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Measurements of air-surface exchange rates of volatile organic compounds

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Abstract: Vertical gradients of volatile organic compounds (VOCs) were measured over a maize field and a soybean field in 1995 and 1996, respectively, in the Lower Coastal Plains of North Carolina. The measurements over the maize field were conducted in its early growth period, during May 1995, and the measurements over the soybean field were conducted in its middle and later growth periods during July through August 1996 at the same location. These measurements were combined with micrometeorological flux measurements to determine emission flux measurements for various VOCs. This measurement programme was part of project NOVA (Natural emissions of Oxidant precursors: Validation of techniques and Assessment) to estimate the flux of VOCs. Methanol was identified as the major biogenic compound for both years with the average flux of $3450 \pm 1456 \mu\text{g}/\text{m}^2/\text{hr}$ over maize and $3079 \pm 2766 \mu\text{g}/\text{m}^2/\text{hr}$ over soybean. Acetone is another compound that was identified as a biogenic compound for both years with the average flux of $425 \pm 223 \mu\text{g}/\text{m}^2/\text{hr}$ over maize and $2701 \pm 1710 \mu\text{g}/\text{m}^2/\text{hr}$ over soybean. In addition to biogenic compounds, a large number of aromatic compounds, including styrene and 1,2,4-trimethylbenzene, were also identified as emissions from the ground over the soybean field.

Keywords: air-surface exchange, biogenic VOCs, hydrocarbons, maize, soybean, VOCs, VOC fluxes.

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1 Introduction

Vegetation provides a major source of reactive carbon entering the atmosphere. The surface fluxes of volatile organic compounds (VOCs) are of interest because of their role in tropospheric chemistry and the global carbon cycle (Fehsenfeld *et al.*, 1992). Most measurements of terrestrial biogenic VOC emissions have focused on isoprene and terpenes, which are believed to be most important for atmospheric chemistry (Zimmerman, 1979; Winer *et al.*, 1989; Singh and Zimmerman, 1992; Fehsenfeld *et al.*, 1992). However, the importance of other VOCs, including light olefins, alcohols, and carbonyls, in the chemistry of the rural troposphere is being increasingly recognized (Isidorov *et al.*, 1985; Zimmerman *et al.*, 1988; Khalil and Rasmussen, 1992; Fehsenfeld *et al.*, 1992; Apel *et al.*, 1994; MacDonald and Fall, 1993; Kirstine *et al.*, 1998; Guenther *et al.*, 2000; Fuentes *et al.*, 2000; Kang *et al.*, 2001; Das *et al.*, 2003). There has been a growing interest in natural hydrocarbon emissions from trees and other foliage in rural areas because, if transported to urban areas, biogenic VOC emissions of long-lived species can add to anthropogenic ozone, i.e. ozone formed from anthropogenically emitted VOCs.

Present estimates place the total annual global emission of biogenically emitted VOCs at 1150 Tg C/yr (Guenther *et al.*, 1995). The authors further surmise that the emissions of isoprene, monoterpenes, other VOCs (OVOC), and other reactive VOCs (ORVOC), to be 503, 127, 260, and 260 Tg C/yr, respectively. However, large uncertainties (sometimes a factor of 3 to 10) remain in these estimates (Guenther *et al.*, 2000). For the USA, the total annual biogenic hydrocarbon emission is estimated to be 29 Tg C/yr (Lamb *et al.*, 1993) whereas the US anthropogenic emission is estimated to be 19 Tg C/yr (Placet *et al.*, 1990). For the biogenic hydrocarbon emissions given in Table 1, ~20% of the emissions are isoprene, ~37% are monoterpenes and the remainder (~42%) are OVOCs with large uncertainties estimated to be a factor of 3 to 10. Though OVOC emissions make the largest contribution to the total emission rate estimates for the USA, it is the least studied and understood component of VOC emissions. This is mainly due to the problems encountered in the sampling, storage, and quantification of these compounds. Some OVOCs have lifetimes of more than a day and hence can be transported large distances from the source of emissions.

For the USA, croplands contribute ~22% to the total VOC budget with OVOCs being the major contributor, ~71%, which amounts to ~15% of the total VOC budget (Geron *et al.*, 1994). Crops were found to emit various VOCs (Arey *et al.*, 1991; Koenig *et al.*, 1995), but emission rates of determined OVOCs were relatively low. Arey *et al.* (1991) investigated in particular emissions of 'leaf-alcohol' and 'leaf-ester', which are compounds involved in the wounding process of leaves. However, our understanding of

biogenic emissions, especially from agricultural crops, such as maize, wheat, or soybean (Geron *et al.*, 1994) is extremely limited. This is attributed to a combination of the limited number of agricultural crop measurements and a lack of accuracy of land-use and biomass density estimates, among other factors that lead to large uncertainties in emission rate factors for agricultural crops. Lamb *et al.* (1985) found that measured emission rates are much higher than the emission rates used in the inventory procedure. In a sensitivity analysis of emission rate factors for agricultural crops by Lamb *et al.* (1993), it was found that uncertainties in the emission factor for maize, the dominant US crop, may produce an ~18% change in the total US inventory.

