High resolution analyses reveal elevated sea-to-air methane fluxes in localized areas in the Gulf of Mexico

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Key Points:

- Localized areas of highly elevated methane concentration were detected that were previously not observable with available methods.

- The use of the new vacuum extraction technique for measuring sea surface methane concentration allowed for the observation of methane sea-to-air flux ranging from 0.01 to 620.02 µmol m⁻² day⁻¹, which is an order of magnitude greater than most previous flux estimates from hydrocarbon seep fields.

- There was no three-dimensional distance relationship between the top of methane bubble plumes and sea surface methane concentration suggesting an unknown alternative source for these surface water features.
Abstract
The sea-to-air flux of methane was measured using a new, high-temporal resolution technique in the northern Gulf of Mexico above previously known methane seeps. The technique vacuum extracts dissolved gases from seawater, enabling the nearly instantaneous measurement of the true dissolved concentration of the gases during transects by a research vessel. This high-resolution technique discovered previously unknown, localized regions of elevated methane concentration, not detectable with previous techniques such as the equilibrator method and discrete sampling. The resulting fluxes were up to an order of magnitude higher than most previous measurements at the same hydrocarbon seep sites and at the higher end of previously reported emissions globally. Surface methane concentration varied from 3.97 to 60.44 nM during these investigations with high temporal variability within and between days. The average methane fluxes between the three sites varied from 13.06 to 102.27 and the total range of methane flux varied from 0.01 to 620.02 µmol m⁻² day⁻¹. The integrated methane fluxes were 3742 for DWH (36 km²), 552 for Gloria Dome (36 km²), and 1700 to 3916 mol day⁻¹ at MC118 (31 to 64 km²). In addition, the locations of the methane bubble emissions from the seafloor were mapped with a hull-mounted Kongsberg EM 302 Multibeam Echosounder. The locations and height above the seafloor of the identified bubble plumes were correlated with the newly identified surface water features. Unfortunately, the results of this correlation analysis were inconclusive, and since numerous other sources of methane could produce these localized features the source of methane to these regions remains unknown. Further research that incorporates methane isotopic data to fingerprint the source as well as three-dimensional ocean circulation models is necessary to identify the source of these methane features. Nonetheless, these newly identified localized features could characterize the oceans as a more substantial source of methane to the atmospheric budget than previously thought.

1 Introduction
Concern over increasing atmospheric concentrations of the greenhouse gases methane and carbon dioxide has motivated investigations to determine the atmospheric budgets of these gases and predict the potential environmental and societal impacts from these increasing concentrations. A current uncertain contributor to the atmospheric methane budget is the reservoir of methane clathrate hydrates. Methane hydrates are molecules of methane that freeze in ice structures under specific pressure and temperature conditions between 600 to 3000 m depth in the seafloor (Reeburgh 2007). The methane can be thermogenic in origin as it migrates towards the seafloor through fault systems from geologic reservoirs or biogenic as it is produced microbially in anoxic sediments (Sassen et al. 1993). Milkov [2004] estimated that methane hydrate systems contain 500 to 2500 Gt of carbon globally. Gas can vent from methane hydrates when temperature changes occur over seafloor hydrate outcrops due to ocean circulation (MacDonald et al. 2002). In the water column, these bubbles of gas can dissolve and/or be metabolically oxidized by microbes to biomass and CO₂ (Valentine et al., 2001). If not oxidized, this methane can reach the sea surface and then increase the flux of methane to the atmosphere through air-sea exchange (Reeburgh 2003).

