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Journal
Geophysical Research Letters, 34(17)

ISSN
0094-8276

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Publication Date
2007

DOI
10.1029/2007gl030528

GEOPHYSICAL RESEARCH LETTERS, VOL. 34, L17808, doi:10.1029/2007GL030528, 2007

A large terrestrial source of methyl iodide

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Received 28 April 2007; revised 2 July 2007; accepted 2 August 2007; published 6 September 2007.

[1] We have identified terrestrial sources of methyl iodide (CH_3I) and assessed their importance in its atmospheric budget using a synthesis of field observations. Measurements include those from NASA DC-8 research flights over the United States and the North Atlantic, the AIRMAP long-term ground-observing network in New England, and a field campaign at Duke Forest, North Carolina. We found an average CH_3I flux of ~2,700 ng m^{-2} d^{-1} to the atmosphere from midlatitude vegetation and soils, a value similar in magnitude to previous estimates of the oceanic source strength. The large-scale aircraft measurements of vertical profiles over the continental U.S. showed CH_3I-mixing ratios comparable to and greater than those observed over the North Atlantic. Overall, midlatitude terrestrial biomes appear to contribute 33 Gg yr^{-1} to the CH_3I global budget.

Citation: Sive, B. C., R. K. Varner, H. Mao, D. R. Blake, O. W. Wingenter, and R. Talbot (2007), A large terrestrial source of methyl iodide, *Geophys. Res. Lett.*, *34*, L17808, doi:10.1029/2007GL030528.

1. Introduction

[2] Methyl iodide (CH_3I) is the most abundant organoiodine compound in the atmosphere and it can influence O_3 chemistry, aerosol formation, and ultimately the atmosphere's oxidizing capacity [e.g., *Solomon et al.*, 1994; *Davis et al.*, 1996; *O'Dowd et al.*, 2002]. Current estimates suggest that oceanic emissions are the major source of CH_3I to the atmosphere [*Smythe-Wright et al.*, 2006], with smaller amounts derived from rice plants/paddies [e.g., *Lee-Taylor and Redeker*, 2005], salt marshes [*Manley et al.*, 2006] and fungi [*Harper*, 1985]. However, significant uncertainties still exist in defining the oceanic CH_3I source strength [*Cox et al.*, 2005] and its loss by photolysis [e.g., *Bell et al.*, 2002].

[3] Plants and soils are known sources of atmospheric methyl halide compounds, as in the case of CH_3Br and CH_3Cl [e.g., *Saito and Yokouchi*, 2006]. We conducted measurements of hydrocarbons and methyl halides in a suite of environments, including aboard airborne research flights over the U.S. and the North Atlantic, the AIRMAP long-term ground observing network in New England, and a mid-latitude forest site. The purpose of these observations was to contrast the CH_3I distribution in continental and marine environments, with the goal of identifying potential terrestrial sources of CH_3I and assessing their importance in its atmospheric budget.

2. Experimental Methods

[4] A long-term continuous record of CH_3I in New England was obtained from January 2004 to October 2006 utilizing daily canister samples collected at local noon from the University of New Hampshire (UNH) AIRMAP Observing Station at Thompson Farm (TF) in Durham, NH (43.11°N, 70.95°W, 24 m). During the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) campaign in July/August 2004 (http://esrl.noaa.gov/csd/ICARTT/) concurrent measurements of CH_3I were made by UNH at TF and Appledore Island (AI) (40.92°N, 70.62°W, 5 m) in the coastal Gulf of Maine. Canister samples were also obtained aboard the NASA DC-8 aircraft by the University of California - Irvine (UCI) during the Intercontinental Chemical Transport Experiment - North America campaign (INTEX-NA) as a component of ICARTT (27.63°–53.03°N, 40.50°–143.83°W). Finally, measurements of CH_3I were conducted above, within and below the canopy of *Pinus taeda* (Loblolly Pine) and *Liquidambar styraciflua* (Sweetgum) at Duke Forest (DF), Chapel Hill, NC (35.58°N, 79.05°W, 163 m) during two intensive study periods of September 8–28, 2004 and June 1–12, 2005. Branch and soil enclosure measurements were performed to determine direct emission fluxes of CH_3I.

