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Coastal New England pilot study to determine fossil and biogenic formaldehyde source contributions using radiocarbon

Haiwei Shen,^{1,2} Brian G. Heikes,¹ John T. Merrill,¹ Ann P. McNichol,³ and Li Xu³

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[1] Compound specific radiocarbon analyses of atmospheric formaldehyde are reported as fraction modern (Fm) for a limited number of winter and summer air samples collected in coastal southern New England in 2007. The 11 of 13 samples with Fm < 0.2 were collected under the influence of the semipermanent Bermuda high-pressure system with transport from the Washington, D. C., to New York City urban corridor. The two samples with Fm > 0.2 (max ~ 0.35) were collected on days with strong northwesterly flow and the least urban impact. The Fm data were combined with VOC observations from the Rhode Island Department of Environmental Management, estimates of oxygenated VOC (OVOC), and back trajectories to interpret the relative contributions of biogenic and fossil carbon sources. It is argued that CH₂O sources were dominated by pollutant VOCs and OVOCs from upwind coastal cities as opposed to more local biogenic VOCs at the times of sample collection.

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1. Introduction

[2] Formaldehyde (CH₂O) is an intermediate product in the photochemical oxidation of volatile organic compounds (VOCs). Its abundance and chemistry relate not only to VOC oxidation, but also to odd-hydrogen chemistry (e.g., HO, HO₂, HO_x), ozone (O₃) production, and global carbon monoxide budgets [e.g., *Finlayson-Pitts and Pitts*, 2000]. By extension of its impact on O₃ and HO_x, CH₂O affects the processing of nearly all compounds in the troposphere; sulfur dioxide to sulfuric acid, nitric oxide to nitric acid, VOCs to carbon monoxide and on to carbon dioxide. Surface O₃ precursors are a combination of natural and anthropogenic nitrogen oxides (NO_x) and VOCs and one of many O₃ control strategies is focused on reducing anthropogenic reactive VOC (RVOC) emissions, thereby, in effect reducing anthropogenic CH₂O as a radical producing source of ozone. The efficacy of this strategy depends upon the relative mix of biogenic and anthropogenic RVOC emissions [e.g., *Trainer et al.*, 1987; *Carter*, 1994; *Russell et al.*, 1995; *Derwent et al.*, 2007; *Luecken and Mebust*, 2008].

[3] Biogenic and anthropogenic VOC emission inventories are under continued development and assessment. For example, CH₂O column measurements from space-based

sensors (GOME, SCIAMACHY, OMI) have been used to constrain bottom-up biogenic isoprene emission estimates [e.g., *Palmer et al.*, 2006; *Fu et al.*, 2007; *Millet et al.*, 2008; *Dufour et al.*, 2009; *Stavrakou et al.*, 2009]. Top-down correction factors to bottom-up inventories can range over a factor of 2 and vary spatially throughout the season. The accuracy of these findings depends on the chemical transport model (CTM) assumptions used to define the relationship between VOC emissions and CH₂O column amounts. Depending on the chemical mechanism employed and the simulated NO_x concentration, first-day CH₂O yields can range from 0.2 to 0.6 moles of CH₂O per atom-C of isoprene [*Dufour et al.*, 2009; *Palmer et al.*, 2006]. *Warneke et al.* [2007], *Buzcu-Guven and Fraser* [2008] and *Mendoza-Dominguez and Russell* [2001] provide examples of similar CTM measurement constraints on anthropogenic VOC emissions for the New York, Houston and Atlanta metropolitan centers, respectively, with adjustment factors again on the order of 2 to 3.

[4] Alternatively, the relative contribution of fossil and biogenic sources of RVOCs to CH₂O can be experimentally evaluated by measuring the radiocarbon (¹⁴C) content of ambient CH₂O [*Tanner et al.*, 1996; *Shen et al.*, 2009]. In this paper, the radiocarbon content is expressed as fraction modern, Fm, as defined by *McNichol and Aluwihare* [2007, and references therein]. Fraction modern is the ¹⁴C/¹²C ratio in a sample relative to the ratio in a “modern” standard where the modern standard represents a theoretical wood sample with a fixed ¹³C/¹²C ratio (δ¹³C = −25‰) in 1950. Fraction modern is calculated from two NIST standards (NIST SRM 4990B and NIST SRM 4990C). Normalizing to a constant δ¹³C is necessary to remove the effects of isotopic

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fractionation on the $^{14}\text{C}/^{12}\text{C}$ ratio and setting 1950 as the reference point for modern removes the impact of nuclear bomb testing and nuclear power production on age determinations. Weapons testing increased the atmospheric inventory of radiocarbon and resulted in fraction modern values of up to 2.0 in atmospheric carbon dioxide in the 1960s. This signal is mixing into the oceans and biosphere and, since 1985, the value has decreased from 1.2 to its present-day value of 1.05. The radiocarbon content of atmospheric methane has also been modified by weapons testing and fossil fuel burning but to a different extent than CO_2 ; the present-day fraction modern value of methane (Fm_{CH_4}) is 1.3. Fraction modern should not be confused with biogenic fraction [Klouta *et al.*, 1996] where measured Fm values are normalized to the fraction modern of contemporary atmospheric carbon dioxide under the assumption that the source of carbon for biogenic matter is the contemporary atmosphere. We make this correction using the present-day value of 1.05 but caution that the complexity of carbon sources for formaldehyde makes the appropriate choice difficult. However, given the error of our measurements and the closeness of the Fm value in contemporary atmosphere to 1.0, the correction is relatively small.