Within current uncertainty bounds methane hydrates are estimated to contribute 5 Gt C, or 1%, to the sources of atmospheric methane (Ciais et al. 2013; Reeburgh 2007). However, it was hypothesized that during the Paleocene Eocene Thermal Maximum (55 mya) that the large
carbon isotopic excursion observable in foraminifera tests in the rock record and the coincident warming of Earth’s surface by 5 to 8°C was due to the dissociation of the isotopically light methane hydrate reservoir (Dickens 2011). This dissociation ultimately increased the mass of atmospheric carbon and exacerbated surface warming. The added mass to the atmosphere may have consisted partially of methane, but most of the reservoir reached the atmosphere as CO₂ due to methane’s instability to microbial oxidation (Archer 2007). Concern that this event could happen again today has motivated extensive study of hydrocarbon seep fields and expeditions to measure the methane fluxes to the atmosphere above these seep fields.

Thus far, there have been three studies estimating methane flux in the Gulf of Mexico. Hu et al. [2012] and Yvon-Lewis et al. [2011] measured methane fluxes of 4.19 to 86.1 and 0.055 to 1.83 µmol m⁻² d⁻¹ respectively using Weiss-type equilibrators. In contrast to these two estimates, Solomon et al. [2009] reported a much larger range of 200 to 10,500 µmol m⁻² d⁻¹ from three plumes in the Gulf of Mexico by discrete sampling via a remotely operated vehicle (ROV), suggesting that less oxidation of methane was occurring than previously thought. Previous studies using Weiss-type equilibrators could have missed these localized plumes detected by ROV due to the long equilibration time of methane (Johnson 1999).

We determined the locations of natural seeps and the location of their plumes in the water column with a Kongsberg EM 302 Multibeam Echosounder mounted on the hull of the E/V Nautilus, and we measured sea surface methane concentration at three sites in the GOM using a new technique developed by Kessler et al. [2016, in preparation]. The first site investigated was the Deepwater Horizon (DWH) oil spill site, which has no natural seepage. Next the natural seep sites Gloria Dome and MC118 were investigated. The new technique vacuum-extracts trace gases from seawater, thereby eliminating the time required for dissolved gases to come to equilibrium with a gaseous headspace, thus enabling a much higher temporal resolution than the equilibrator and discrete sampling methods. We used this data to quantify the sea-to-air methane flux at each site. Finally, we investigated the spatial relationship between surface water methane concentration and the locations of methane plumes in the water column above the survey sites. We hypothesized that surface data points closer to the peaks of the bubble plumes would be higher in concentration. This result would indicate that a minimal amount of deflection of the methane dissolving in the water column occurs and that this simple distance relationship could be used to link methane in the water column and at the surface.

2 Methods

2.1 Measuring surface water CH₄ concentration with a vacuum extraction system

The new technique for measuring the surface water methane concentration uses a vacuum extraction system (VES) to remove trace gases from the water and pumps them into a Cavity Ring-down Spectrometer (CRDS) at a high sampling frequency. This is a significant improvement over Weiss-type equilibrators, in which long equilibration times for gases with low solubility such as methane (Johnson, 1999) may preclude the detection of high spatial variation of dissolved methane over a survey area and thus produce inaccurate integrated flux estimates.
Surface water was pumped into the VES and filtered before flowing into a manifold to deliver the water to the vacuum extraction system, two Weiss-type equilibrators (to compare against the VES measurements), and another output for discrete samples. The VES extracted the trace gases from the water as the water flowed through a membrane contactor, and the flow rate of the water was measured. Water was removed from the gas stream, and then the temperature, pressure, and flow rate of the gas were measured before the gas was delivered to the CRDS. The CRDS reports concentration of gas in the sample in parts per million (ppm).