Table 1 Biogenically emitted US VOC emission rate estimates by source and class of compound; values are in TgC/yr (source: Lamb *et al.*, 1993).

Source	Isoprene	Monoterpene	OVOC	Total VOC
Woods	3.93	6.42	4.72	15.07
Crops	0.20	1.66	4.51	6.37
Shrub	1.66	2.56	2.94	7.16
Inland waters	0.02	0.12	0.07	0.21
Urban areas	0.08	0.10	0.08	0.26
All	5.9	10.9	12.3	29.1

In this study, the average VOC emission fluxes from maize and soybean were estimated from the measured gradients in VOCs. The fluxes were calculated by similarity using the observed concentration gradient and concurrent measurements of fluxes and gradients of heat as well as water vapour (Wesley *et al.*, 1989). The measurement of methanol, acetone and other VOC fluxes in this study could possibly improve our understanding of the chemistry and budgets of these compounds, which have been investigated in previous studies (Singh and Zimmerman, 1992; Fuentes *et al.*, 2000; Das *et al.*, 2003).

2 Experimental

2.1 Sampling site

Vertical gradients of VOCs were measured over an intensively managed agricultural maize field situated in the Lower Coastal Plain region of North Carolina. The research site is located in the southwest corner of Washington County, NC, approximately 20 km southeast of Plymouth, North Carolina (124.63 °W, 48.30 °N, 43 m MSL), ~4 km inland from the Albemarle Sound, and ~120 km from the Atlantic Ocean (Figure 1). The research site itself consisted of approximately 136 hectares of continuous cropland maize, 1067 m wide and 1280 m long. The site is accessible by a canal road off NC Route 99/45, which lies approximately 2 km to the northeast. Measurements were confined to the northeast edge of the field to capture the emission footprint. There are no major industrial sources of VOCs within a radius of ~75 km from the site, which classifies it as a rural agricultural area. Intensive measurement campaigns were conducted from 21 May to 25 May 1995 and from 21 July to 14 August 1996 for gradient measurements of VOCs. Ambient VOC levels were measured during the first week of June 1995. The maize was planted on 12 April 1995 and the plants were about 0.5 m tall and had an estimated biomass density of ~100 g/m² (dry weight, DW, of the whole harvested plants) during the measurement period.

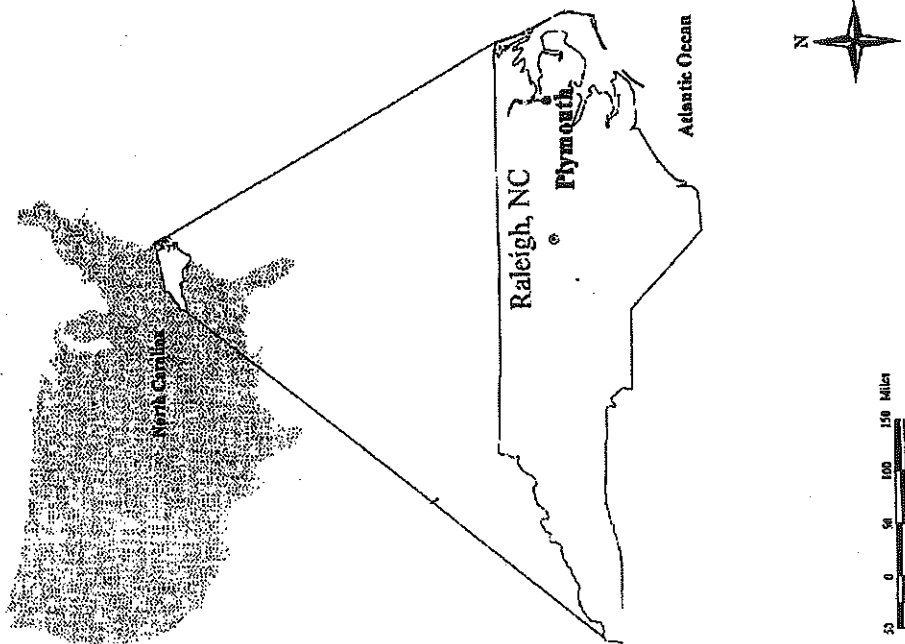


Figure 1. Map of North Carolina indicating research site, Plymouth, NC

2.2 Sampling and analytical methods

Differences in VOC concentrations between heights of approximately 2.5 m and 10 m above the tops of the maize and soybean plants were measured by analysis of air samples collected through stainless steel sampling tubes. Two micrometeorological approaches, the modified Bowen ratio technique and a bulk aerodynamic technique, were used to determine the vertical transfer coefficient, V_t , which was subsequently multiplied by the concentration differences for selected VOCs to estimate their vertical mass flux densities. With the modified Bowen ratio technique, V_t is found as

