Terrestrial and Marine Sources of Methyl Iodide in the Rural Southeast

Justine L. Stocks¹, Yong Zhou², Michael Link², Carley Brunton¹, Matthew West¹, Ryan Cook², Brian Morgan², Christopher Thaxton¹,³, and Barkley C. Sive¹,²

¹Environmental Science Program, Appalachian State University, Boone, NC
²Department of Chemistry and Atmospheric Sciences, Appalachian State University, Boone, North Carolina, USA.
³Department of Physics and Astronomy, Appalachian State University, Boone, North Carolina, USA.

Abstract
Methyl iodide (CH₃I) is the most abundant organo-iodine compound in the atmosphere and is influential in aerosol formation and tropospheric ozone depletion. It is used in the production of pesticides and pharmaceuticals and is also produced biogenically by marine algae and terrestrial vegetation and soils. Short and long-term methyl iodide exposure via inhalation can be harmful to humans. In order to investigate the sources and distributions of methyl iodide in the rural southeastern U.S, a two-week long campaign was conducted at the Appalachian Atmospheric Interdisciplinary Research (AppalAIR) site in Boone, NC, from June 15 through July 2, 2013. Whole air samples were collected hourly and analyzed for a comprehensive suite of volatile organic compounds (VOCs), including methyl iodide. In this paper, relative levels of methyl iodide are compared to other terrestrial regions in the U.S. and anthropogenic and biogenic tracers are used to elucidate the summertime sources of methyl iodide observed in the rural southeast.

1.0 Introduction
Methyl iodide (CH₃I) is an important intermediate for aerosol formation and also plays a key role in tropospheric ozone depletion. It is produced predominately by marine phytoplankton, at levels around 2 Tg/year [1]. Methyl iodide and bromoform (CHBr₃) are sources of the halogen oxide radicals IO and BrO. These radicals influence oxidation processes in the troposphere, as their formation consumes ozone both in the troposphere and the stratosphere. During strong atmospheric uplift in the equatorial regions, methyl iodide and bromoform can reach the stratosphere and contribute to ozone depletion, via the formation of halogen oxide radicals.

Most previous studies have focused on marine sources of methyl iodide, with levels measured in coastal regions and marine environments. Sive et al. (2007) [2] investigated terrestrial sources of methyl iodide at Thompson Farm in Durham, New Hampshire and Duke Forest in Durham, North Carolina, and found terrestrial fluxes of methyl iodide of 2,655 ng m⁻² d⁻¹ and 1,790 ng m⁻² d⁻¹, respectively. These values are comparable to the estimated oceanic flux of ~2,600 ng m⁻² d⁻¹ [2]. In an effort to expand this investigation, several key tracers are used to deduce the source of methyl iodide observed in the sampling area; these gases include trichloroethene (C₂HCl₃) and tetrachloroethene (C₂Cl₄), isoprene (C₅H₈), bromoform (CHBr₃), and ethene (C₂H₄). Tetrachloroethene has a longer lifetime in the atmosphere, with a lifetime of ~96 days as opposed to trichloroethene, which has an atmospheric lifetime of 4-15 days [3]. The atmospheric ratio of trichloroethene to tetrachloroethene can indicate the proximity of the anthropogenic source. Trichloroethene and tetrachloroethene are both used as industrial solvents and are produced predominately in mid-northern latitudes. If the ratio is small, then trichloroethylene has had time to be removed from the air mass being sampled, which indicates a long travel time and distance for the solvents. If the ratio is high, then the source is in close proximity, as trichloroethene has not had time to be removed from the air.
mass. This concept is also applied to the methyl iodide to bromoform ratio and the methyl iodide to isoprene ratio.

Bromoform is a marine-derived gas. It is produced in the oceans by marine algae and phytoplankton. Methyl iodide has a lifetime in the atmosphere of 5.2 days averaged for all latitudes, shorter than bromoform’s lifetime of 2-4 weeks [4]. A high ratio of methyl iodide to bromoform at an inland location would indicate a proximal terrestrial source for methyl iodide, and a low ratio of methyl iodide to bromoform would indicate that there is not a significant proximal terrestrial source of methyl iodide. Isoprene is a volatile organic compound (VOC) emitted almost exclusively by leafy vegetation and has an atmospheric lifetime of around 20 minutes. The methyl iodide to isoprene ratio was used to provide insight on the magnitude of emissions of methyl iodide from vegetation in the area by Sive, et. al. (2007) [2], but the strong diurnal cycle of isoprene drove the variation in methyl iodide to isoprene ratios in this study, as the sampling period was much shorter. Therefore, isoprene will not be used as a tracer gas in this investigation. Ethene is produced biogenically (it is the ripening chemical in plants) in soils and from vegetation, in addition to having an array of anthropogenic sources; it is primarily a product of fossil fuel combustion. Ethene has a lifetime in the atmosphere of around 1.45 days. Although it has both biogenic and anthropogenic sources, in this case, ethene is used in a manner similar to isoprene in a rural environment, but to assess the influence and magnitude of a soil source.