[5] Radiocarbon analysis has been used in numerous studies to determine the fraction of fossil and modern carbon sources of trace gases and atmospheric particles. The radiocarbon results for VOCs and carbonyl compounds are of specific interest. The Fm values cited below have been rounded to the nearest tenth percentile. Klouta *et al.* [1996, 2002] found that only 10–20% of VOCs were derived from modern sources in Atlanta, Georgia, during summer, although they state their sample timing might have missed the diel peak in biogenic VOCs, and the VOCs were 0–40% modern carbon in September 1997 at Azusa, California. Larsen *et al.* [2001, and references therein] showed carbonyl compounds contained about 30–85% modern carbon at semiremote sites in Italy and Portugal, and about 60–90% modern carbon at a rural area in Germany during autumn. Kato *et al.* [2008] found acetaldehyde inside an unoccupied home located in a suburb of Tokyo was 50–70% modern carbon. Tanner *et al.* [1996] reported 80–90% modern carbon in CH_2O at Chebogue Point, Nova Scotia, in summer 1993.

[6] Ambient $^{14}\text{CH}_2\text{O}$ is expected to vary widely, as well, and especially in Rhode Island (RI) given the rural-to-urban character of the State and the air masses transported to it. Warneke *et al.* [2004] and de Gouw *et al.* [2005] illustrated the extent of urbanization in New England and its impact on VOC and oxygenated VOC (OVOC) sources and chemistry. They also showed RI as a “hot spot” of biogenic isoprene emission. Further, several major metropolitan areas lie 24 h upwind of southern New England including New York City (~19 million people, ~220 km away), Baltimore–Washington–Northern Virginia (~8 million, 550 km), Philadelphia–Southern New Jersey (~5 million, ~350 km), Montreal (~4 million people, 475 km), and Boston (~4 million, 100 km) and transported air masses from these urban centers to RI are expected to be depleted in biogenic RVOCs [e.g., Warneke *et al.*, 2004; Sommariva *et al.*, 2008], to have large fossil VOC mixing ratios and thus to have small biogenic contributions to CH_2O . de Gouw *et al.* [2005] further

showed a suite of OVOCs in the Boston–NYC plume to have estimated biogenic contributions less than 30%.

[7] The results of a pilot study exploring ambient $^{14}\text{CH}_2\text{O}$ at a southern New England coastal site are reported and interpreted here. The objectives of the study were the development of a compound specific radiocarbon analysis method (CSRA) for CH_2O and to answer the questions: What are the Fm values in ambient CH_2O impacting the site? Are CH_2O sources dominated by biological emissions or fossil pollutants? Does the source mix vary seasonally with a winter maximum in fossil contributions and a summer maximum in biogenic contributions?

2. Methods

2.1. Site Description

[8] In the pilot study, a limited number of CH_2O samples were collected on the roof of the CACS building (~15 m above ground) at the University of Rhode Island's Narragansett Bay Campus (NBC) and their ^{14}C content measured. The locations of the University of Rhode Island's Narragansett Bay (NBC) and Alton Jones (AJC) campuses are shown on the map in Figure 1. AJC is located in the town of West Greenwich, RI, and hosts a Rhode Island Department of Environmental Management (RIDEM) air-monitoring site. The AJC site is referred to as West Greenwich in the manuscript. A second RIDEM sample air-monitoring site at the Francis School in East Providence, RI (EP) is also indicated.

[9] The NBC $^{14}\text{CH}_2\text{O}$ hi-vol sampler was located on the southwest corner of the CACS building roof, approximately 15 m off the ground and 40 m MSL. CACS is approximately 250 m from Narragansett Bay to the east and 65 m from a woodlot to the west. The general area outside of the NBC is a mix of high-density suburban homes (0.4 km south) and small businesses (0.3–1 km southwest to west). Boston Neck Rd (rte 1A), a main secondary road, runs north and south ~1 km to the west. The inset on Figure 1 shows housing, vegetation and roadways near NBC.

[10] Sample dates and times are listed in Table 1. Sample days were selected to be nonprecipitating and mostly sunny to avoid CH_2O wet deposition, to maximize the likelihood of high CH_2O mixing ratios, and, in summer, to correspond with meteorological conditions conducive to surface ozone production. Average daytime temperature was ~5°C for the winter samples and ~23°C for the summer (July) samples.

2.2. CH_2O Instrumental Method

[11] The $^{14}\text{CH}_2\text{O}$ was determined using the CSRA method described by Shen *et al.* [2009] and reported as fraction modern, Fm. Briefly, ambient CH_2O was collected on sodium bisulfite coated glass-fiber filters using a high-volume air sampler. The exposed NaHSO_3 -coated filter was rolled within a piece of precombusted aluminum foil, folded, and stored in a capped glass bottle at 4°C until analyzed. The exposed filter was extracted with water and CH_2O was derivatized to thiazolidine using cysteamine. The thiazolidine was extracted into dichloromethane and separated from other organic compounds present in the extract by an automated preparative capillary gas chromatography system and collected as a phosphate salt. The thiazolidine salt carbon was combusted to CO_2 and subsequently con-



Figure 1. Map showing the locations of the Narragansett Bay Campus (NBC) sample site in Narragansett, RI, and RIDEM air monitoring sites in East Providence and West Greenwich (image covers $69^{\circ}45'W$ – $74^{\circ}15'W$ and $40^{\circ}15'N$ – $43^{\circ}40'N$). East Providence (EP) is an urban site often downwind of the Providence metropolitan area. The Alton Jones Campus (AJC) is a semirural site in West Greenwich. The red line indicates the coastal climate zone specified for Connecticut, Massachusetts, and Maine and interpolated through New Hampshire and Rhode Island. It roughly corresponds with the inland extent of the coastal sea breeze. The inset details the NBC, CACS sample location, and surrounding vegetation and housing density (CACS is located at $71^{\circ}25'24''W$, $41^{\circ}29'26''N$). The CH_2O sampling site is about 30 km southeast of the AJC site, about 40 km south of EP and in the interpolated coastal zone. Base images from Google Earth 2008© showing state boundaries and major highways.

verted to graphite using established procedures for AMS analysis at National Ocean Sciences Accelerator Mass Spectrometry Facility, Woods Hole Oceanographic Institution [McNichol *et al.*, 1992; Pearson *et al.*, 1998]. The Fm limit of detection was <0.05 [Shen *et al.*, 2009]. Radiocarbon results are reported as Fm as defined by McNichol and Aluwihare [2007].