$$V_t = F_s / \Delta s \quad (1)$$

where F_s is the flux density of a reference scalar quantity and Δs is the difference in scalar concentration across points located as closely as possible to the measurement points for the chemical of interest; this approach assumes that the vertical eddy diffusivities for the chemicals are the same as those for the reference quantity (e.g., Businger, 1986; Baldocchi and Meyers, 1991). In the present study, an energy balance Bowen ratio system of the type described by Fritschen and Simpson (1989) was used to measure the surface energy balance and the temperature and water vapour content differences between points that were nearly collocated with the inlets of the VOC sampling tubes. Water vapour content was chosen as the reference scalar quantity, and the water vapour flux was derived from the latent heat flux found by the energy balance computations.

With the bulk aerodynamic technique, the transfer coefficients were computed as

$$V_t = k u_* [\ln(z_2/z_1) + \psi_2 - \psi_1]^{-1} \quad (2)$$

where $k = 0.4$ is the von Karman constant, u_* is the friction velocity computed as the square root of the negative of the kinetic momentum flux, and ψ_1 and ψ_2 represent corrections for the effects of non-neutral atmospheric stability at the two heights (e.g., Kanemasu *et al.*, 1979). The values of z_1 and z_2 represent the upper and lower heights, respectively, above the soil surface minus the aerodynamic displacement height, which was assumed to be 0.5 times the canopy height. Values of u_* and the vertical fluxes of heat and moisture, all of which are necessary to estimate ψ_1 and ψ_2 , were found from eddy correlation measurements at a height of approximately 10 m on a tower located about 10 m cross-wind from the VOC sampling site. The fluctuations of the three components of velocity and of the temperature needed to compute the momentum and heat fluxes were measured with a sonic anemometer-thermometer (model SWS-211/3Sx from Applied Technology, Inc. (ATI)). A krypton hygrometer was mounted nearby to measure turbulent fluctuations of water vapour density, for the estimates of the water vapour flux. The analogue signal from the water vapour sensor was pre-amplified and passed to ATI analogue-to-digital converters. The digital signals were transmitted to a computer system housed in a trailer approximately 100 m east of the tower. The system was able to monitor the data stream in real time and to compute fluxes and various statistics for every half hour. The turbulence data were sampled 20 times per second. Deviations from a 200-s moving average were used to compute the covariances. Coordinate rotations were carried out to set the mean vertical velocity to zero, and adjustments for density variations were included in the flux calculations.

Hourly integrated air samples were collected in evacuated SUMMA® polished stainless steel canisters using pumps (Nutech Sampling System). Pumps and canisters for both levels and frequently blank canisters were placed in air-conditioned enclosures. Flow-rates for the pumps were initially calibrated to be 200 cm³/min, and calibration checks were performed before and at the end of the study period. At the start and end of the sampling period, side-by-side collection of canisters was made at the 2.5 m level by moving both the samplers to this height. The average percentage difference for total VOC was found to be ~22% (of 36 samples). This value can be considered to be the precision of the entire measurement and calibration process.

The collected sample canisters were taken to the National Exposure and Research Laboratory (NERL) of the US Environmental Protection Agency (USEPA) located in the Research Triangle Park, NC, to be analysed. The one-hour integrated samples were analysed by two gas chromatographic flame ionization detection (GC-FID) systems, which included cryogenic sample preconcentration.

The C₂-C₁₄ compounds were separated on a 60 mm × 0.32 mm I.D. DB-1 fused silica column with a 1 μm liquid phase film thickness (J&W Scientific, Folsom, CA). The column condition consisted of a 50 °C initial temperature for 2 minutes followed by temperature programming to 200 °C at a rate of 8 °C/min. The final temperature was held for 11.75 minutes. The C₂ and C₃ hydrocarbons were analysed on a 30 × 0.53 mm I.D. GSQ gas-solid fused silica column (J&W Scientific, Folsom, CA). The column conditions included a 40 °C initial temperature for 4 min followed by temperature programming at 10 °C/min to 200 °C. Cryogenic preconcentration was employed to analyse a 500 cm³ sample volume. Further details of the GC systems are published elsewhere (Seila *et al.*, 1989). Both GC systems were calibrated with propane in air with a National Institute of Standard and Technology (NIST) standard reference material (SRM) cylinder. Some samples were analysed by a mass-selective detector with peak identification by computer search of the EPA/NIH mass spectral library. The existence of methanol, styrene, and other abundant compounds listed in Table 2 was confirmed by MS.

