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Measurements of hydrocarbon air–surface exchange rates over maize

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Abstract

Vertical gradients of volatile organic compounds (VOCs) were measured over a maize (*Zea mays*) field, in its early growth period, during May 1995, in the Lower Coastal Plains of North Carolina. These measurements were combined with micrometeorological flux measurements to determine emission flux measurements for various VOCs. This measurement program was part of project NOVA (Natural emissions of Oxidant precursors: Validation of techniques and Assessment) to estimate the flux of VOCs. Average emissions of VOCs (and standard error) was estimated to be $4900 \pm 700\,\mu g/m^2/h$ out of which emission for methanol averaged $(3450 \pm 420)\,\mu g/m^2/h$. A methanol emission rate of $35\,\mu g/g/h$ was calculated for maize from the estimated emission of methanol and biomass density for the site.

Keywords: VOCs; Maize; *Zea mays*; Biogenic VOCs; VOC fluxes; Hydrocarbons; Air–surface exchange

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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 rural tropospheric chemistry is being increasingly recognized (Isidorov et al., 1985; Zimmerman et al., 1988; Khalil and Rasmussen, 1992; Fehsenfeld et al., 1992; MacDonald and Fall, 1993; Apel et al., 1994; Kirstine et al., 1998; Guenther et al., 2000; Fuentes et al., 2000; Kang et al., 2001). There has been a growing interest in natural hydrocarbons 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 man-made 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, and 260 Tg C/yr, respectively. However, large uncertainties (sometimes a factor of 3–10) remain in

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[1] This paper is dedicated to the memory of Dr. M. L. Wesely. Marv was an excellent scientist, a visionary leader, a special person, gentleman, and a scholar. He always had time for us and our students. He will be sorely missed.

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Table 1
Biogenically emitted US VOC emission rate estimates (Tg C/yr) by source and class of compound

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

Source: Lamb et al. (1993).

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 emissions are estimated to be 19 Tg C/yr (Placet, 1990). For the biogenic hydrocarbon emissions given in Table 1, ~20% of the emissions are from isoprene, ~37% from monoterpenes and the remaining (~42%) from OVOCs with large uncertainties estimated to be factor of 3–10. Though OVOC emissions have the largest contribution to the total emission rate estimates for the US, 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 >1 day and hence can be transported large distances from the source of emissions.

For the US, 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; Koening 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 agriculture 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, produce an 18% change in the total US inventory.

In this study, the average VOC emission flux from maize is 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 vapor Wesely et al., 1989. The measurement of methanol, acetone and other VOC fluxes in this study could possibly improve our understanding to the chemistry and budgets of these compounds that have been investigated in previous studies (Singh and Zimmerman, 1992; Fuentes et al., 2000).

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 (Fig. 1). The research site itself consisted of approximately 136 ha 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. An intensive measurement campaign was conducted from 21 May to 25 May for gradient measurements of VOCs. Ambient VOC levels were measured during the first week of June 1995. The crop was planted on 12 April 1995 and the plants were about 0.5 m tall and had an estimated biomass density of ~100 g/m^2 (dry weight (DW) of the whole harvested plants) during the measurement period.

2.2. Sampling and analytical methods

Differences in VOC concentration between heights of approximately 0.5 and 2.5 m above the tops of the maize 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 produce values of the vertical transfer coefficient, V_t, which were 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