2.3. RIDEM VOC and Ozone Measurements

[12] VOC composition and CH_2O source contributions were investigated using RIDEM VOC measurements made at two sites, West Greenwich and East Providence, representing rural and urban RI, on days surrounding the CH_2O sampling dates. Site locations relative to NBC are shown in Figure 1. Monthly mean VOC mixing ratios were used for this analysis since the RIDEM data are from 24 h integrated samples collected at 6 day intervals and their sample days did not correspond with CH_2O sample days. The two VOC mixes are detailed in Table 2 for July and shown in Figure 2 for February, March and July. VOCs attributed to anthropogenic-fossil emissions were in greater abundance than biogenic VOCs in all three months. There was little or no isoprene in the air during February and March and it increased in July as expected.

[13] Hourly ozone mixing ratio data were obtained from RIDEM for Narragansett (200 m north of CACS), West Greenwich, and East Providence RI. Site locations are given in Figure 1.

2.4. CH_2O Source Model and Estimated Fm

[14] Estimates of VOC contributions to CH_2O production, P_i , are shown in Figure 3. P_i was calculated following the work of Lee *et al.* [1998] and Sumner *et al.* [2001],

$$P_i = k_i[VOC]_i[HO]\varphi_i, \quad (1)$$

using representative VOC concentrations ($[VOC]_i$), their respective HO reaction rate coefficients (k_i), their corresponding molar CH_2O yield (φ_i), and HO concentration ($[HO]$). RIDEM VOC measurements and the literature were used below to develop several VOC case study mixes. Table 2 lists the selected VOCs, their reaction parameters,

Table 1. Ambient Air CH_2O Fraction Modern at Narragansett

Sample Identification	Date 2007	Start (EST)	Sample Time (hours)	Air Volume (m^3)	Thiaz ^a (μgC)	AMS Carbon ^b (μgC)	Fm CH_2O^c	Biogenic Fraction CH_2O^d
OS-60452	6 Feb	1000	8.9	61	77.4	42.5	0.11 ± 0.01	0.10
OS-60450	26 Mar	0700	12.0	55	70.6	48.5	0.16 ± 0.01	0.15
OS-60454	27 Mar	0700	12.3	49	66.2	44.2	0.10 ± 0.01	0.10
OS-60455	29 Mar	0700	12.6	52	58.8	30.4	0.35 ± 0.05	0.33
OS-60456	31 Mar	0700	11.9	54	45.2	22.4	0.13 ± 0.02	0.12
OS-62341	1 Jul	0700	11.9	46	101.6	38.9	0.28 ± 0.02	0.27
OS-62039	3 Jul	0700	11.9	47	127.2	51.6	<0.05	<0.05
OS-62447	7 Jul	0700	13.2	50	87.8	45.5	0.10 ± 0.01	0.10
OS-62343	8 Jul	0700	12.2	47	85.0	35.0	0.16 ± 0.01	0.15
OS-62037	10 Jul	0800	12.1	45	116.5	59.4	<0.05	<0.05
OS-62448	12 Jul	0800	12.1	45	99.5	43.7	0.12 ± 0.01	0.11
OS-62445	17 Jul	0800	12.1	44	98.5	46.4	0.09 ± 0.01	0.09
OS-62038	24 Jul	1000	12.0	44	114.2	56.3	0.11 ± 0.01	0.10

^aTotal amount of thiazolidine collected, in μgC , estimated before preparative capillary gas chromatography.

^bTotal amount of carbon converted to graphite.

^cFraction modern (Fm) carbon \pm propagated errors.

^dBiogenic carbon fraction based on $Fm_{biol} = 1.05$.

Table 2. Reaction Rate Coefficients, Initial CH₂O Yields, and Selected VOC Mixing Ratios^a

Compound	k_{OH} ($\times 10^{12}$, $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)	φ (CH ₂ O yield per molec)	West Greenwich (pmol/mol)	East Providence (pmol/mol)	Northeast U.S. Urban Plume (pmol/mol)
<i>Anthropogenic VOCs</i>					
Ethane	0.24	1	909	1535	2701
Propane	1.1	0.4	556	1056	1798
n-Butane	2.3	0.2	91	281	393
i-Butane	2.19	0.8	154	286	235
n-Pentane	4	0.3	56	184	360
i-Pentane	3.7	0.5	224	625	928
2, 2-Dimethylbutane	2.34	0.3	0	2	28
Cyclopentane	5.2	0.3	4	12	NA
2-Methylpentane	5.3	0.35	20	138	257
3-Methylpentane	5.4	0.35	43	66	297
n-Hexane	5.34	0.3	20	100	249
Cyclohexane	7.21	0.3	0	12	66
n-Heptane	7	0.3	20	100	93
Methylcyclohexane	10	0.3	0	14	NA
n-Octane	8.71	0.3	1	15	46
n-Nonane	10.4	0.3	2	16	NA
n-Decane	12.1	0.3	2	25	23
Ethylene	7.9	1.8	264	468	1061
Propene	29	1	82	164	317
1-Butene	31.4	1	46	90	32
t-2-Butene	67	1	2	20	12
c-2-Butene	65	1	2	11	14
1-Pentene	31.4	0.5	0	15	26
1, 3-butadiene	15	1	10	18	NA
<i>Biogenic VOC</i>					
Methane, ~70% bio	0.0064	1	1,800,000	1,800,000	1,800,000
2-Methyl-1, 3-butadiene	100	0.7	1099	251	250
α -Pinene	53.7	0.22	1034	92	1