Molar concentration of these gases in the surface water was calculated as follows. First, once the volumetric flow rate \( (Fr) \) of the water through the membrane contactor, the total volumetric flow rate of all the gases extracted from the water, the vacuum extraction efficiency (VEE) for the analyte, and the concentration of the analyte in ppm are known, the volumetric concentration of the analyte \( (V_c) \) can be calculated:

\[
V_c = \frac{t_a}{t_w} = \left( \frac{VEE \cdot Fr_a \cdot \text{ppm}_a}{10^6} \right) / Fr_w
\]

The subscripts “a” and “w” denote the analyte and water respectively. Once \( V_c \) is known, the molar concentration, \( M_c \), can be determined using the ideal gas law \( PV = nRT \), where \( R \) is the ideal gas law constant, \( n \) is the moles of gas, \( V \) is the volume of the gas, \( P \) is the pressure of the gas, and \( T \) is temperature of the gas before being analyzed by the CRDS:

\[
M_c = \frac{mol_a}{t_w} = \frac{PV_c}{RT}
\]

Because the VEE is not unity for methane, discrete water samples are used to calibrate the VES. A simple linear calibration curve between the discrete samples and the VES concentrations was used to determine the VEE.

### 2.2 Equilibrator method for measuring surface water CH\(_4\) concentrations

For part of the last day of the survey, only the Weiss-type equilibrators were used to measure sea surface methane concentration. In an equilibrator, water is pumped into a chamber that contains a headspace and the dissolved gases are allowed to reach equilibrium between the gas phase and the aqueous phase. The time to reach full equilibration is proportional to the solubility of the gases. A first order closed system model of this equilibration process gives rise to the concentration of the headspace gas as a function of time:

\[
C_e(t) = \left( C_{ei} - \frac{C_w}{\alpha} \right)e^{-\frac{t}{\tau}} + \frac{C_w}{\alpha}
\]

where \( C_e \) is the headspace gas concentration, \( C_{ei} \) is the initial headspace gas concentration in disequilibrium, \( C_w \) is the concentration of the gas in the aqueous phase being pumped into the equilibrator, \( \tau \) is the time constant, and \( \alpha \) is the Ostwald solubility coefficient (Johnson 1999). Samples of headspace gas from the primary equilibrator were pumped into the CRDS for analysis.
2.3 Air-sea flux calculations

To measure atmospheric concentration \( C_{atm} \) of and methane, air was pumped from off the bow of the vessel into the manifold and dried by a glass bead trap and Nafion dryer before being delivered to the CRDS for analysis. Once \( C_w \) is known and \( C_{atm} \) is determined, the following equation from Wanninkhof et al. [2014] can be used to calculate the flux:

\[
F = k_w (C_w - C_{atm})
\]

(4)

where \( F \) is the flux in \( \mu \text{mol m}^{-2} \text{d}^{-1} \) and \( k_w \) is the gas transfer velocity (m d\(^{-1}\)), as defined by Wanninkhof et al. [2014]:

\[
k_w = 0.27 u_{10}^{0.2} \left( \frac{Sc}{660} \right)^{-0.5}
\]

(5)

where \( Sc \) is the Schmidt number and \( u_{10} \) is the wind velocity ten meters above sea level. Flux is highly dependent on the wind velocity, which stresses the air-sea interface and creates turbulence in the surface.

2.4 Bubble plume data collection

The locations of seeps and their methane bubble emissions from the seafloor were mapped with a hull-mounted Kongsberg EM 302 Multibeam Echosounder.

2.4 Spatial analysis of the data

ESRI ArcMap and ArcScene 10.3.1 were used to perform spatial analyses on the data.

3 Results

3.1 Heterogeneous sea surface methane concentration with temporal variability was observed
Figure 1. a) Survey site. b) Cruise tracks from all five days of the cruise data and the three study sites. Points \((n = 16890)\) are labeled by surface water methane concentration in 10 bins using the Natural Breaks (Jenks) method, ranging from 4.0 to 60 nM. c) Close up of MC118 showing the four major seep locations (A, B, C, D), the locations of their resultant bubble plumes in the water column, and the surface points.
Elevated surface seawater methane concentrations relative to the typical mixed layer maximum concentration of ~5 nM were observed at MC118 and the DWH site but not at Gloria Dome. C2, C3, and C4 hydrocarbons with average concentrations of 0.47, 0.30, and 0.27 nM respectively throughout the cruise were also detected at the surface above the natural seep sites, indicating that the hydrocarbons were at least partially of geologic origin (Bernard et al., 1976). High spatial variability was observed in surface methane concentration and sea-to-air flux (fig. 1 and fig. 2). Table 1 summarizes the range of values observed at each location and also gives the total flux calculated from an inverse distance weighted interpolation (grid cell size = 30 m). Atmospheric methane concentration fluctuated between 1.83 ppm to 1.89 ppm, which was notably lower than the upper bound of atmospheric concentration of 4.01 ppm observed previously by Hu et al. [2012].
Table 1. Summary of ranges of surface methane concentration and integrated methane flux during the survey.