From this work, a significant source of methyl iodide is proposed using different trace gases corresponding to anthropogenic, biological terrestrial, and biological marine sources. Variable lifetimes of trace gases used for analysis will provide an indication of the proximity of the sources using ratios of short-lived to long-lived compounds.

2.0 Methods

2.1. Field Site Description

Hourly air samples were collected during the sampling period of June 15 to July 2, 2013 at the Appalachian Atmospheric Interdisciplinary Research (AppalAir) facility (36.213°, -81.691°; 1110m), located on the campus of Appalachian State University in Boone, NC. The site is in a rural area of Western North Carolina, and is surrounded by a mixed forest. Air was drawn from the top of a 34-m tower [5] using a 5/8-inch O.D. PFA Teflon sampling line at a flow rate of ~75 liters per minute, of which a sub-sample of air was directed to the canister sampling manifold.

2.2. Hourly canister sample collection and analysis

Whole air samples were collected in two-liter electro polished stainless steel canisters (University of California, Irvine, CA). These canisters were prepared for sampling by first flushing with UHP helium, which had been passed through an activated charcoal/molecular sieve (13X) trap immersed in liquid nitrogen. The sample canisters were then evacuated to 10-2 torr. Prior to sampling, the can was connected to a sampling manifold, which used a metal bellows pump to sub-sample air from the main sample inlet line. The sampling manifold was first flushed 10 times by pressurizing it to 30 psig; then venting to ambient pressure, and then the can was opened and “pumped and flushed” five times in the same manner. The sample was then collected by filling the canister to 30 psig and closing the canister’s valve. Whole air samples were collected hourly beginning on June 15 at 12:00 pm and ending on July 2, 2013 at 12:00 pm. The samples were analyzed in the laboratory at Appalachian State University for hydrocarbons, halocarbons, alkyl nitrates, OVOCs, and sulfur compounds using a custom-built, multi-channel gas chromatographic system. Canister samples were injected in 1500 cc aliquots [6] into a gas chromatograph (GC) system equipped with two flame ionization detectors (FID) and two electron capture detectors (ECD), and a mass spectrometer (MS). A 1500 cc aliquot from one of several working standards was run every twelfth analysis.

2.3. Analysis

In order to assess and understand the factors controlling distributions of methyl iodide and its tracer gases, plots of the ratios will be presented, along with correlation plots between significant tracers and methyl iodide, diurnal plots of methyl iodide and significant tracers, and wind rose plots showing local wind directions and levels of each gas measured. Included in this analysis are the basic statistics of each compound, which are presented in Table 1.
2.4 Numerical Analysis

All mixing ratios are presented in parts per trillion by volume (pptv). The mixing ratios are calculated by dividing the peak area of the compound in the sample (PAsa) by the response factor (RF) of the compound (Eq. 1):

\[ MRSA = \frac{PAsa}{RF} \]  

(1)

The response factor (RF) is calculated by dividing the peak area from the standard (PAstd) by the mixing ratio of the compound in the standard (MRstd), as shown in the following expression (Eq. 2).

\[ RF = \frac{PAstd}{MRstd} \]  

(2)

3.0 Data and Analysis

The mean mixing ratios ± standard deviation measured at AppalAIR for methyl iodide, bromoform, trichloroethene, tetrachloroethene, isoprene, and ethene were 0.57 ± 0.27, 1.25 ± 0.64, 0.96 ± 0.93, 7.31 ± 4.10, 604.0 ± 488.5, and 177.4 ± 112.1 pptv, respectively. The highest variability observed was with trichloroethene, as it had a relative standard deviation (RSD) of 97.1% (Table 1). The high variability observed for this compound can be explained by its relatively short lifetime (4-15 days) and its sources are inferred to be distant from the sampling site, as reflected by the low values of the trichloroethene to tetrachloroethene ratio (0.14 ± 0.14). Mixing ratios of trichloroethylene and tetrachloroethene measured during the sampling period were 0.96 ± 0.93 and 7.31 ± 4.10 pptv, respectively, which are low compared to those measured by Zhou et. al. (2005) [7] at Thompson Farm in rural New Hampshire from June-August, 2002 (3.3 ± 3.7 and 17 ± 13.4 pptv, respectively). The low values for these compounds indicate that the site is rural and relatively pristine.