The OVOCs listed in Table 2 were identified by retention time location using GC-FID systems. All concentrations are reported in parts per billion carbon (ppbC). GC-MS (HP5890-5970, Hewlett-Packard) was used in the scan mode in an attempt to confirm peak identification. Low concentrations prevented reliable peak confirmation. The GC peaks for methanol and acetone eluted at the expected retention times and provided the anticipated mass spectra, although at low abundance.

The average concentrations of individual compounds detected at the two levels are given in Table 2. The gradients were calculated as the differences between the VOC concentrations at the upper level and those at the lower level. Thus a negative gradient implies emission and a positive gradient implies deposition. Though a number of measurements from 7:00 am to 4:00 pm were made at these two levels, VOC results are reported only for paired samples collected during the period that measurements were obtained using the modified Bowen ratio technique. There are 12 paired samples collected during 21-25 May in the afternoon (between 1200 to 1500 EDT) over maize in 1995 and 11 paired samples collected during 21 July to 14 August at noon (1200 to 1300 EDT) over soybean in 1996.

Table 2 List of identified VOCs and their average concentrations (ppb) at the two heights.

Compound	Maize		Soybean	
	2.5 m	10 m	2.5 m	10 m
ALKANES				
Ethane	3.31	3.20	30.3	5.79
Propane	26.77	10.09	5.44	14.84
Isobutane	1.61	0.42	0.75	1.00
n-Butane	0.77	0.82	0.88	9.87
Isopentane	0.51	1.03	2.14	9.85
n-Pentane	0.28	1.19	0.92	0.64
2-Methylpentane		2.7	0.77	1.28
3-Methylpentane	0.98	0.27	0.21	0.09
n-Hexane		0.75	0.27	0.31
3-Methylhexane	0.76		0.29	0.25
2,3,5-Trimethylhexane			2.46	1.07
3,3-Dimethylheptane			7.75	0.55
2,3-Dimethyloctane			3.75	0.40
ALKENES				
Ethylene	2.10	2.64	2.98	2.06
Acetylene		2.14	13.00	1.70
Propylene	1.11	0.46	0.35	0.57
Isobutylene		2.59	0.69	0.25
Isoprene			0.85	0.83
2-Methyl-2-butene			4.63	0.15
AROMATICS				
Benzene		0.55	4.45	0.99
Toluene	0.67	0.93	1.81	1.68
Ethylbenzene		0.26	0.84	0.23
<i>m</i> & <i>p</i> -xylene		0.15	2.18	0.53
Styrene		0.61	36.70	2.99
n-Propylbenzene			3.29	0.52
<i>m</i> -Ethyltoluene			8.69	0.81
1,3,5-Trimethylbenzene		0.93	3.41	0.55
<i>o</i> -Ethyltoluene			2.32	0.35
1,2,4-Trimethylbenzene			12.82	1.43
Isobutylbenzene			1.16	0.17
1,2,3-Trimethylbenzene			1.78	0.28
1,3-Diethylbenzene			2.28	0.27
1,4-Diethylbenzene			1.60	0.63
MONOTERPENES				
α -Pinene	0.47		1.66	1.20
β -Pinene	0.57		1.87	0.65
d-Limonene	0.33		0.89	0.19
Linalool	0.90	0.97	0.50	0.49
OVOC				
Methanol	28.01	13.99	20.5	8.2
Ethanol			11.5	0.8
Acetone	2.95	1.18	20.4	9.1

2.3 Flux calculations

The VOC fluxes were computed as the product of the transfer velocity and the concentration gradient ($\Delta[\text{VOC}]$ or g_{VOC}) of the compounds across the two heights:

$$F_{\text{VOC}} = -V_t g_{\text{VOC}} \quad (3)$$

With the current sign conventions, V_t is always positive or zero, F_{VOC} is positive for fluxes directed upward, and g_{VOC} is positive when the concentration increases with height. Hourly averages of each of the quantities were constructed from the field observations. The value of V_t was computed with the previously described modified Bowen ratio technique and the bulk aerodynamic technique, but only results from the latter method are reported here because a humidity sensor on the Bowen ratio apparatus failed part way through the experiment. The assumption that the aerodynamic displacement height could be estimated as 0.5 times the canopy height was made on the basis of comparing water vapour fluxes derived by the two techniques when the energy-balance Bowen ratio system was fully operational. For 15 hourly periods during the times of interest when the Bowen ratio apparatus was fully operational, the ratio of the transfer coefficient from the bulk aerodynamic approach to that from the modified Bowen ratio approach had an average of 1.17, with a standard deviation of 0.27. From these values, the micrometeorological measurement uncertainty in the ensemble averages of VOC fluxes can be found to be approximately $\pm 31\%$ at a confidence level of 90% ($\pm 38\%$ at a confidence level of 95%). Past experience with micrometeorological systems indicates that the levels of uncertainty in transfer coefficients are typically $\pm 10\%$ to 30% with a 90% level of confidence, for each hourly average.