[5] Canister samples were analyzed by gas chromatography (GC) using flame ionization and electron capture detection in conjunction with quadrupole mass spectrometry [*Sive et al.*, 2005; *Zhou et al.*, 2005]. At TF during the ICARTT campaign, measurements of volatile organic compounds were made *in situ* using an automated 4-channel GC system [*Sive et al.*, 2005; *Zhou et al.*, 2005]. The UNH and UCI analytical systems have similar configurations and calibration methods[1]. Inter-comparison of the canister and in situ measurement techniques over a four day period in June 2004 provided high confidence in the comparability of the CH_3I measurements (n = 80): UNH GC = 0.48 ± 0.27 pptv; UNH canisters = 0.49 ± 0.26 pptv; UCI canisters = 0.49 ± 0.26 pptv. The corresponding slope and r^2 values for the correlations between each set of measurements were the following: UNH GC/UNH canisters, slope = 0.93, r^2 = 0.95; UNH GC/UCI canisters, slope = 0.93, r^2 = 0.95; UNH canisters/UCI canisters, slope = 0.99, r^2 = 0.97. The CH_3I measurement precision was ±3% for the canister

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0094-8276/07/2007GL030528

[1] Auxiliary material data sets are available at ftp://ftp.agu.org/apend/gl/2007gl030528. Other auxiliary material files are in the HTML.

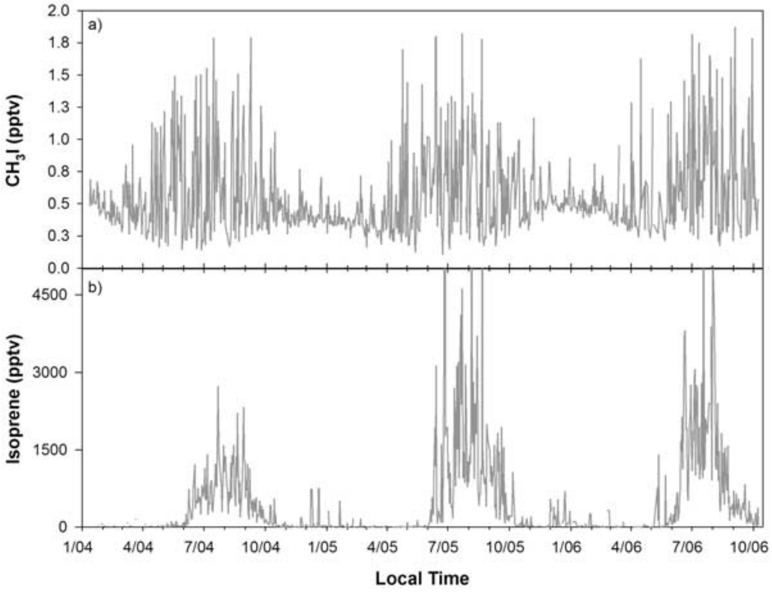

Figure 1. Measurements of (a) CH_3I and (b) isoprene from daily samples collected at Thompson Farm in Durham, NH from January 2004–October 2006.

samples and ±5% for the in situ system; the overall accuracy for all CH_3I measurements was ±5% based on primary reference halocarbon standards generated from static dilutions of pure compounds prepared in the UCI laboratory [*Wang*, 1993].

3. Temporal Variation

[6] Three years of daily measurements of CH_3I at TF exhibited a seasonality that is similar to isoprene (Figure 1), with highest mixing ratios occurring in July and August. Overall averages and standard deviations for January and July were 0.45 ± 0.09 pptv (n = 82) versus 0.74 ± 0.44 pptv (n = 81) respectively. A distinct feature of the time series was the broader time period of enhanced mixing ratios for CH_3I (late March – mid-October) compared to isoprene (mid-June – early September). The CH_3I time period compares favorably with the growing season in New England, whereas isoprene corresponds to a narrower interval of active leafy vegetation. Moreover, the mixing ratios of CH_3I at TF exhibited 2-fold larger seasonal variation than at sites such as Cape Grim, Tasmania, Australia which is primarily a marine source region [*Cox et al.*, 2005].