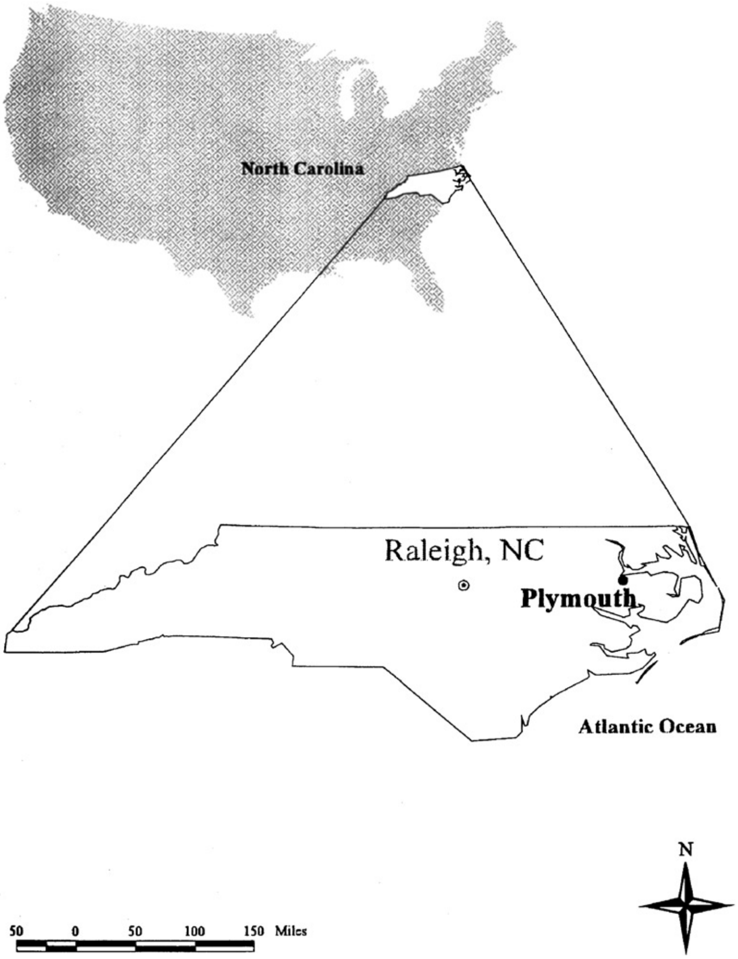

Fig. 1. Map of North Carolina indicating research site, Plymouth, NC.

found as

$$V_t = F_s/\Delta s, \tag{1}$$

where F_s is the flux density 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; Balcochi and Meyers, 1991). In the present study, an energy balance Bowen ratio system of the type described by Fritschen and Simpson (1989) measured the surface energy balance and the temperature and water vapor content differences between points that were nearly collocated with the inlets of the VOC sampling tubes. Water vapor content was chosen as the reference scalar quantity, and the water vapor 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

$$V_t = KU^*[\ln(z_2/z_1) + \psi_2 - \psi_1]^{-1}, \tag{2}$$

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 the 0.5 times the maize 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 vapor density, for the estimates of the water vapor flux. The analog signal from the water vapor sensor was pre-amplified and passed to ATI analog-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 an 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 6 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 cm^3/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 were made at the 3 m level by moving both the samplers to this height. The average % 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 analyzed. The 1 h integrated samples were analyzed by two gas chromatographic—flame ionization detection (GC-FID) systems that included cryogenic sample pre-concentration.

The C_2–C_{10} compounds were separated on a 60 mm × 0.32 mm ID DB-1 fused silica column with a 1 mm liquid phase film thickness (J&W Scientific, Folsom, CA). The column condition consisted of a −50°C initial temperature for 2 min followed by temperature programming to 200°C at a rate of 8°C/min. Final temperature was held for 11.75 min. The C_2–C_3 hydrocarbons were analyzed on a 30 × 0.53 mm ID GSQ gas solid fused silica column (J&W Scientific, Folsom, CA). Column condition included a 40°C initial temperature for a 4 min period followed by temperature programming at 10°C/min to 200°C. Cryogenic pre-concentration was employed to analyze a 500 cm^3 sample volume. Further details of the GC systems are published elsewhere (Seila and Lonneman, 1989). Both GC systems were calibrated with propane in air with a National Institute of Standard and Technology (NIST) standard reference material (SRM) cylinder.

Table 2
List of identified VOCs and their average concentrations at the two levels

Name	Avg conc (2.5 m) Level 1 ($n = 12$)	Avg conc (0.5 m) Level 2 ($n = 12$)
Ethane	3.43	3.69
i-Butane	1.43	0.25
n-Butane	0.73	0.64
Methanol	11.03	16.44
Acetone	5.35	6.57
n-Pentane	0.64	0.47
3-Methylpentane	1.41	1.13
Benzene	0.79	0.69
Toluene	0.71	0.95
α-Pinene	0.65	2.01
β-Pinene	0.63	1.05
d-Limonene	0.49	0.99

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

The average concentration of individual compounds detected at the two levels is given in Table 2. The gradients were calculated as the differences of the VOC concentrations at the upper level from the concentrations at the lower level. Thus a negative gradient implies emission whereas a positive gradient implies deposition. Though a number of measurements (21 at 2.5 m and 15 at 0.5 m) from 10:00 a.m. to 4:00 p.m. were made at these two levels, only VOC results are reported for paired samples collected during the periods measurements were obtained using the modified Bowen ratio techniques. These 12 paired samples were collected during 21–25 May in the afternoon (between 1200–1500 EDT) to minimize errors due to variations in temperature and solar radiation.