3 Results and discussion

3.1 Difference of VOC concentrations at the two heights

Figure 2 displays the concentrations of total non-methane organic compounds (TNMOC), styrene, methanol, and isoprene at 2.5 m and 10 m heights over soybean in 1996 and the statistical tests between the paired samples. The two circles on the right of each figure denote the mean and the variance of the paired samples. The two circles on the right of each figure mean and the edge representing the variance of the sample. If the two circles of the paired samples intersect at the points for which the angle between the two tangential lines is less than 90° , there exists significance difference between the paired samples at the confidence level of 95%. The further the two circles are away from each other, the larger the difference is. As Figure 2 indicates, there are significant differences between the concentrations of TNMOC, styrene and methanol at the two heights. However, no significant differences exist for isoprene at the two heights, indicating that no significant isoprene is emitted from the surface. The data strongly signify the source at the surface (either soybean plants and/or soil) for TNMOC, styrene and methanol.

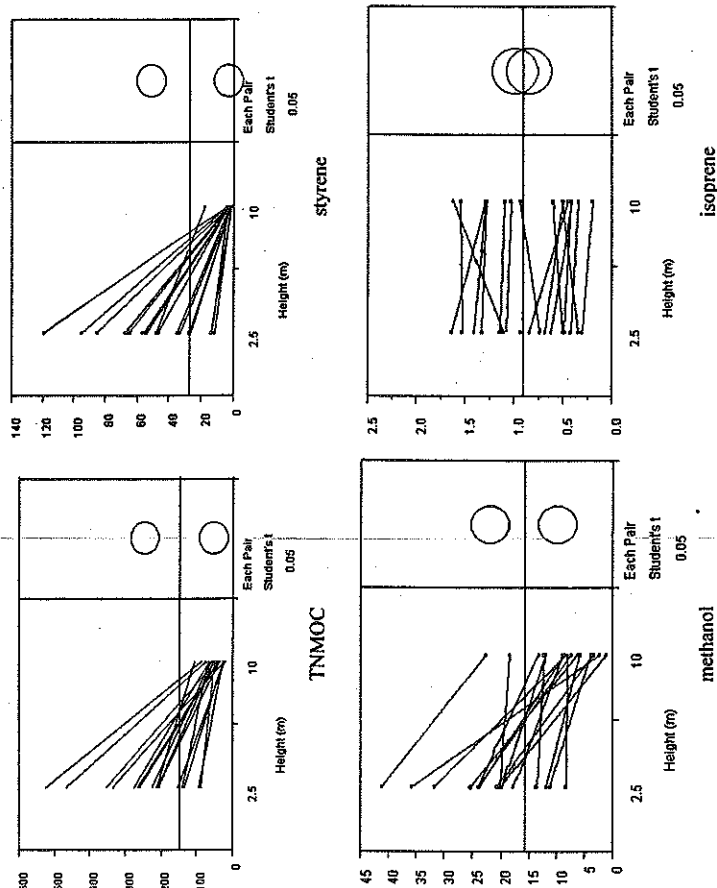


Figure 2 Concentration (ppbC) distribution of total non-methane organic compounds (TNMOC) and other selected compounds at two heights and the statistical test.

3.2 Ambient VOC concentrations

Table 2 lists the average concentrations of the VOCs at the 2.5 m and 10 m heights for the two years' measurements. As Table 2 indicates, methanol, acetone, propane, ethane, and ethylene were the most abundant compounds over both maize and soybean fields. However, ethanol and several aromatic compounds, including styrene and 1,2,4-trimethylbenzene, were identified over soybean in 1996 in relatively large concentrations, especially at the lower height. In 1995, only 1,2,4-trimethylbenzene was identified to have higher concentrations at 2.5 m over maize. Isoprene concentrations were mostly below the level of detection over maize, and below 1 ppbC over soybean at both levels. The most abundant compounds, including methanol, acetone and styrene, were observed in the GC-MS samples at the expected retention times with the anticipated mass spectra. Methanol, acetone, ethanol, and the monoterpenes are considered to have biogenic origin, while some other compounds, such as propane, butane and acetylene, are associated with automobile exhaust, gasoline and industrial processes. Their presence at this rural site can be attributed to transport.

However, the reason for the existence of large amounts of styrene, 1,2,4-trimethylbenzene, and other aromatic compounds over soybean in 1996 is not clear. As far as we know, the farmer didn't apply anything because the soybean was planted until the conduction of the measurements, so there were no direct anthropogenic sources related to these higher concentrations of aromatic compounds. They cannot be explained by advection transport from neighbouring anthropogenic sources either, because the concentration of these compounds were much lower at 10 m than at 2.5 m, and the fluctuation of concentrations was not influenced by the wind direction. Styrene is primarily a synthetic chemical and exists in a variety of products, including rubber, plastics, insulation, fiberglass, pipes, automobile parts, food containers, and carpet backing. Low levels of styrene also occur naturally in a variety of foods, such as fruits, vegetables, nuts, beverages, and meats. One possible explanation for the large amount of styrene in this field is that it may come from the degradation of some substances that the farmer might have applied to the soil before planting.