^aReaction rate constants, k_{OH} , are from Atkinson [1997] and Atkinson *et al.* [2006]. Formaldehyde molar yields for alkanes, alkenes, alkynes, and aromatics are from Lee *et al.* [1998] and Sumner *et al.* [2001]. West Greenwich and East Providence VOC mixing ratios are July 2007 averages. Northeast U.S. urban plume mixing ratios are from Sommariva *et al.* [2008] but with reduced isoprene (2-Methyl-1, 3-butadiene) per the text. NA denotes not available.

and case study mixing ratios. A 12 h average [HO] of $1.6 \times 10^6 \text{ molec cm}^{-3}$ [Seinfeld and Pandis, 1998] was assumed and while the CH₂O production rate from each species is proportional to the assumed [HO], their relative contributions are independent of the chosen [HO]. The production estimates, P_i , were combined to calculate an estimated CH₂O Fm,

$$Fm_{CH_2O} = b_{fossil}Fm_{fossil} + b_{isoprene}Fm_{isoprene} + b_{CH_4}Fm_{CH_4} \quad (2)$$

where the b_i s represent the fraction of CH₂O from various sources and given by

$$b_{fossil} = \frac{\sum_{fossil} P_i}{\sum_{fossil} P_i + P_{CH_4} + P_{isoprene}}, \quad (3a)$$

$$b_{CH_4} = \frac{P_{CH_4}}{\sum_{fossil} P_i + P_{CH_4} + P_{isoprene}}, \quad (3b)$$

$$b_{isoprene} = \frac{P_{isoprene}}{\sum_{fossil} P_i + P_{CH_4} + P_{isoprene}}. \quad (3c)$$

Since $Fm_{fossil} \equiv 0$, equation (2) is reduced to

$$Fm_{CH_2O} = b_{isoprene}Fm_{isoprene} + b_{CH_4}Fm_{CH_4}$$

$Fm_{CH_4} \approx 1.3$ and $Fm_{isoprene} \approx 1.05$ based upon work by Lassey *et al.* [2007] and the value of contemporary photosynthetic material [e.g., Hsueh *et al.*, 2007] and experiments showing biogenic isoprene is produced from contemporary photosynthetic material [e.g., Sharkey and Yeh, 2001]. In 2007, if all atmospheric formaldehyde was derived without fractionation from contemporary photosynthetic material (e.g., isoprene), atmospheric methane, or fossil carbon (e.g., coal or petroleum), the Fm_{CH_2O} would have been 1.05, 1.3 or 0.0, respectively.

2.5. Air Mass Trajectories

[15] Air mass histories (transport) were examined at the regional-to-national scale using meteorological back trajectories calculated using HYSPLIT (R. R. Draxler and G. D. Rolph, HYSPLIT—HYbrid Single-Particle Lagrangian Integrated Trajectory Model, 2003, accessed via NOAA ARL READY Web site, <http://www.arl.noaa.gov/ready/hysplit4.html>). The back trajectory calculations used the EDAS meteorological data set with 3 h 40 km resolution. A set of seven 48 h back trajectories was run for each CH₂O sample. The first back trajectory in a set was initiated at a

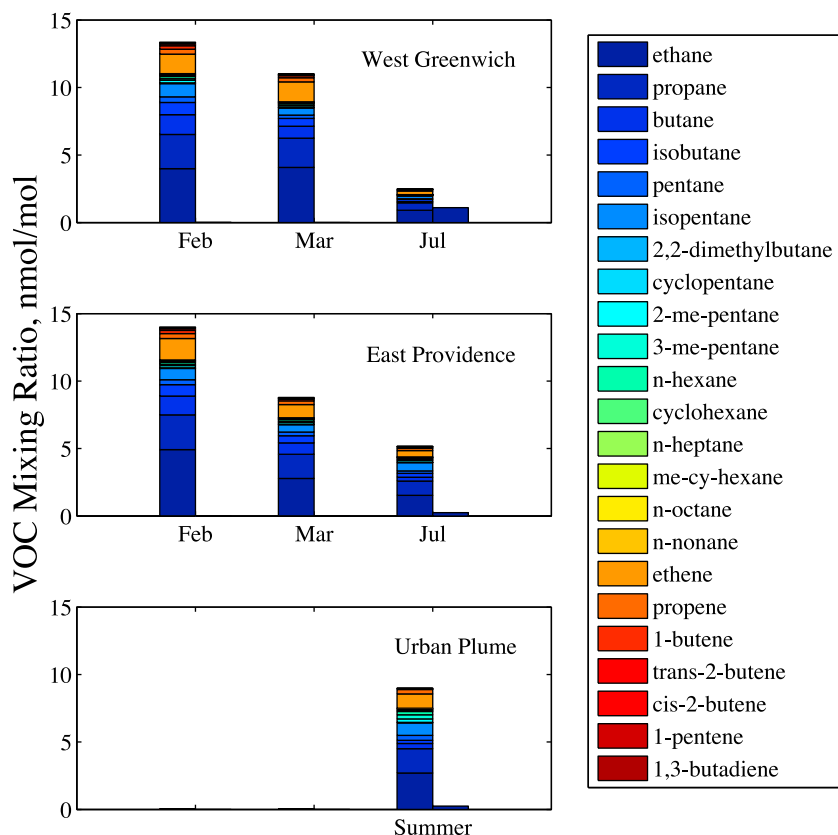


Figure 2. Mean monthly VOC mixing ratios, nmol/mol, for February, March, and July 2007 using RIDEM VOC data from (top) West Greenwich and (middle) East Providence, and (bottom) a summer synthetic urban plume. There are two columns for each month. The left column of a pair shows anthropogenic VOCs, and the right column of a pair shows biogenic isoprene. Only July (summer) had biogenic mixing ratios large enough to be seen above the axis. Anthropogenic VOCs include 23 selected compounds indicated by a separate color (blues and greens are alkanes; oranges and reds are alkenes).

sample's end time and the others initiated at 2 h intervals back in time. Each back trajectory was geographically started at 71.4231°W, 41.4901°N and 300 m altitude. Another set of trajectories were begun 10 km south of this location and a third set ~10 km west; these were done as a catastrophe check on the meteorological data set and resulting trajectory calculation. All three sets showed the same flow paths.