[7] The AIRMAP data obtained during ICARTT provide a basis for direct comparison of selected methyl halides between the terrestrial and marine environments. At TF mean values (± standard error) were: CH_3I = 1.24 ± 0.02 pptv; $CHBr_3$ = 6.4 ± 0.2 pptv; CH_2ClI = 0.15 ± 0.01 pptv. The corresponding values at AI were: CH_3I = 1.39 ± 0.02 pptv; $CHBr_3$ = 14.3 ± 0.3 pptv; CH_2ClI = 0.68 ± 0.03 pptv. The overall difference in CH_3I between the two sites was small compared to large gradients (AI/TF) of 2-fold for $CHBr_3$ and 4-fold for CH_2ClI. The lifetime due to photolysis of CH_3I (~4 days) is intermediate to that of $CHBr_3$ (~2 weeks) and CH_2ClI (~2 hours), so an easily measurable gradient in CH_3I would be expected if its primary source was solely of marine origin. In a related study, *Zhou et al.* [2005] observed a 14% gradient in mixing ratios of CH_3I between coastal-to-inland sites in New Hampshire; during ICARTT the observed gradient between TF and AI was 11%.

[8] Strong evidence for a terrestrial source of CH_3I is derived from the time series record of the ratio $CH_3I/CHBr_3$ (Figure 2). In the marine environment the ratio varied over a small range of 0.1–0.5 with a mean value of 0.12 ± 0.06 (n = 994). In contrast, the mean value inland at TF was nearly 3-fold greater at 0.34 ± 0.27 (n = 1284), and covered a wide range of 0.1–1.9, resulting from the much lower levels of $CHBr_3$ and larger variation in CH_3I. There were several time intervals where the ratio at TF was close to the

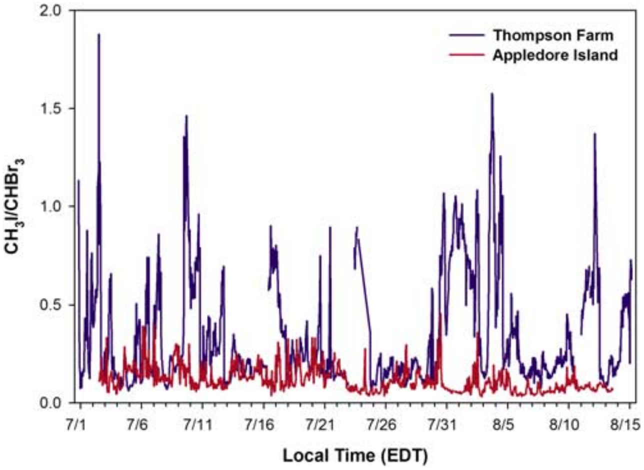

Figure 2. Time series of the $CH_3I/CHBr_3$ ratio from Thompson Farm and Appledore Island during the ICARTT campaign (July 1–August 15, 2004).

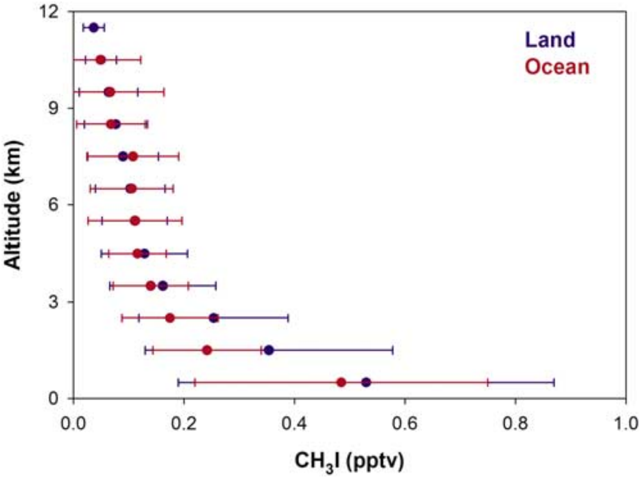

Figure 3. Vertical distributions of CH_3I over the land and ocean from measurements onboard the NASA DC-8 aircraft during INTEX-NA as part of the ICARTT 2004 campaign. Error bars represent the standard deviation.

marine value at AI, but in general its distribution exhibited values >0.3 over more than 50% of the ICARTT period.