3.3 Fractional distribution

Figure 3 presents the fractional contribution of various VOC classes to the total VOCs at both heights over maize and soybean. The contribution of alkanes is 22% over both maize and soybean at 2.5 m, increasing to 30% over maize and 37% over soybean at 10 m. The variation of the contribution of alkenes (from 8 to 11%) is small, both between the two heights and from maize to soybean. Monoterpenes have larger contributions over maize than over soybean, and the OVOCs vary from 17 to 31%. The Unknowns account for about 21–25% at both heights over both fields. The largest difference exists in the Aromatics, which make the largest contribution (26%) at 2.5 m over soybean, but only 3% at the same height over maize. However, the contributions from Aromatics at 10 m are the same over both fields. The differences in VOC concentrations and class contributions between the two fields are largely due to the higher concentrations of aromatic compounds observed over soybean.

3.4 VOC flux estimates

The average VOC fluxes estimated during the measurement periods are given in Table 3. It is to be noted that these flux values represent average fluxes for midday, summertime conditions. Emissions of ethane, methanol, acetone, α -pinene, β -pinene and d -limonene are observed, whereas the rest of the compounds deposit over maize. However, except for two compounds, propane and isobutane, which have deposition rates similar to those over maize, other compounds have positive fluxes (emissions) over soybean. Also note that some of the compounds in Table 3 have large standard deviation values associated with the average flux estimates, indicating large uncertainties associated with the flux values.

From Table 3, methanol ($3450 \pm 1456 \mu\text{g}/\text{m}^2/\text{hr}$) is observed as having the largest emission flux, followed by acetone ($425 \pm 223 \mu\text{g}/\text{m}^2/\text{hr}$) and α -pinene ($391 \pm 115 \mu\text{g}/\text{m}^2/\text{hr}$) over maize. Styrene ($4560 \pm 4221 \mu\text{g}/\text{m}^2/\text{hr}$), methanol ($3079 \pm 2766 \mu\text{g}/\text{m}^2/\text{hr}$), acetone ($2701 \pm 1710 \mu\text{g}/\text{m}^2/\text{hr}$), and 1,2,4-trimethylbenzene ($1431 \pm 1312 \mu\text{g}/\text{m}^2/\text{hr}$) have the largest emission rates over soybean. The emission fluxes of methanol are very similar over the two different plant fields, but the flux of acetone over soybean is more than six times greater than that over maize. The fluxes of aromatics over maize are negative (deposition), but significant emissions of these compounds are observed over

soybean. As we argued above, it is not clear where these compounds come from. The fluxes of α -pinene and d -limonene are greater over maize than over soybean, and the flux of β -pinene over soybean is about three times greater than over maize.

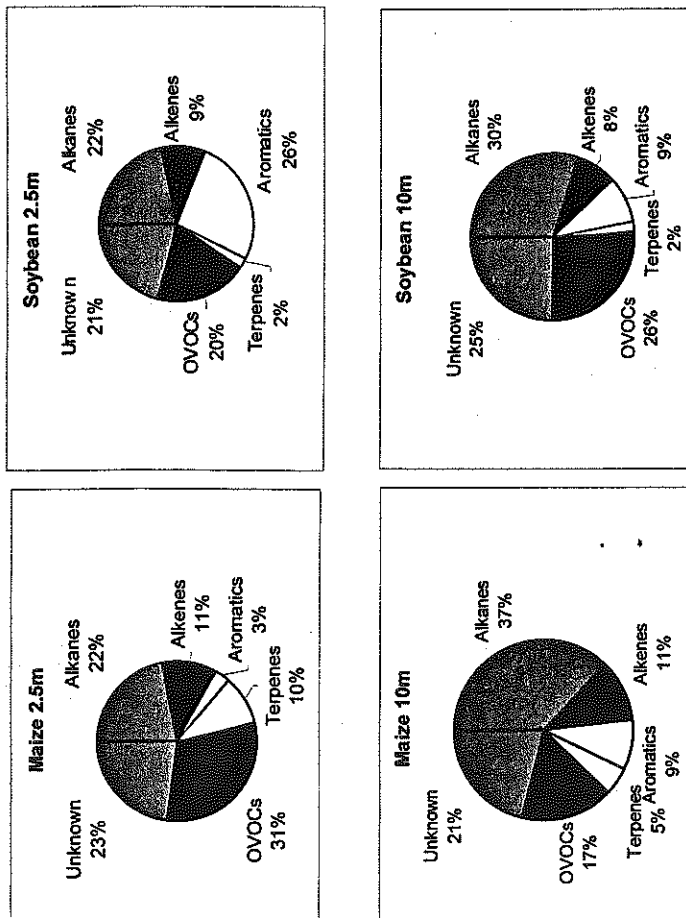


Figure 3 Fractional contribution of the various classes of VOCs to the total VOCs, at two heights above two crops.