3. Results and Discussion

3.1. The $^{14}\text{CH}_2\text{O}$ Observed

[16] The CH_2O F_m , biogenic fraction and ancillary data are listed in Table 1. The late winter F_m values ranged from 0.10 ± 0.01 to 0.35 ± 0.05 and those for summer varied from <0.05 to 0.28 ± 0.02 . Four of five winter samples contained less than 20% modern carbon. Seven of eight summer samples also contained less than 20% modern carbon. Only 2 of 13 samples contained more than 20% modern carbon: 28% and 35% on 1 July and 29 March, respectively. CH_2O derived solely from contemporary biogenic materials should have a $F_m > 1.00$ because of the current enhancement in atmospheric ^{14}C due to nuclear bomb testing and nuclear power generation relative to the pre-nuclear standard reference material used. CH_2O from purely fossil carbon origin

should contain no detectable ^{14}C and have $F_m = 0.00$. The airflow on the two days with the highest F_m , 29 March and 1 July, was from the northwest. The other days were characterized by airflow from the southeast to west. The results indicated CH_2O precursors were dominated by fossil VOC sources on all sample days during winter and summer at NBC. Further, an increased proportion of biogenically derived CH_2O was not observed in summer compared to winter, contrary to expectation. The initial expectation is reexamined and alternative explanations are explored below.

3.2. The $^{14}\text{CH}_2\text{O}$ Source Attribution: Local VOCs

[17] Estimated initial CH_2O production rates, nmol/mol h^{-1} , for West Greenwich and East Providence are shown in Figure 3 for July following *Lee et al.* [1998] and *Sumner et al.* [2001]. Three columns are shown for each VOC case studied. The left, middle and right columns for a case show initial CH_2O production rates from anthropogenic VOCs, isoprene, and methane, respectively. The contribution from α -pinene was calculated, was much smaller than isoprene and is not shown. The contribution from methane was constant at $0.066 \text{ nmol/mol h}^{-1}$. Currently, 70% of atmospheric methane is estimated to be from biological sources [*Lassey et al.*, 2007] and its contribution to CH_2O is distributed proportionately.

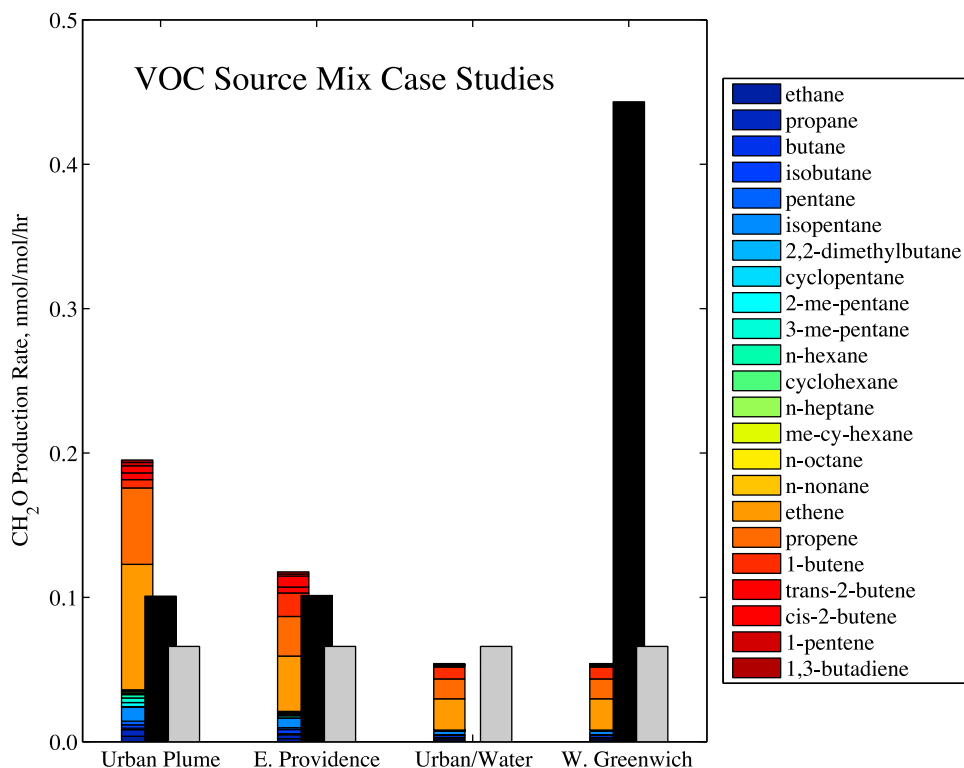


Figure 3. Initial CH₂O production rates, nmol/mol h⁻¹, for summer VOC case studies. Each case shows three columns: anthropogenic VOCs (blue to red), isoprene (black), and methane (gray). Anthropogenic VOC contributions are from 23 selected compounds indicated by the color legend (blues and greens are alkanes; oranges and reds are alkenes). VOC mixes are developed and discussed within the text.

[18] The calculations (not shown) indicated fossil VOCs were the major sources of CH₂O during the winter season at the RIDEM sites, as observed. The biogenic methane and isoprene fraction was predicted to contribute about 10% to CH₂O production in February, about 30% in March and this was mostly due to methane. In July, the biogenic isoprene and methane fractions were estimated to contribute about 80% of the CH₂O production at West Greenwich and 60% at East Providence (Figure 3). Hence, a large summer Fm value or a large biogenic contribution to CH₂O was predicted but not observed.