<table>
<thead>
<tr>
<th>Sampling period</th>
<th>Location</th>
<th>Surface water CH$_4$ range (nM)</th>
<th>Sea-to-air CH$_4$ flux (µmol m$^{-2}$ d$^{-1}$)</th>
<th>Average flux from points (µmol m$^{-2}$ d$^{-1}$)</th>
<th>Average flux interpolated (µmol m$^{-2}$ d$^{-1}$)</th>
<th>Area (km$^2$)</th>
<th>Total flux over area (mol d$^{-1}$) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/16/15</td>
<td>DWH site</td>
<td>4.96 – 28.15</td>
<td>7.64 – 289.66</td>
<td>102.27</td>
<td>103.89</td>
<td>36.02</td>
<td>3741.74</td>
</tr>
<tr>
<td>4/17/15</td>
<td>Gloria Dome</td>
<td>4.05 – 7.99</td>
<td>0.01 – 93.42</td>
<td>16.63</td>
<td>15.36</td>
<td>35.96</td>
<td>552.31</td>
</tr>
<tr>
<td>4/18/15</td>
<td>MC118</td>
<td>5.29 – 26.09</td>
<td>0.00 – 134.85</td>
<td>13.06</td>
<td>11.78</td>
<td>179.46</td>
<td>2114.06</td>
</tr>
<tr>
<td>4/19/15</td>
<td>MC118</td>
<td>4.46 – 22.39*</td>
<td>0.05 – 321.94*</td>
<td>58.34</td>
<td>54.53</td>
<td>31.18</td>
<td>1700.08</td>
</tr>
<tr>
<td>4/20/15 all</td>
<td>MC118</td>
<td>3.97 – 23.69</td>
<td>0.01 – 389.13</td>
<td>42.87</td>
<td>61.18</td>
<td>64.01</td>
<td>3916.34</td>
</tr>
<tr>
<td>4/20/15 part 1$^a$</td>
<td>MC118</td>
<td>7.71 – 11.41</td>
<td>5.79 – 47.98</td>
<td>20.59</td>
<td>24.86</td>
<td>12.90</td>
<td>320.63</td>
</tr>
<tr>
<td>4/20/15 part 2</td>
<td>MC118</td>
<td>3.97 – 23.69</td>
<td>0.01 – 389.13</td>
<td>53.33</td>
<td>70.79</td>
<td>52.37</td>
<td>3707.15</td>
</tr>
</tbody>
</table>

* The weather excursion during this day contained the highest surface methane concentration (58.97 nM) and flux (580.69 µmol m$^{-2}$ d$^{-1}$), but these maxima were far away from MC118 (see fig. 2A).

$^a$ Part 1 (5:48am to 8:09am) is a shorter time interval than part 2 (8:09am to 2:13 pm), thus the total flux is much smaller.