The objective of this study is to investigate the VOC emissions from maize and soybean plants. Hence, the following discussion is limited to emissions of biogenic compounds.

Recently, substantial emissions of methanol from plants to the atmosphere have been observed (MacDonald and Fall, 1993a; Fuentes *et al.*, 2000). The presence of substantial amounts of methanol in rural air raised the question of whether plants could be a significant source of methanol to the atmosphere. MacDonald and Fall listed methanol emissions from eleven species of plants, including maize and soybean. In their study, methanol emission originated within the leaf, was affected by leaf temperature, and closely followed changes in stomatal distribution and conductance. The physiology of methanol emission has been further studied by Nemeck-Marshall *et al.* (1995). They relate the rate of methanol emission to leaf development, with emission generally declining with increasing leaf age after leaf expansion.

Table 3 Average fluxes estimated from the measured gradients in the VOC concentrations during the sampling periods 21–25 May 1995 (maize) and 22 July to 14 August 1996 (soybean).

Compound	Maize field		Soybean field	
	Flux ($\mu\text{g}/\text{m}^2/\text{hr}$)	STD (\pm)	Flux ($\mu\text{g}/\text{m}^2/\text{hr}$)	STD (\pm)
Ethane	157	185	91	123
Propane	-154	138	-178	144
Isobutane	-49	32	-36	169
n-Butane	-14	41	7	36
Methanol	3450	1456	3079	2766
Acetone	425	153	2701	1710
Ethanol			811	487
n-Pentane	-61	21	65	55
3-Methylpentane	-28	44	11	18
Benzene	-17	7	529	386
3-Methylhexane	-32	31	27	41
Toluene	-83	24	62	31
α -Pinene	391	39	12	34
β -Pinene	110	23	309	223
d-Limonene	160	80	43	44
Styrene			4560	4221
1,2,4-Trimethylbenzene	-92	44	1431	1312

Though the biochemical source of methanol in leaves is not known with certainty, it has been hypothesized by MacDonald and Fall (1993a) that methanol is produced when cell walls expand, a process during which pectin is demethylated. Methanol is also known to be a product of pectin demethylation in the cell walls of roots, stems, and fruits by pectin methyltransferase (Fuentes *et al.*, 2000). Other possible sources could be protein methyltransferase and protein repair reactions that occur in all plant tissues, and fungal degradation of lignin in plant secondary cell walls (Nemeck-Marshall *et al.*, 1995).

The source of acetone emission could not be verified. In a study by MacDonald and Fall (1993b), little or no acetone emission was detected in the leaf emissions of the species they sampled. Maize was not one of the species sampled. However, they found substantial production of acetone by the buds of each species they sampled (mostly conifers), and this emission was found to be independent of the differences in the temperature regimes to which these organs are normally exposed. The acetone observed in our study could be a secondary product of photochemical reactions of the biogenic compounds emitted in the ambient air (Fuentes *et al.*, 2000).

Doskey *et al.* (<http://www.atmos.gov/ACP/Doskey.pdf>) found that ethanol is emitted from grassland vegetation and the emission rates of it subjected to hypoxia and frost are a factor of six greater than the average emission rates. Emissions of ethanol from other vegetation and crop plants are rarely reported.

Ethane is generally considered to have anthropogenic sources. However, ethane is formed in plants as a result of a free radical oxidation of unsaturated lipids (Lindskog,

1997), and may represent a marker for membrane damage. The production is increased by a wide variety of stresses, such as wounding, flooding, chemical stress, freezing and chilling, and continues to increase with increasing injury. Hahn *et al.* (1990) and Steinbrecher *et al.* (1992) found that the wheat canopy acted both as a source and a sink for ethane, but the soil only as a source. They reported emission fluxes of ethane from soil up to $144 \mu\text{g}/\text{m}^2/\text{hr}$, which is surprisingly similar to the $157 \mu\text{g}/\text{m}^2/\text{hr}$ and $91 \mu\text{g}/\text{m}^2/\text{hr}$ emission flux of ethane in this study.

The emission flux of methanol is converted into an emission rate using a biomass density of $\sim 100 \text{ g}/\text{m}^2$ estimated for the site over maize. The calculated emission rate, density of $\sim 35 \mu\text{g}/\text{g}/\text{hr}$, is similar to the value of $\sim 45 \mu\text{g}/\text{g}/\text{hr}$ reported by MacDonald and Fall (1993a). In our study the biomass is calculated for the entire plant, including the stalk. The biomass used for the calculation in this study is higher than would be expected for maize leaves only of the same age, thus the calculated emission rate is somewhat low.