3.3. The ¹⁴CH₂O Source Attribution: Transport and Regional Urban VOCs

[19] The combined effects of transport and reactivity suggest the VOC concentrations measured at the inland RIDEM sites were not representative of the VOC mix at the NBC sampling site. Our sample day selection criteria preferentially chose days when prevailing southwesterly winds were predicted with likely transport over water. A regional sea breeze reinforces this flow in daylight hours in summer [e.g., Fisher, 1960; Angevine *et al.*, 2004]. In contrast with the NBC site the inland RIDEM sites are beyond the landward penetration of the sea breeze front. The pattern of hourly surface ozone shown in Figure 4 illustrates this contrast. The inland sites, especially West Greenwich, show depletion ascribed to titration through surface deposition and reactions with NO and reactive VOC emissions under a nocturnal inversion. Angevine *et al.* [2004] and Darby *et al.*

[2007] similarly attributed variations in O₃ in coastal New Hampshire to transport effects.

[20] We examined summer transport patterns using back trajectories. Figure 5 illustrates the spatial domain enclosed by the 7 trajectories for each sample in July, truncated at 12 h. The photochemical lifetime of CH₂O is <3 h in daylight at 41°N in July. Consequently, if the CH₂O concentration is constant, >95% of the CH₂O sampled would have been produced in the previous 12 h; or >95% of the CH₂O present 12 h upstream will have been lost by the time of sampling. The trajectory envelopes indicate sampling of coastal air masses, including the New York City urban plume, with the exception of one sample. The 1 July 2007 sample has the least urban influence of all of the July samples, as the transport path lies well west of the Boston metropolitan area, and Montreal is 15–18 h upwind. The 1 July sample has the second-highest Fm value. The February and March trajectories showed similar behavior but with longer paths owing to stronger winds. The 29 March case has a trajectory envelope nearly identical with the 1 July case; this sample has the highest Fm value.

[21] Two additional VOC mixes were developed to better reflect transport and upwind VOC sources, an urban plume case and a coastal inflow case. The northeast urban plume case was developed following Sommariva *et al.* [2008] with one exception: isoprene was significantly reduced from their value of 1740 pmol/mol to 250 pmol/mol. Isoprene concentrations at West Greenwich in July 2007 were less than the values used by Sommariva *et al.* [2008] for their urban plume case study. Further, whole-air-sample VOC mea-