$^b$ Calculated as average flux interpolated $\times$ area.
The vacuum extraction system allowed for the observation of localized areas of highly elevated methane concentration. These localized features had not been observed in previous cruises. Weiss equilibrators on the cruise were able to detect broad plumes of methane on the last day of the cruise. Fig. 2 shows the complete time series of the data with a selection of concentration spikes ranging in intensity labeled 1 – 10, which Table 2 provides more detail on. This table provides the beginning, peak, and end times and concentrations of the spikes as well as the distance over which the spike occurred, i.e. the line integral of the cruise track over the spike. \( \Delta [\text{CH}_4] \) shows roughly how much the concentration changed over the spike. A small spike (3) of 1.71 nM occurred over the Gloria Dome site persisting for an hour and 12.66 km, while a very ephemeral spike (5) of 16.83 nM occurred at MC118 lasting only 12 minutes and persisting for only 2.5 km. The greatest spike (8) of change in concentration of 44.88 nM occurred during a bad weather excursion in which the vessel travelled southwest of MC118. The vessel did not go all the way over the plume but instead doubled back, which can be seen in fig. 2a where there is a long dark-red colored excursion. The last spike (10) shows a broad, long spike that was captured by the equilibrators between MC118 and the DWH site. (4) also shows a spike occurring in transit between Gloria Dome and MC118, demonstrating the existence of concentration spikes outside of the immediate areas of the seeps investigated. These could be occurring due to transport of the plumes from the seep sites investigated or they could be coming from one of the many other seeps in the region. The minimum non-zero flux was \( 3.00 \times 10^{-3} \) and the maximum was 389.13 \( \mu \text{mol m}^{-2} \text{d}^{-1} \), excluding the bad weather excursion in which a flux of 620.02 \( \mu \text{mol m}^{-2} \text{d}^{-1} \) was observed.

Another noteworthy feature in the data was that as the vessel circled around the seep sites, there were often different values of surface methane concentration observed at approximately the same latitude/longitude; thus there was high temporal variability in concentration and flux. This variability was particularly evident at MC118, which was surveyed for three days (fig. 3). The overlapping cruise tracks at MC118 reveal that a location’s methane concentration could change significantly in the same day or between days. There are numerous locations in fig. 3 where there are clearly two or three data points in the same location but with differing concentration measurements.
Figure 2. a) Time series of data. Blue points show sea-to-air methane flux and orange points show surface water methane concentration. The DWH site was sampled first on 4/16/2015, Gloria Dome was sampled on 4/17/2015, and MC118 was sampled for the remainder of the cruise through 4/20/2015. Labels 1 – 10 are a selection of methane concentration spikes. b) Close ups of spikes 1 and 2. c) Close ups of spikes 5, 6 and 7.
Table 2. Beginning, peak, and end times and concentrations of notable methane plumes observed. Methane concentration is in nmol L\(^{-1}\).

<table>
<thead>
<tr>
<th>Plume #</th>
<th>Sampling period</th>
<th>Location</th>
<th>Beginning [CH(_4)] and time</th>
<th>Peak [CH(_4)] and time</th>
<th>Ending [CH(_4)] and time</th>
<th>(\Delta [\text{CH}_4])^a</th>
<th>Duration of plume (hr:min)</th>
<th>Length of plume (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4/16/15</td>
<td>DWH</td>
<td>19.3, 19:33</td>
<td>24.8, 19:41</td>
<td>19.09, 19:45</td>
<td>5.61</td>
<td>00:12</td>
<td>2.11</td>
</tr>
<tr>
<td>4</td>
<td>4/17/15</td>
<td>Transit from Gloria Dome to MC118</td>
<td>5.67, 10:25</td>
<td>12.2, 12:31</td>
<td>5.3, 13:17</td>
<td>6.72</td>
<td>02:52</td>
<td>43.65</td>
</tr>
<tr>
<td>5</td>
<td>4/18/15</td>
<td>MC118</td>
<td>10.43, 5:07</td>
<td>26.09, 5:15</td>
<td>8.10, 5:19</td>
<td>16.83</td>
<td>00:12</td>
<td>2.50</td>
</tr>
<tr>
<td>6</td>
<td>4/18/15</td>
<td>MC118</td>
<td>10.04, 5:55</td>
<td>15.69, 6:06</td>
<td>10.27, 6:16</td>
<td>5.54</td>
<td>00:21</td>
<td>4.04</td>
</tr>
<tr>
<td>7</td>
<td>4/18/15</td>
<td>MC118</td>
<td>6.74, 8:45</td>
<td>10.72, 9:41</td>
<td>6.34, 9:50</td>
<td>4.18</td>
<td>01:05</td>
<td>20.36</td>
</tr>
<tr>
<td>8(^b)</td>
<td>4/19/15</td>
<td>Southwest of MC118</td>
<td>14.65, 14:19</td>
<td>60.44, 15:31</td>
<td>16.48, 16:26</td>
<td>44.88</td>
<td>01:53</td>
<td>33.70</td>
</tr>
<tr>
<td>9</td>
<td>4/19/15</td>
<td>MC118</td>
<td>16.71, 18:18</td>
<td>22.39, 19:00</td>
<td>16.7, 19:30</td>
<td>5.685</td>
<td>01:12</td>
<td>15.54</td>
</tr>
<tr>
<td>10</td>
<td>4/20/15(^c)</td>
<td>Transit from MC118 to DWH</td>
<td>4.32, 12:27</td>
<td>29.63, 15:35</td>
<td>10.44, 17:20</td>
<td>22.25</td>
<td>04:53</td>
<td>41.84</td>
</tr>
</tbody>
</table>