4. Terrestrial Source

4.1. Large Scale

[9] The vertical distribution of CH_3I from 0.15–12 km was examined over the U.S. using the UCI aircraft data partitioned into terrestrial and oceanic subsets and 1 km altitude bins (Figure 3 and Table S2). Flights over the continent occurred east of 100°W, while the oceanic flights were mainly off the Northeast coastline eastward to 40°W (Figure S1). Mixing ratios of CH_3I at altitudes <1 km ranged from 0.11–1.40 pptv and 0.15–1.36 pptv over land and ocean respectively. If CH_3I had an exclusive marine source, such a geographic distribution would not be expected to persist over the six-week period of the airborne campaign. Air transported inland from the marine environment could result in regionally elevated CH_3I mixing ratios over land, especially in coastal areas. However, for inland locations, loss of CH_3I by photodissociation would be important. For example, using the average mixing ratio of 0.49 pptv observed over the ocean at ≤1 km altitude, a photolysis frequency of 3×10^{-6} s^{-1} [*Rattigan et al.*, 1997] and 12 hours of photochemical processing time per day, the mixing ratio would be reduced to ~0.38 pptv after two days. Such low values were rarely observed in the boundary layer over the U.S. Evidence for a large-scale terrestrial source of CH_3I is further corroborated by the fact that some of the highest CH_3I mixing ratios (>1 pptv) were found over the continent with correspondingly low levels of $CHBr_3$ (<0.9 pptv).

4.2. Forest Setting

[10] A suite of measurements conducted in DF provide direct evidence for a terrestrial source of CH_3I. Vertical profiles were obtained in June 2005 with 5 m resolution to evaluate sources of trace gases in the forest ecosystem. Comparison of the average vertical profiles at 0000 and 1500 EDT show a nighttime buildup beneath the canopy (~18 m), with the largest mixing ratios occurring near the forest floor (Figure 4a). Note that the mid-day mixing ratio at 20 m is very similar to the average value we observed on ≤1 km flight legs over the U.S. However, below canopy mixing ratios were elevated significantly over this value, indicating a strong persistent ecosystem (i.e, vegetation and soil) source of CH_3I.

[11] The above canopy hourly averaged mixing ratios of CH_3I from DF and TF exhibited a distinct diurnal pattern, with elevated levels at night and 25% lower levels during daytime (Figure 4b). The DF profile data show that the observed enhancements result from buildup associated with local biogenic emissions under a stable nocturnal boundary layer. The diurnal pattern in CH_3I is similar what we have observed for monoterpenes [*Talbot et al.*, 2005]; both are removed relatively rapidly during the daytime (OH for monoterpenes and photolysis for CH_3I) and exhibit elevated levels at night due to continuous terrestrial emissions. Moreover, the land breeze and otherwise prevalent weak wind conditions (<2 m s^{-1}) at TF during the night (>70% of the time) [*Mao and Talbot*, 2004] minimize transport inland from the coastal environment. Direct marine influences on the chemistry are negligible at DF because it is located ~250 km inland.

[12] The average diurnal cycles allow determination of the terrestrial flux required to sustain the above canopy levels of CH_3I at DF and TF. The diurnal variation of the