2.3. Flux calculations

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

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

Table 3
Average fluxes and coefficient of variance of the fluxes estimated from the measured gradients in the VOC concentrations and transfer coefficients during the sampling period 21–25 May 1995

Compound	V_t (cm/s)	σV_t (cm/s)	g_{VOC} (ppbC)	σ_{VOC} (ppbC)	F_{VOC} ($\mu g/m^2/h$)	$\lvert\sigma F_{VOC}\rvert$ ($\mu g/m^2/h$)	CV (%)
Ethane	1.17	0.27	−0.26	0.3	157	184	118
i-Butane	1.17	0.27	1.18	1.02	−49	44	89
n-Butane	1.17	0.27	0.09	0.11	−14	18	124
Methanol	1.17	0.27	−5.4	1.91	3450	1456	42
Acetone	1.17	0.27	−1.23	0.58	425	223	52
n-Pentane	1.17	0.27	0.17	0.17	−61	62	103
3-Methylpentane	1.17	0.27	0.28	0.43	−28	43	155
Benzene	1.17	0.27	0.1	0.14	−17	25	142
3-Methylhexane	1.17	0.27	0.24	0.22	−32	30	95
Toluene	1.17	0.27	0.24	0.18	−83	65	78
α-Pinene	1.17	0.27	−1.36	0.25	391	115	29
β-Pinene	1.17	0.27	−0.42	0.12	110	40	37
d-Limonene	1.17	0.27	−0.5	0.23	160	82	51

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 maize canopy height was made on the basis of comparing water vapor 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 ±31% at a confidence level of 90% (±38% at a confidence level of 95%). Past experience with micrometeorological systems indicate that the levels of uncertainty in transfer coefficients are typically ±10% to 30% with a 90% level of confidence, for each hourly average.

2.4. VOC flux error analysis

Individual VOC flux calculations have errors associated with them, both random as well as systematic. Systematic errors are more difficult to determine. Hence the random errors propagated through flux calculations are discussed here. VOC fluxes from Eq. (3) are given as:

$$F_{VOC} = -V_t g_{VOC}.$$

Assuming that errors in V_t and g_{VOC} are random and independent, the absolute standard deviation (σ) for a determination of F_{VOC} can be calculated from (Goldstein et al., 1996)

$$\sigma(F_{VOC}) = [(\sigma(V_t)/V_t)^2 + (\sigma(g_{VOC})/g_{VOC})^2]^{1/2}. \tag{4}$$

The coefficient of variation ($\sigma(F_{VOC})/F_{VOC}$) for the individual flux determinations as well as the values for each of the terms in Eq. (4) are given in Table 3.

Random errors will vary with ambient conditions, including magnitude of the flux, atmospheric stability, diurnal variation, and absolute hydrocarbon concentrations. Most of the uncertainty is associated with quantifying the VOC and water vapor gradients. When fluxes are small, the gradients are more difficult to quantify owing to the small concentration difference. Also, uncertainties increase with increased atmospheric concentration as the precision of the gradient measurement is a function of absolute hydrocarbon concentration. Though random errors are inherent in the flux data, much of the variability in the results may be attributed to the variability of the atmosphere and surface conditions, especially on a day-to-day basis.

3. Results and discussion

3.1. Ambient VOC concentrations

Table 2 lists the average concentrations of the VOCs at the two levels calculated from the 12 paired samples collected from 12 May to 25 May, which are the base concentrations to calculate VOC fluxes shown in

Table 3. As Table 2 indicates, methanol is the most abundant compound (11.03 ppbC at 2.5 m). A number of monoterpenes including α-pinene, β-pinene, d-limonene, and linalool, are determined, again by retention time, location, but only the first three are quantified at the concentration levels from 0.49 to 0.65 ppbC at 2.5 m; however, isoprene concentrations are mostly below the level of detection. As mentioned earlier, compound concentration levels are too low for GC/MS confirmation for most peaks reported. Both methanol and acetone are observed in the GC/MS samples at expected retention times with anticipated mass spectra. Methanol, acetone, and the monoterpenes are considered to have biogenic origin, while others in Table 2 are associated with automotive exhaust, gasoline and industrial processes and their presence at this rural site can be attributed to transport.