\(^a\) \(\Delta [\text{CH}_4] \approx [\text{CH}_4]_{\text{peak}} - \text{average}([\text{CH}_4]_{\text{begin}}, [\text{CH}_4]_{\text{end}})\)

\(^b\) Bad weather excursion.

\(^c\) Sampled via equilibrator rather than the VES.
Figure 3. a) Close up of temporal variability in sea surface methane concentration over the three survey days at MC118. A, B, C and D denote seep sites. b) Data from April 20th, 2015 shows that there was intra-day temporal variability in methane concentration as well. Note the differing color scales.
The use of the multibeam echosounder at MC118 determined the locations of the seep sites as well as the general locations of their bubble plumes in the water column, but the multibeam data were too low resolution at Gloria Dome to pinpoint these features. At MC118, four main seep sites labeled A – D were identified (fig. 1C), which each have a depth of approximately 889 mbsl. The tops of the methane plumes were at variable heights: $A_{\text{top}} = 314$, $B_{\text{top}} = 517$, $C_{\text{top}} = 451$, and $D_{\text{top}} = 608$ mbsl. The locations of the tops of these plumes were used to explore the spatial relationship between the plumes and the heterogeneous surface methane concentrations (see 3.3).

3.2 Surface concentration interpolation and flux

Although the VES was able to attain a new level of temporal resolution, the study region was still too vast to comprehensively sample within the span of a few days. Thus, surface water methane concentration and sea-to-air methane flux were interpolated using an inverse distance weighting method (fig. 4 and 5 respectively). For MC118, the interpolations help communicate that there was temporal variability from day to day. MC118 on the first day showed very low concentrations, leading to a small total daily flux comparable to the Gloria Dome survey (Table 1, last column), but its concentration climbed on the second day to almost triple the total daily flux. The third day was divided into two parts, in which part 1 was from 5:48am to 8:09am and part 2 was from 8:09am to 5:23pm, to show an example of the intra-day temporal variability. Concentration was low during part 1 and then increased dramatically in part 2, causing many of the same latitude/longitude locations to have multiple concentration values as was discussed earlier. Presumably dividing April 20th 2015 into two parts would help make the correlation between three-dimensional distance and surface methane concentration more robust (see 3.3). A correlation was not made between three-dimensional distance and flux because the flux is more erratic and highly dependent on wind speed, and thus did not linearly match the surface methane concentration. Average methane flux for each sampling interval was calculated based on the original data points and the interpolated data points; daily flux extrapolated regionally was also calculated (Table 1).
Figure 4. IDW interpolation of surface water methane concentration in the three major study sites of the cruise. d) and e) show the day 4/20/15 divided into part 1 (5:48am to 8:09am) and part 2 (8:09am to 2:13 pm) respectively.
Figure 5. IDW interpolation of sea-to-air methane flux for each region.
3.3 Correlation between concentration and 3D distance to water column plumes

