes in highest concentration were limonene and myrcene, with lesser amounts of α - and β -pinene. Isoprene was about 10% of the terpene emissions. Winer et al. [1989] identified limonene and α - and β -pinene in emissions from annual grasslands in California. The trend in the emission of the monoterpenes at our site was very similar to that of methanol. Monoterpene emissions are believed to be controlled largely by changes in ambient temperature and are frequently modeled by using the relationship between the compound vapor pressure and temperature [Tingey et al., 1991; Guenther et al., 1993]. The relationships between the measured emission rates of limonene and myrcene, the calculated vapor pressures for the two compounds, and the measured ambient temperature for our study site are presented in Figure 3. The relationship between emission rate and temperature is logarithmic, like that between vapor pressure and temperature. Samples represented by the lowest ambient temperatures were collected in late summer and early fall, while the midrange and highest temperatures were recorded for samples collected during mid and early summer, respectively. The live standing crop of vegetation at this site declined throughout the growing season. Consequently, the slopes of the vapor pressure and emission rate curves would probably be similar if the emission rates were based on the weight of living phytomass rather than the covered surface area. Our results also indicate that the emission rates were greater than those predicted from vapor pressure alone. This phenomenon has been attributed to changes in the pathway conductance or monoterpene pool size in plants [Tingey et al., 1991].

We harvested the vegetation on five occasions to derive biomass-based emission rates. Methanol emission rates ranged from 0.46 to 2.0 $\mu\text{g g}^{-1} \text{hr}^{-1}$, below the average value of 13.2 $\mu\text{g g}^{-1} \text{hr}^{-1}$ measured by MacDonald and Fall [1993] for several species of plants. The monoterpene emission rate decreased from about 0.25 $\mu\text{g g}^{-1} \text{hr}^{-1}$ on 17 July 1992 to 0.015 $\mu\text{g g}^{-1} \text{hr}^{-1}$ by the end of September. During this time the live vegetation in the plots

decreased from 90% to 68% of the total harvested biomass, but the mass of living bluegrass and crown vetch, the dominant species in the plots, remained fairly constant. A monoterpene emission rate of $0.034 \mu\text{g g}^{-1} \text{hr}^{-1}$ was measured on 12 October 1992 for vegetation that had grown back in a plot exhibiting an emission rate of $0.25 \mu\text{g g}^{-1} \text{hr}^{-1}$ on 17 July 1992. An emission measurement for similar vegetation in another plot on 29 September 1992 that had never been clipped was lower by a factor of 2 than the October measurement, even though the mass of both bluegrass and crown vetch were significantly lower during October.

To observe seasonal variations of the monoterpene emission rates, the emission rates of limonene and myrcene were normalized to 25°C by using the ratio of the vapor pressure at 25°C to the vapor pressure at ambient temperature (Figure 4). The normalized emission rates based on both area and biomass generally decreased from late June to October. It was expected that the slope of the line for emission rates based on area would be nearly zero if they were normalized to biomass because the weight of living biomass decreases throughout the growing season. Yokouchi et al. [1984] found that monoterpene emissions from *Pinus densiflora* during winter were lower than those expected on the basis of temperature alone, they attributed the difference to the effect of lower light intensities on the production of monoterpenes. Isidorov et al. [1985] found that monoterpene emissions for *Populus balsamifera* were highest in spring but had ceased by summer. Investigators have observed that the composition of the monoterpene pool in plants varies seasonally, but the effects on emission rates have not been investigated [Tingey et al., 1991]. Our data may indicate that the growth stage of the vegetation has a major effect on monoterpene emissions from herbaceous plants. Guenther et al. [1991] reported a trend toward decreasing monoterpene emissions with increasing age for eucalyptus leaves. The herbaceous plants in our investigation apparently exhibit a similar trend.

We measured an average total NMOC emission rate for perennial grasslands of about $2.3 \mu\text{g g}^{-1} \text{hr}^{-1}$, with approximately 10% of the identified emissions composed of monoterpenes. The average temperature during the measurements was 24°C , and the range