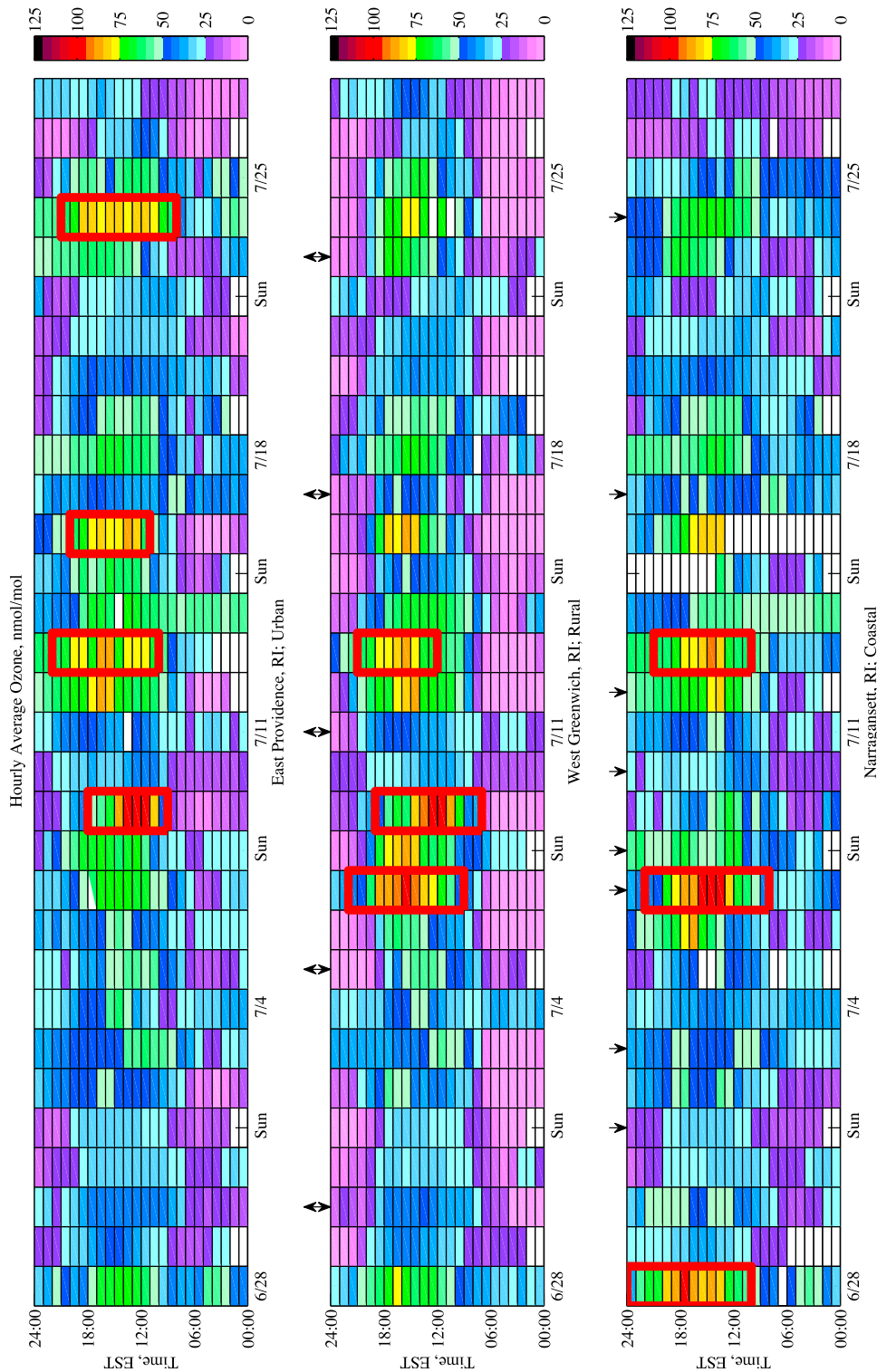


Figure 4. Hourly average O₃ for Narragansett, West Greenwich, and East Providence, RI. Month/day and Sundays are indicated along the x axis and hour of day (EST) is indicated along the y axis. Colors denote O₃ mixing ratios ranging from light pink (<5 nmol/mol) to dark red (>120 nmol/mol). The green-to-yellow transition indicates 75 nmol/mol. Missing data are indicated by white. The arrows along the top of Figure 4 (bottom) show ¹⁴CH₂O sample days at the Narragansett Bay Campus. The double arrows along the top of Figure 4 (middle) show RIDEM VOC sample days. Bold red boxes show periods over which the 8 h average ozone standard of 75 nmol/mol was exceeded at each site.

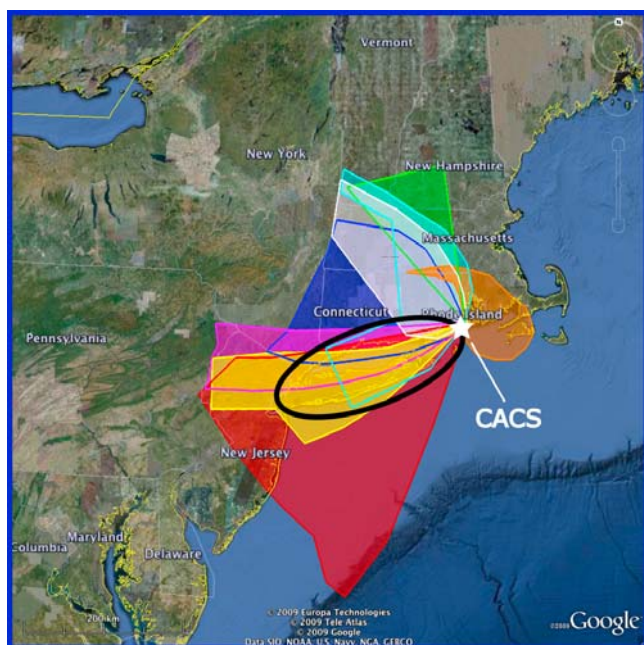


Figure 5. Air mass envelopes defined by 12 h back trajectories initiated every 2 h from sample start to end times. Dates 1, 3, 7, 8, 10, 12, 17, and 24 July are indicated by the colors green, cyan, blue, magenta, red, white, orange, and yellow, respectively. With the exception of 1 July, each envelope included a significant coastal air component and the New York City metropolitan area, highlighted by the black ellipse. Sample site location is shown by the orange star labeled CACS. Image covers approximately 69°W–76°W, 38°N–44°N. Base image from Google Earth 2008©.

measurements collected on the NOAA WP-3 in ICARTT-2004 near New York City and within the near-field NYC urban plume contained less than 250 pmol/mol isoprene when two or more of ethane, propane, ethene or propene were in excess of 2000, 1000, 500 and 100 pmol/mol, respectively (E. Atlas, University of Miami, personal communication, 2009). The later mixing ratios were in keeping with the Sommariva urban plume case and East Providence urban data. Hence, isoprene was set at 250 pmol/mol for the urban plume case mix whose VOC mixing ratios are listed in Table 2.

[22] A southern New England coastal onshore flow VOC case study was defined using the West Greenwich measurements and the whole-air-sample measurements from ICARTT-2004 over Rhode Island Sound, Block Island Sound, Long Island Sound and the coastal North Atlantic south of Long Island, NY (E. Atlas, University of Miami, personal communication, 2009). The “Coastal” over-water VOC mixing ratios were near those listed in Table 2 for the West Greenwich rural site with the exception of isoprene and α -pinene, which were both < 1 pmol/mol. VOC and OVOC plume studies over New England support using reduced isoprene values in the over-water VOC case. Warneke *et al.* [2004], Goldan *et al.* [2004], de Gouw *et al.* [2005] and Sommariva *et al.* [2008] have argued biogenic VOCs (isoprene and monoterpenes) are oxidized during both day and nighttime hours by HO and nitrogen trioxide (NO_3), respectively, whereas, the anthropogenic VOCs are

oxidized mostly during daylight hours by HO. The oxidation of VOCs by HO is expected to lead to the formation of CH_2O and the oxidation of isoprene and monoterpenes by NO_3 is expected to yield organic nitrates [e.g., Tuazon *et al.*, 1999; Atkinson and Arey, 2003] and so is not expected to yield significant amounts of CH_2O . Rhode Island is approximately 10 h to 1 day transport time from New York City (200 km) or Washington, D. C. (500 km), respectively, and urban polluted air masses transported over water are expected to have their biogenic VOCs depleted relative to the longer-lived anthropogenic VOCs. The consequences of day/night oxidation, biogenic/anthropogenic VOC emission patterns and transport path over water/land should have a marked impact on O_3 production [Warneke *et al.*, 2004] and CH_2O sources. Hence, the defined “Coastal” inflow VOC case has the anthropogenic VOC mixing ratios of the West Greenwich case listed in Table 2 but without isoprene or α -pinene.

[23] The CH_2O source contribution results for the additional urban plume and the urban plume over water cases are shown on Figure 3. Both cases indicated fossil VOCs contribute $\sim 60\%$ of the CH_2O . While these two cases developed Fms indicating larger fossil contributions than the original East Providence or West Greenwich cases, their biogenic VOC contributions were still higher by about 0.2 to 0.3 in Fm than those observed and additional fossil sources of CH_2O were sought.