Before and during the sampling period, high levels of rainfall were experienced by the Boone area. These high rainfall events affected dilution with clean, free tropospheric air associated with

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mean</th>
<th>Minimum</th>
<th>1st Quartile</th>
<th>Median</th>
<th>3rd Quartile</th>
<th>Maximum</th>
<th>SD</th>
<th>%RSD</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3I</td>
<td>0.57</td>
<td>0.23</td>
<td>0.43</td>
<td>0.54</td>
<td>0.65</td>
<td>2.66</td>
<td>0.27</td>
<td>47.1</td>
<td>409</td>
</tr>
<tr>
<td>CHBr3</td>
<td>1.25</td>
<td>0.56</td>
<td>1.03</td>
<td>1.22</td>
<td>1.45</td>
<td>1.99</td>
<td>0.64</td>
<td>51.1</td>
<td>401</td>
</tr>
<tr>
<td>C2HCl3</td>
<td>0.96</td>
<td>0.16</td>
<td>0.45</td>
<td>0.67</td>
<td>1.06</td>
<td>9.55</td>
<td>0.93</td>
<td>97.5</td>
<td>409</td>
</tr>
<tr>
<td>C2Cl4</td>
<td>7.31</td>
<td>3.00</td>
<td>5.10</td>
<td>6.12</td>
<td>8.07</td>
<td>36.74</td>
<td>4.10</td>
<td>56.1</td>
<td>409</td>
</tr>
<tr>
<td>C5H8</td>
<td>604.0</td>
<td>20.0</td>
<td>246.5</td>
<td>460.1</td>
<td>822.0</td>
<td>2708.7</td>
<td>488.5</td>
<td>80.9</td>
<td>409</td>
</tr>
<tr>
<td>C2H4</td>
<td>177.4</td>
<td>45.4</td>
<td>110.8</td>
<td>144.6</td>
<td>200.8</td>
<td>917.1</td>
<td>112.1</td>
<td>63.2</td>
<td>409</td>
</tr>
</tbody>
</table>

Table 1. Basic statistics of methyl iodide (CH3I) and tracers analyzed (bromoform (CHBr3), trichloroethene (C2HCl3), tetrachloroethene (C2Cl4), isoprene (C5H8), and ethene (C2H4) mixing ratios (pptv).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mean</th>
<th>Minimum</th>
<th>1st Quartile</th>
<th>Median</th>
<th>3rd Quartile</th>
<th>Maximum</th>
<th>SD</th>
<th>%RSD</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3I:CHBr3</td>
<td>0.50</td>
<td>0.14</td>
<td>0.34</td>
<td>0.44</td>
<td>0.58</td>
<td>3.54</td>
<td>0.33</td>
<td>66.2</td>
<td>409</td>
</tr>
<tr>
<td>C2HCl3:C2Cl4</td>
<td>0.14</td>
<td>0.010</td>
<td>0.07</td>
<td>0.11</td>
<td>0.16</td>
<td>1.63</td>
<td>0.14</td>
<td>100.8</td>
<td>409</td>
</tr>
<tr>
<td>CH3I:C5H8</td>
<td>0.002</td>
<td>0.0001</td>
<td>0.0006</td>
<td>0.001</td>
<td>0.002</td>
<td>0.02</td>
<td>0.002</td>
<td>120.4</td>
<td>409</td>
</tr>
<tr>
<td>CH3I:C2HCl3</td>
<td>0.95</td>
<td>0.06</td>
<td>0.45</td>
<td>0.79</td>
<td>1.20</td>
<td>8.13</td>
<td>0.77</td>
<td>80.7</td>
<td>409</td>
</tr>
<tr>
<td>CH3I:C2Cl4</td>
<td>0.09</td>
<td>0.01</td>
<td>0.06</td>
<td>0.08</td>
<td>0.11</td>
<td>0.41</td>
<td>0.05</td>
<td>54.4</td>
<td>409</td>
</tr>
<tr>
<td>CH3I:C2H4</td>
<td>0.004</td>
<td>0.0006</td>
<td>0.002</td>
<td>0.004</td>
<td>0.005</td>
<td>0.02</td>
<td>0.003</td>
<td>63.8</td>
<td>409</td>
</tr>
</tbody>
</table>

Table 2. Basic statistics of ratios of methyl iodide (CH3I) to bromoform (CHBr3), trichloroethene (C2HCl3) to tetrachloroethene (C2Cl4), methyl iodide to isoprene (C5H8), methyl iodide to trichloroethene (C2HCl3), methyl iodide to tetrachloroethene, and methyl iodide to ethene (C2H4).
the convective activity of storms for many of the gases measured at the site during the 2-week period, leading to a decrease in mixing ratios observed.