was 17-29°C. Winer et al. [1992] reported a total NMOC emission rate of $0.1 \mu\text{g g}^{-1} \text{hr}^{-1}$ for annual grasslands in California. The average temperature during their measurements was 33°C, with a range of 17-43°C. Approximately 20% of the emissions from the California grasslands were monoterpenes. Lamb et al. [1987] reported average total NMOC emission rates of 25 and $12 \mu\text{g g}^{-1} \text{hr}^{-1}$ (at 30°C) for oak and pine trees, respectively, with 93 and 24% of the emissions for oak and pine composed of terpenes. Using biomass estimates for deciduous and coniferous trees in grassland regions from Lamb et al. [1987], we estimated the contributions of total NMOCs and terpenes from trees at 30°C to be 1800 and $1100 \mu\text{g m}^{-2} \text{hr}^{-1}$, respectively. Our estimates of total NMOC and terpene emission rates for grassland varieties of herbaceous plants in our undisturbed plot were 110-660 $\mu\text{g m}^{-2} \text{hr}^{-1}$ and 10-74 $\mu\text{g m}^{-2} \text{hr}^{-1}$, respectively. Herbaceous vegetation apparently is not a significant source of terpenes in grasslands. However, our measurements indicate that the contribution of oxygenated hydrocarbon emissions from herbaceous vegetation may be significant. Interestingly, ambient air samples collected in forests of the southeastern United States [Fehsenfeld et al., 1992] contained many of the same OxHCs that we identified as emissions from a grassland in the Midwest. Additional study is needed to identify and quantify the emissions of OxHCs from forested regions.

The half-lives of the OxHCs identified in this investigation with respect to oxidation by OH (except for acetaldehyde), are relatively long compared to those of the terpenes [Warneck, 1987]. However, these low reactivities will facilitate long-range transport of the OxHCs and subsequent formation of ozone in remote regions. To improve the predictive capability of tropospheric chemistry models, accurate emission inventories of NMOCs must be assembled. These inventories must also include OxHC emissions from biogenic sources.

Conclusions

The total NMOC emission rate for a plot dominated by bluegrass and crown vetch decreased rather consistently from $580 \mu\text{g m}^{-2} \text{yr}^{-1}$ in early summer to $150 \mu\text{g m}^{-2} \text{yr}^{-1}$

during fall, with a minor increase during August. Terpenes and OxHCs contributed about 10 and 90% of the identified NMOC emissions, respectively. Terpene emissions consisted mainly of isoprene, limonene, myrcene, and α - and β -pinene. OxHCs included methanol, ethanol, acetaldehyde, and acetone. In addition to vegetation, microbial oxidation of organic matter in soils may produce methanol. Emissions of ethanol, acetaldehyde, and acetone may be related to anaerobic respiration in plants. The source of the isoprene and monoterpenes appears to be herbaceous vegetation. The monoterpene emission rates followed a logarithmic relationship with temperature, like the one between compound vapor pressure and temperature. Monoterpene emission rates normalized to temperature and based upon both area and biomass decreased throughout the growing season. Comparison of measured emissions from a new-growth plot during fall with those from an old-growth plot during late summer indicated that the emission rate may vary with plant growth stage. Consequently, factors that take into account the temporal variations of environmental conditions like soil moisture and nutrient deposition as they affect plant phenology and the seasonal pattern of species dominance must also be included in parameterizations of emission rates of NMOCs from vegetation.

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Table 1. Emission rates of hydrocarbons ($\mu\text{g m}^{-2} \text{hr}^{-1}$) from a grassland site.

	Julian Day								
	173	189	217	231	243	257	265	278	295
Methanol	120	360	150	180	120	91	75	87	89
Acetaldehyde	32	-0.45	11	58	19	14	24	12	15
Acetone	28	11	53	30	18	27	7.4	17	14
Isoprene	1.7	3.1	4.4	3.8	1.2	-0.88	1.1	0.86	0.80
Monoterpenes ^a	18	71	16	27	11	12	2.8	9.0	14
Alkanes ^b	10	-6.0	-7.9	-13	4.4	3.7	-1.9	-8.9	10
Aromatics ^c	-0.32	-0.97	-8.5	-3.1	-0.74	-1.9	-1.4	-8.4	-4.3
Total NMOC ^d	580	560	660	470	300	190	160	110	190

^a Σ limonene, myrcene, α - and β -pinene.

^b Σ propane, 2-methylpropane, n-butane, 2-methylbutane, n-pentane.

^c Σ benzene, toluene.

^d Calculated from total FID response.

Figure Captions

- Fig. 1. Enclosure system with 6-L Summa[®] passivated stainless steel canister for sample collection.
- Fig. 2. NMOC concentrations in enclosure for covering periods up to 7 min long.
- Fig. 3. Relationships between ambient temperature, monoterpene emission rates, and vapor pressures for a single grassland plot.
- Fig. 4. Seasonal variation of monoterpene emission rates, normalized to 25°C for a single grassland plot and five plots where the vegetation was harvested.

Fig. 1

Fig 2

Fig. 3