Fig. 2 presents the variation of methanol concentrations at 2.5 m with temperature and solar radiation on August 23, 1995. No significant relationship between methanol concentrations and temperature exists, but the solar radiation seems to have effect on methanol concentrations. From 10:00 a.m. to 1:00 p.m., both solar radiation and methanol concentration decrease with time. But the influence of radiation on methanol concentration is not linear and seems to accumulate with time (the variation of methanol concentration has about 1 h delay following the variation of solar radiation).

3.2. VOC flux estimates

The average VOC flux estimated during the measurement period of 21 May–25 May, 1995 along with the % coefficient of variance (CV) of these estimates is given in Table 3. It is to be noted that these flux values represent average fluxes for midday, summer time conditions. The procedure for calculating CV has been described in an earlier section. From Table 3 it is seen that some of the compounds have very high coefficient of variances associated with the average flux estimates indicating large uncertainties associated with the flux values. Emissions of ethane, methanol, acetone, α-pinene, β-pinene, d-limonene, are observed whereas the rest of the compounds are found to be deposited. The objective of this study is to investigate the VOC emissions from maize leaves. Hence, the following discussion is limited to emission.

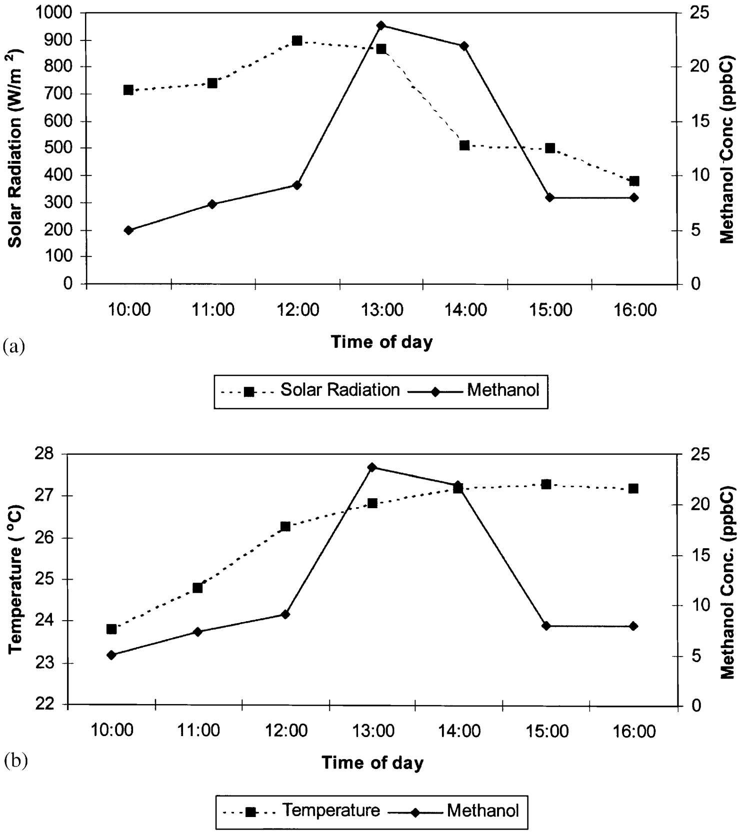

Fig. 2. Variation of ambient methanol with: (a) solar radiation, and (b) temperature on 23 August 1995.

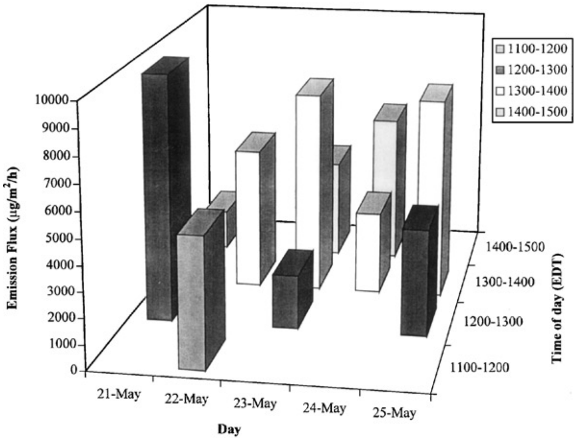

Fig. 3. Total VOC flux emission during the measurement period.