3.1 Ratio Plot Analysis

Figure 1 shows the time series plots of the recorded values (pptv) of methyl iodide, bromoform, ethene, isoprene, trichloroethene and perchloroethene. Figure 2 shows the time series plots of the ratios of of trichloroethene to tetrachloroethene, methyl iodide to perchloroethene, methyl iodide to trichloroethene, methyl iodide to ethene, and methyl iodide to bromoform. Elevated values in the methyl iodide ratios to all tracer gases around June 27, 2013 (Figure 2-b-e) likely indicate a significant, proximal emission of methyl iodide. This peak corresponds to a slight peak in the ratio of trichloroethene to tetrachloroethene on June 27, likely indicating a possible anthropogenic influence to the methyl iodide levels.

The mean value for the ratio between methyl iodide and bromoform was 0.49 ± 0.33. This is greater than the mean value for the ratio of methyl iodide to bromoform measured by Sive et al. (2007) [2] at Thompson Farm during July and August, of 0.34 ± 0.27. In evaluating the Thompson Farm data using only continental levels of bromoform (≤ 3pptv), which is more comparable to bromoform levels observed at AppalAIR, the mean value for the methyl iodide to bromoform ratio at Thompson farm was 0.54 ± 0.33. The comparability of the mean value of ratios of methyl iodide to bromoform observed at AppalAIR to those observed at Thompson

Figure 1. Time series of mixing ratios of a) methyl iodide, b) bromoform, c) ethene, d) isoprene, e) trichloroethene, and f) perchloroethene from samples collected at AppalAIR during the sampling period of June 15, 2013 to July 2, 2013.
Farm, where there is a known significant terrestrial source of methyl iodide (Sive et al., 2007) [2], supports the case for terrestrial sources of methyl iodide in the greater Boone area. The variation of methyl iodide observed was less than that of bromoform (47% RSD and 51% RSD, respectively). In contrast, Sive et al. (2007)[2] observed a larger variation in methyl iodide levels than in bromoform levels, driven by the seasonal variations of methyl iodide from the terrestrial sources and that both methyl iodide and bromoform are coupled with marine influences (5). The sampling period for this study was only two weeks long, so seasonal variations could not be observed with the AppalAIR data.

The methyl iodide to tetrachloroethene ratios (Figure 2) had similar values, compared to those of trichloroethene to tetrachloroethene (0.09 ± 0.05 and 0.14 ± 0.14, respectively). This could suggest an anthropogenic source of methyl iodide, but it is likely fortuitous that the ratios are similar. Depending on source strength, the similar ratio values could indicate that methyl iodide has had approximately the same transport time in the atmosphere as trichloroethene and tetrachloroethene, as methyl iodide and trichloroethene have similar atmospheric lifetimes (5.2 days and 4-15 days, respectively).

While isoprene was anticipated to be a useful terrestrial marker from methyl iodide emissions, ultimately, it could not be used as a tracer for methyl iodide, as its strong diurnal cycle (Figure 3) drove the variation in the ratios between methyl iodide and isoprene. Additionally, ethane is a good marker for soil microbe emissions which would be useful to further assess the terrestrial

![Figure 2. Time series of ratios of a) trichloroethene to tetrachloroethene, b) methyl iodide to perchloroethene, c) methyl iodide to bromoform, d) methyl iodide to trichloroethene, and e) methyl iodide to ethene.](image-url)
source of methyl iodide. However, ethene levels observed in the area were found to be local and anthropogenically driven, based on the diurnal cycles observed. Ethene was found to have an inverse diurnal cycle to isoprene and concentrations peaked during the morning and evening, when the boundary layer is stable, which is a characteristic of local anthropogenic emissions.