3.4. The $^{14}\text{CH}_2\text{O}$ Source Attribution: Regional Urban VOCs and OVOCs

[24] The inclusion of oxygenated volatile organic compounds (OVOCs), organic nitrates and organic peroxy nitrates as precursors to CH_2O formation could further help bridge the gap between that expected from the CH_2O source analyses and the summer Fm measurements. Shen [2008] analyzed near surface CH_2O sources using the same point-model method and data as presented by Fried *et al.* [2008] for high-altitude INTEX-NA data and found the OVOC group (methanol, acetaldehyde, acetone), together with peroxy compounds (PAN and peracetic acid), contributed 10–40% of the total CH_2O production at altitudes < 1 km over eastern North America. An analysis of VOCs and OVOCs in urban plumes over the Gulf of Maine by de Gouw *et al.* [2005] showed acetaldehyde, propanal, acetone, methyl ethyl ketone, methanol, peroxy propyl nitrate, and peroxy isopropyl nitrate to each have biogenic source contributions below 20%. They also showed formic and acetic acids and peroxy acetyl nitrate to each have biogenic source contributions of 20–30% and only the isoprene derived product, peroxy methacryloyl nitrate, had a biogenic source contribution (86%) larger than $> 30\%$. From these two studies, the urban OVOC contribution to CH_2O is presumed to have a predominantly fossil source character, which would increase the fossil source component in the urban plume cases and would lower the expected Fm for urban air by another 0.1 to 0.3 from the concomitant reductions in b_{isoprene} and b_{CH_4} .

[25] The combination of metropolitan plume VOCs and OVOCs with over water transport brought the calculated fossil contribution into plausible agreement with the Fm observed at NBC. However, this analysis is by no means complete. Other OVOC components not considered such as

methyl vinyl ketone or methacrollyn, products of isoprene oxidation and potential secondary biogenic sources of CH₂O away from the primary emission location [e.g., *de Gouw et al.*, 2005; *Millet et al.*, 2006], would increase the disagreement. Unaccounted for near-site local CH₂O and HRVOC emissions, (e.g., propane tanks, diesel traffic, light industry) would decrease the disagreement. The data to quantitatively evaluate these factors are unavailable.

3.5. The ¹⁴CH₂O Source Attribution: Prior Work

[26] In the only other ¹⁴CH₂O study, *Tanner et al.* [1996] reported ~87% modern carbon for samples collected at Chebogue Point, Nova Scotia, in the summer during NARE-1993. They concluded that the majority of CH₂O measured was derived from biogenic precursors. Their interpretation was based upon air samples collected at 10 m above the surface for 24 to 48 h. Analyses of meteorological conditions and air mass composition from both ground and airborne measurements indicated surface air at their site was frequently isolated from polluted air aloft as the relatively warm polluted air from the northeast United States and Canada was advected over relatively cold North Atlantic waters upwind of Chebogue Point. This led to a strong temperature inversion isolating the pollutants from the surface site [e.g., *Tanner et al.*, 1996]. The CH₂O concentrations observed (0.3–1.5 nmol/mol) by *Tanner et al.* were in the same range as airborne observations of CH₂O made over this region below 500 m altitude during INTEX-NA 2004 [*Shen*, 2008; *Fried et al.*, 2008]. From the analysis by *Shen* [2008], 60 to 70% of the CH₂O in maritime air near Nova Scotia was attributed to the oxidation of methane and methyl hydroperoxide (mainly derived from methane). The relatively high ¹⁴C content of CH₄ (Fm = 1.3 [*Lassey et al.*, 2007]), together with the source analysis by *Shen* [2008] indicated a mix of 60–70% methane and 30–40% anthropogenic VOC would yield CH₂O with an Fm of 0.8 to 0.9 and consistent with that observed by *Tanner et al.* [1996]. It should be noted that *Millet et al.* [2006] suggested long-range transport of biogenic OVOCs as the source of the biogenic CH₂O at Chebogue Point and these sources would be in addition to that from methane. The *Tanner et al.* study and the one presented here emphasize the need to carefully consider transport, as well as, local chemistry in the interpretation of CH₂O radiocarbon observations.

4. Conclusions and Future Work

[27] Gaseous CH₂O samples were collected at Narragansett, RI during winter and summer 2007 and their radiocarbon content determined. The results show a significantly large fraction of fossil carbon in collected CH₂O, 11 of 13 samples had Fm < 0.2, and indicated the precursors of CH₂O were dominated by fossil sources at the NBC site during each sample's collection period. The winter-spring Fm values were in agreement with those expected based upon a CH₂O source contribution analysis. The summer Fm values were considerably lower than first expected from this same analysis using VOC observations from rural and urban Rhode Island locations. It is suggested that pollutants from upwind coastal metropolitan areas were transported to the sample site, a local sea breeze circulation reinforced this pollutant transport flow regime and that urban fossil VOCs and OVOCs

could have dominated the CH₂O source chemistry at NBC. Additional CH₂O radiocarbon measurements and more sophisticated chemical transport modeling of atmospheric CH₂O in a variety of environments, e.g., urban, semiurban, and rural areas, are needed to confirm this interpretation of CH₂O sources and to further develop strategies to regulate its precursor VOCs and OVOCs and potential contributions to surface O₃.

Notation

- b* fraction of CH₂O production from a specific source.
- Fm fraction modern.
- HRVOC highly reactive volatile organic compound.
- i* chemical species or process index.
- k* chemical reaction rate coefficient.
- OVOC oxygenated volatile organic compound.
- P* CH₂O production rate from species *i*.
- VOC volatile organic compound.
- RVOC reactive volatile organic compound.
- φ effective CH₂O yield from VOC reaction with HO.
- [] molecular concentration.

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