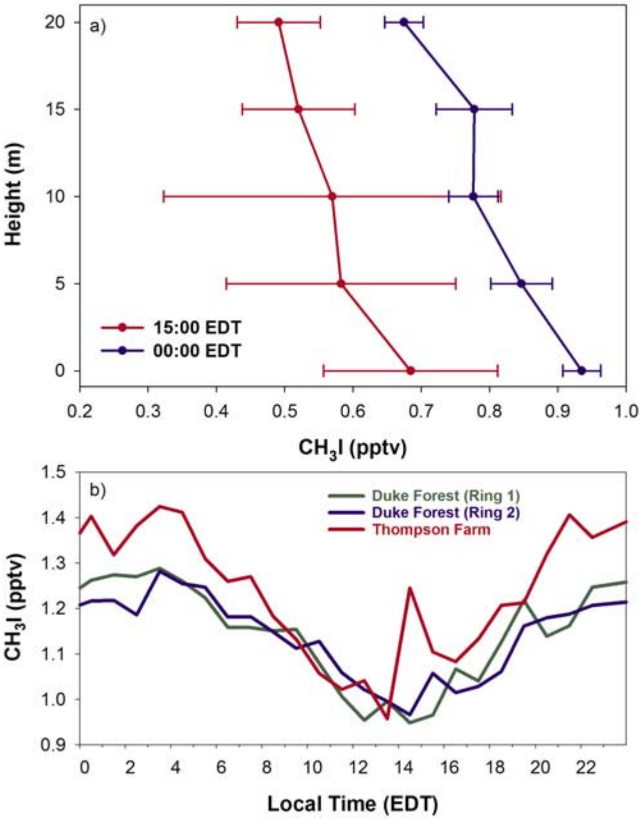

Figure 4. (a) Daytime and nighttime vertical profiles of CH_3I at Duke Forest from samples collected at Rings 1–6 in June 2005. (b) Average diurnal profiles of CH_3I at Thompson Farm (July 1–August 15, 2004) and at Duke Forest for Rings 1 and 2 (September 16–28, 2004).

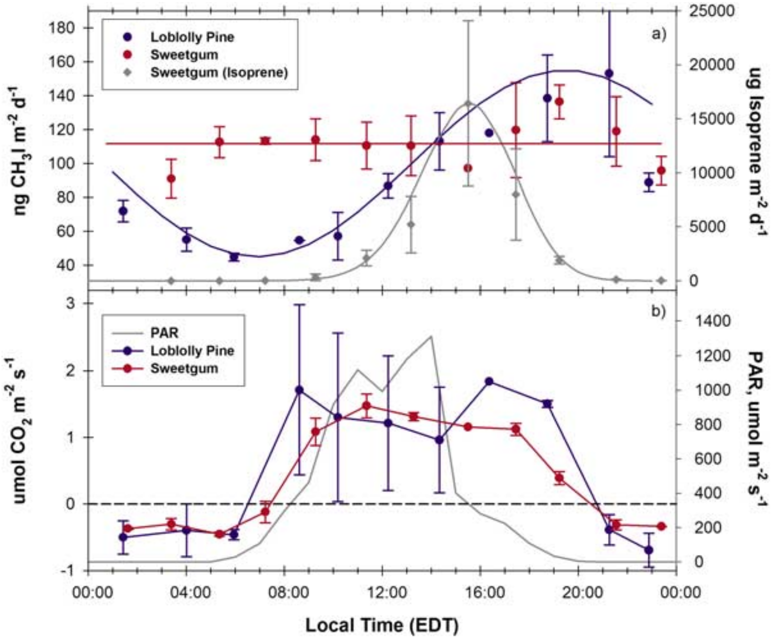

Figure 5. Results from the branch enclosure measurements of the Loblolly Pine and Sweetgum showing the (a) fluxes of CH_3I and isoprene (Sweetgum only) per unit leaf area and (b) photosynthetically active radiation (PAR) and the net exchange of CO_2 at Duke Forest (June 1–12, 2005).

CH_3I cycle at TF was 0.46 pptv, yielding an average terrestrial flux of 2,655 ng m^{-2} d^{-1} using the diurnal profile of planetary boundary layer height from *Mao and Talbot* [2004]. The diurnal amplitudes were smaller at DF and averaged 0.31 pptv, with a CH_3I flux of 1,790 ng m^{-2} d^{-1}.

[13] The soil emission flux of CH_3I was determined at DF during the September and June time periods (Table S2). In June the measurements were obtained during a period of heavy precipitation with essentially water saturated soils. The emissions exhibited a diurnal cycle with values indistinguishable from zero at night (2100–0900), reaching 15 ng m^{-2} d^{-1} by mid-morning and peaking around 1300 EDT at 45 ng m^{-2} d^{-1}. The mean soil flux of CH_3I to the atmosphere was 39 ± 10 ng m^{-2} d^{-1} (n = 12). Warmer (27.6 ± 2.1°C versus 24.5 ± 1.5°C) and much drier conditions prevailed in September, and soil fluxes were measured in two study plots yielding values of 578 ± 376 and 118 ± 52 ng m^{-2} d^{-1} (n = 8). The emissions were continuous and did not exhibit a diurnal cycle under dry weather conditions.