### 3.2 Regression Plots

The regression plots of various tracers with methyl iodide are shown in Figure 4. The R² values for each trace gas in the correlations were all on the order of magnitude of 10⁻² or lower, meaning that there is no statistically significant correlation amongst these gases. Worth noting is that the methyl iodide to bromoform correlation was the strongest, with an R² value of 0.014 (see Figure 4). None of the plots in Figure 4 show a significant correlation with methyl iodide. What the low correlation values suggest is that a single significant source of methyl iodide can not be distinguished in this area for the time period, and is likely a result of the persistent storms during the study. This does not discount the methyl iodide to bromoform ratio and its reflection on a terrestrial source in this area, as this ratio is key to finding a robust marker based on the results from Thompson Farm.

Methyl iodide showed a slight positive correlation (slope) with all of the tracers except for tetrachloroethene (Figure 4-c). The equation for the correlation line between methyl iodide and tetrachloroethene was \( y = -8.5e^{-4}x + 0.57 \). The
negative correlation between these two species suggests low correlation. This low correlation suggests little or no relationship between the methyl iodide levels observed in the area and emissions of tetrachloroethene (anthropogenically sourced). The highest slope found was in the equation for the line between trichloroethene and tetrachloroethene (Figure 4-e), which was $y=0.034x+0.5024$. This slope shows a positive correlation between the two gases, suggesting similar emission patterns. The lower correlation values shown for these gases ($r^2=0.072$) is characteristic of areas that are far from an emission source of these species, such as Boone. The high variation in trichloroethene, due to its lower and variable (4-15 days) atmospheric lifetime, drives the correlation down as the travel time increases.

### 3.3 Wind Direction

The wind rose plot of methyl iodide (Figure 5-a) indicates that the high levels of methyl iodide (1.5 pptv and above) were observed during westerly wind flow. Bromoform levels were similar.

![Figure 4](image)

**Figure 4.** Correlation plots of a) methyl iodide to trichloroethene ($R^2=0.0024$, $y=0.021x+0.55$, $n=409$); b) methyl iodide to ethene ($R^2=0.0043$, $y=1.4e^{-4}x+0.54$, $n=409$); c) methyl iodide to tetrachloroethene ($R^2=0.00021$, $y=-8.5e^{-4}x+0.57$, $n=409$); d) methyl iodide to bromoform ($R^2=0.014$, $y=0.0793x+0.47$, $n=401$); and e) trichloroethene to tetrachloroethene ($R^2=0.072$, $y=0.034x+0.5024$, $n=363$).
between westerly and easterly wind flow events. The higher levels of methyl iodide from the westerly winds correlate to wind flow patterns in the area, as most winds in Boone come from the southwest. Bromoform levels observed appear consistent from all directions.

### 4.0 Conclusions

The similarities in methyl iodide to bromoform ratios observed at AppalAIR to those observed at Thompson Farm (with continental bromoform levels) support a terrestrial source of methyl iodide in the region. Thompson Farm is in close proximity to the coast, while Boone is an inland site, so the comparability of these ratio values are a very significant indication of terrestrial source(s) of methyl iodide in the Boone area.

Low R² values calculated for the regressions between methyl iodide and its tracer gases indicate that, of the sources analyzed with the tracer gases used, a single significant source cannot be suggested from the data gathered in the two week period.

Wind rose plots showed higher levels of methyl iodide during westerly wind flows, which follows local meteorology patterns (winds out of the south and west). This indicates that some methyl iodide observed in the Boone area is not from local sources, as higher values follow major wind patterns.

The spike in methyl iodide ratio levels across the board around 27 June, 2013 indicates a proximal emission of methyl iodide, and the corresponding spike in the ratio between trichloro-

![Figure 5. Wind rose plots of a) methyl iodide, b) isoprene, c) ethene, d) trichloroethene, and e) bromoform mixing ratios (pptv) represented on the axes.](image-url)
ethene and perchloroethene around the same time suggests a strong anthropogenic influence. Weather conditions at the site during the sampling period were not ideal for measuring concentrations of compounds representative of their emission rates from different sources. There were frequent and intense rainfall events throughout June and July, 2013, ultimately resulting in the mixing and dilution of air masses with clean, free tropospheric air, making it difficult to assess various sources of methyl iodide.

Future observations of methyl iodide in the area should be done on the time scale of at least a year. The sampling period of this study was not long enough to adequately elucidate the main sources of methyl iodide in the area, especially with the frequent rain events during that time period. A longer sampling period would effectively negate the effects of weather events such as this one. Also, seasonal variability of the compounds analyzed can be observed with a year-long sampling period.

Acknowledgments
I wish to thank the Environmental Science program and the Office of Student Research at Appalachian State University for funding during this investigation.

References