The emission flux estimates for maize and soybean calculated in this study are compared with the estimates of Lamb *et al.* (1993). The total emission flux of $4900 \pm 700 \mu\text{g}/\text{m}^2/\text{hr}$ (± 1 standard error) over maize calculated in our study is comparable with the estimate of Lamb *et al.* ($3542 \mu\text{g}/\text{m}^2/\text{hr}$). The total emission flux over soybean is much larger than both the emission flux over maize and the estimate of Lamb *et al.*, owing to the large emission flux of aromatic compounds observed over soybean. However, if only the compounds that have emission fluxes over maize are taken into consideration of total flux estimate over soybean, the total emission flux of $6955 \mu\text{g}/\text{m}^2/\text{hr}$ is about double the estimate by Lamb *et al.* and 50% larger than that over maize in this study. The difference is attributed to the fact that the value reported in this study is site-specific, whereas the values reported by Lamb *et al.* are calculated from the emission rates in conjunction with available biomass and land-use data for the US to derive an estimated total emission flux of $3542 \mu\text{g}/\text{m}^2/\text{hr}$. For the entire US, the inventory of biogenic emissions for maize, as provided by Lamb *et al.*, shows that 10% of the total is contributed by each of α -pinene and other monoterpenes with OVOCs making up the rest (80%). This study reports the fractional contribution of α -pinene and other monoterpenes to be $\sim 6\%$ and $\sim 4\%$, respectively, and OVOCs contributing up to $\sim 90\%$ of the total over maize, and α -pinene and other monoterpenes combined contributing $\sim 5\%$ and OVOCs $\sim 95\%$ of the total over soybean.

Table 4 Emission flux ($\mu\text{g}/\text{m}^2/\text{hr}$) estimates for maize and soybean at 25°C .

Reference	α -Pinene	Other monoterpenes	Other VOCs	Total flux ($\mu\text{g}/\text{m}^2/\text{hr}$)
Lamb <i>et al.</i> (1993)	354	354	2834	3542
This study (maize)	390	270	4030	4690
This study (soybean)	12	352	6591	6955

4 Conclusions

Gradients of VOCs were measured over a maize field in its early growth period in May 1995, and over a soybean field at the same place during July to August 1996. A fairly large number of VOCs, biogenic as well as anthropogenic in origin, were detected. Most of the compounds detected were of anthropogenic origin. The compounds attributed to

biogenic origin include methanol, α -pinene, β -pinene, d-limonene, acetone, and ethanol. No direct relationship between temperature and methanol concentrations exists, but solar radiation appears to have a non-linear effect on methanol concentrations.

VOC fluxes were calculated from the measured VOC gradients. Large VOC emissions of methanol were detected from both the maize and the soybean fields, which provides the first evidence of strong methanol emissions from a developing maize canopy and a fast-growing soybean canopy. As maize and soybean are major crops in the US, this could be a major source of methanol to the atmosphere. Thus the contribution of methanol emission (the average flux of 3450 $\mu\text{g}/\text{m}^2/\text{hr}$ compares favourably with previous work performed in the laboratory on expanding maize leaves) from maize and soybean could be a significant source of organic carbon to the rural troposphere. Considerable emissions of acetone (425 $\mu\text{g}/\text{m}^2/\text{hr}$ from maize and 2701 $\mu\text{g}/\text{m}^2/\text{hr}$ from soybean), α -pinene (391 $\mu\text{g}/\text{m}^2/\text{hr}$ from maize), β -pinene (110 $\mu\text{g}/\text{m}^2/\text{hr}$ from maize and 309 $\mu\text{g}/\text{m}^2/\text{hr}$ from soybean), d-limonene (160 $\mu\text{g}/\text{m}^2/\text{hr}$ from maize), and ethanol (811 $\mu\text{g}/\text{m}^2/\text{hr}$ from soybean) were also detected. Isoprene, the most abundant biogenic compound emitted by forests, was not observed from either of these plant species.

In addition to the above compounds that are considered to have a biogenic origin, an emission flux of some anthropogenic compounds, including styrene (4560 $\mu\text{g}/\text{m}^2/\text{hr}$), 1,2,4-trimethylbenzene (1431 $\mu\text{g}/\text{m}^2/\text{hr}$), and benzene (425 $\mu\text{g}/\text{m}^2/\text{hr}$) was also identified from the soybean field. These compounds may come from the biodegradable materials that were applied to the soil underneath the soybean plants, but the exact sources and characteristics of these emissions need further investigation. Considering the large methanol flux emission from maize and soybean, and given its relatively long lifetime, it can be transported to nearby urban areas and influence the concentration of the anthropogenically derived methanol in urban areas. Hence, a substantial flux of methanol and other compounds from agricultural crops may affect urban as well as rural air quality. Owing to its lower reactivity, methanol has not been considered important in the formation of ozone though in the southeastern US. With better estimates of the emission rates of this compound, the importance of methanol in ozone formation may increase in the future.

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