4.3. Enclosure Measurements of Tree Branches

[14] Tree branch enclosure measurements were performed at DF with particular emphasis on CH_3I and isoprene. The measured emission fluxes of CH_3I (259–1,728 ng cm^{-2} d^{-1}) and isoprene are shown in Figure 5a. The fluxes are based on a per leaf area basis and demonstrate that Loblolly Pine and Sweetgum are sources of CH_3I to the atmosphere. The average daily fluxes from the Sweetgum and Loblolly Pine were 993 and 778 ng m^{-2} d^{-1} respectively. As illustrated in Figures 5a and 5b, the highest CH_3I flux occurs after the maximum in photosynthetically active radiation (PAR), isoprene emission, and net exchange of CO_2. Moreover, there are distinct features of the CH_3I emissions: (1) they are continuous from Sweetgum with no apparent diurnal cycle, (2) they are continuous from Loblolly Pine and exhibit a diurnal cycle and, (3) they do not appear to be stomatally controlled.

5. Terrestrial Source of CH_3I: Global Budget Considerations

[15] As outlined by *Cox et al.* [2005], the CH_3I budget appears to be balanced; however, there are sizable uncertainties in the magnitude of the oceanic source with estimates ranging from 128–500 Gg yr^{-1} [*Cohan et al.*, 2003] and 214–1,300 Gg yr^{-1} [*Cox et al.*, 2005]. As described by *Cohan et al.* [2003], a comprehensive analysis of shipboard data over a range of latitudes (60°N–40°S) and oceanic regions (Atlantic, Pacific), during several seasons indicates a global ocean-to-atmosphere flux of ~130–360 Gg yr^{-1}, at the low end of the earlier estimates used by *Cox et al.* [2005]. Therefore, if the average estimate for the oceanic source strength from *Cohan et al.* [2003] (315 Gg yr^{-1}) is combined with the area of the oceans (331 × 10^6 km^2), the resulting oceanic flux is ~2,600 ng m^{-2} d^{-1}.

[16] In this study, the terrestrial CH_3I flux was estimated to be 2,655 ng m^{-2} d^{-1} at TF and 1,790 ng m^{-2} d^{-1} at DF, respectively, assuming that the rate of CH_3I change in the average diurnal cycles is determined by the terrestrial source and photolysis sink. Our measurements from DF indicate that vegetation dominated the terrestrial flux with 900 ± 1,100 ng m^{-2} d^{-1} and soils contributed 500 ± 400 ng m^{-2} d^{-1}. This suggests that the terrestrial and oceanic fluxes are comparable in magnitude, which accounts for the similarity in the vertical profiles of CH_3I in the marine and terrestrial environments.

[17] On a global basis, the average terrestrial flux of 2,270 ng m^{-2} d^{-1} over an active season of 240 days, together with biome areas for temperate forest and wood-

lands (28.5×10^{12} m^2) and temperate grasslands (31.9×10^{12} m^2) [*Guenther et al.*, 1995], yield a source strength of 33 Gg yr^{-1}. Measurements are needed in tropical and boreal areas to improve and expand upon our terrestrial flux estimates and facilitate development of a more accurate global budget.

[18] **Acknowledgments.** Financial support for this work was provided through the Office of Oceanic and Atmospheric Research at the National Oceanic and Atmospheric Administration under grants NA04OAR4600154 and NA05OAR4601080. Additional support for the research conducted on Appledore Island was provided by the National Science Foundation through grant 0401622, the U.S. EPA-STAR program through grant RD-83145401 for Duke Forest, and the NASA GTE program for INTEX-NA. This paper is contribution 143 to the Shoals Marine Laboratory. A special thanks to Y. Zhou, M. White, R. Russo, J. Ambrose, K. Haase, P. Beckman, and E. Frinak at UNH and I. Simpson at UCI.

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