The total VOC emission flux calculated during the afternoon periods of 21–25 May 1995 is given in Fig. 3. Total emission ranges from ~2000 to ~9000 μg/m^2/h with a large variability from hour to hour as well as day to day. The average total emission flux is estimated to be 4900 ± 2420 μg/m^2/h (±1 standard deviation). From Table 3, methanol (3450 ± 1456 μg/m^2/h) is observed as having the largest emission flux followed by acetone (425 ± 223 μg/m^2/h) and α-pinene (391 ± 115 μg/m^2/h). The other monoterpenes, β-pinene and d-limonene, also appear to be emission compounds with emissions fluxes less than half of α-pinene.

Recently, substantial emissions of methanol from plants to the atmosphere have been observed (MacDonald and Fall, 1993; 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 list methanol emissions from 11 species of plants including maize. 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 Nemecek-Marshall et al. (1995). They relate methanol emission rate to leaf development with emission generally declining with increasing leaf age after leaf expansion.

Though the biochemical source of methanol in leaves is not known with certainty, it has been hypothesized by MacDonald and Fall (1993) 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 dimethylation in the cell walls of roots, stems, and fruits by pectin methylesterase (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 (Nemecek-Marshall et al., 1995).

The source of acetone emission could not be verified. In an emission study of acetone by MacDonald and Fall (1993), 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).

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 (Linkdskog, 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 μg/m^2/h, which is surprisingly similar to the 157 μg/m^2/h emission flux of ethane in this study.

The emissions flux of methanol is converted to an emission rate using a biomass density of ~100 g/m^2 estimated for the site. The calculated emission rate, ~35 μg/g/h, is similar to the value of ~47 μg/g/h reported by MacDonald and Fall (1993). 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 what 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 calculated in this study is compared to the estimates of Lamb et al. (1993). Total emission flux of 4900 ± 700 μg/m^2/h (±1 standard error) calculated in our study is comparable with the estimate of Lamb et al. (3542 μg/m^2/h). 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 μg/m^2/h. 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 each by 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 ~6% and ~4% with OVOCs contributing up to ~90% of the total (Table 4).

Table 4
Total emission flux ($\mu g/m^2/h$) estimates for maize at 25°C

Reference	α-pinene	Other monoterpenes	Other VOCs	Total flux ($\mu g/m^2/h$)
Lamb et al. (1993)	354	354	2834	3542
This study	390	270	4030	4690

4. Conclusions

Gradients of VOCs are measured over a maize field in its early growth period in May 1995. A fairly large number of VOCs both biogenic as well as anthropogenic in origin are detected. Most of the compounds detected are of anthropogenic origin. The compounds attributed to biogenic origin include methanol, α-pinene, β-pinene, and d-limonene. No direct relationship between temperature and methanol concentrations exists, but solar radiation appears to have non-linear effect on methanol concentrations. VOC fluxes are calculated from the measured VOC gradients. Large VOC emissions of methanol are detected from the maize field, which provides the first evidence of strong methanol emissions from a developing maize canopy; considering maize being one of the major crops of the US, this could be a major source of methanol to the atmosphere. Thus the contribution of methanol emission (average flux of $3450\,\mu g/m^2/h$ compares favorably with previous work performed in the laboratory on expanding maize leaves) from maize could be a significant source of organic carbon to the rural troposphere. Considerable emissions of acetone ($425\,\mu g/m^2/h$) and α-pinene ($391\,\mu g/m^2/h$), β-pinene ($110\,\mu g/m^2/h$), and d-limonene ($160\,\mu g/m^2/h$) are also detected. Total VOC emission ranges from ~ 2000 to $\sim 9000\,\mu g/m^2/h$ with an average value of $4900 \pm 700\,\mu g/m^2/h$ (± 1 standard error). Methanol contributes $\sim 75\%$ to the total emission flux at this site. The emission flux of methanol is converted to an emission rate ($\sim 35\,\mu g(C)/g/h$) using the biomass density at the site ($\sim 100\,g/m^2$). From the large methanol flux emission of maize and given its relatively longer lifetime it can be transported to nearby urban areas and influence the concentration of the anthropogenically derived methanol in urban areas. Other agricultural crops, like soybean is also known to emit large quantities of methanol. Hence, a substantial flux of methanol from agricultural crops may affect rural as well as urban air quality. Due 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 our knowledge of ozone formation may increase in the future.

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