While investigating the complete methane dynamics of these sea surface features was beyond the scope of this thesis, we did a spatial analysis between MC118’s four major seep sites’ (A, B, C, and D) water column methane plumes and the surface methane concentration with a simple correlation between 3D distance from the top of the plume and concentration. A script was created in ArcScene to automate the measurement of the 3D distance between the top of each water column plume and the surface points within a specified 3D radius of the top of the plume. Because of the wide range in the values of the depths of the tops of the plumes with a maximum depth of 608 mbsl at plume D, a search radius of 700 m from each plume’s top was selected to ensure that surface data points were within range. Fig. 6 shows the results from this analysis at MC118.
Figure 6. Correlation between three-dimensional distance from the top of each plume (A – D) to each point within a 700 m radius of the top of the plume and the surface methane concentration at each point. Each row (1–4) is a different day, with the last two rows being part 1 and part 2 of 4/20/2015 respectively.
4 Discussion

4.1 Performance of the VES and comparison to previous studies

The VES was able to detect localized areas of highly elevated methane concentration that had not been previously detectable with the equilibrator method. The implication of this new level of temporal resolution is that this new technique will be able to refine the contribution hydrocarbon seeps make to the atmospheric methane budget. As shown in the maps, the cruise tracks can be clearly seen with this technique and the high sampling frequency allowed the VES to capture subtle concentration gradients and concentration spikes. Among the three locations and the transit paths between them, this study found a range in surface methane concentration of 3.96 to 60.44 and flux of $3.00 \times 10^{-3}$ to $620.02 \mu\text{mol m}^{-2}\text{d}^{-1}$. The flux in this study was higher than Hu et al.’s values of 4.19 to 86.1 $\mu\text{mol m}^{-2}\text{d}^{-1}$ by an order of magnitude but lower than Solomon et al.’s [2009] 200 to 10,500 $\mu\text{mol m}^{-2}\text{d}^{-1}$ measurements made by ROV. The integrated fluxes were 3742 for DWH (36 km$^2$), 552 for Gloria Dome (36 km$^2$), and 1700 to 3916 mol day$^{-1}$ at MC118 (31 to 64 km$^2$). Our measurements at MC118 were significantly higher than Hu et al.’s 0.744 to 300 mol d$^{-1}$, although their survey coverage at MC118 was much smaller (0.06 to 15.15 km$^2$). Nonetheless, doubling the area and the flux of Hu’s upper bound leads to a flux of 600 mol d$^{-1}$, a third of the lower bound we observed with vacuum extraction system.

Sites that could be compared in more detail directly to previous studies using the equilibrator method were the DWH site and MC118 done by Yvon-Lewis et al. [2011] and Hu et al. [2012] respectively. At the DWH site a flux range of 7.64 to 289.66 was found in this study while the previous study found a range of -0.05 to 1.83. A similarly large discrepancy was found at MC118, where the previous equilibrator study found a flux range of 7.75 to 19.8 and this study found a range of 0.01 to 389.13 $\mu\text{mol m}^{-2}\text{d}^{-1}$. With respect to averages, the average at DWH measured via equilibrator was 0.02 while this study found an average flux of 102.27 $\mu\text{mol m}^{-2}\text{d}^{-1}$. At MC118, this difference in averages was not as well pronounced; the average was 11 in the equilibrator study and 38 $\mu\text{mol m}^{-2}\text{d}^{-1}$ in this study. Despite this difference in averages, there were still a significant amount of flux measurements greater than 100 $\mu\text{mol m}^{-2}\text{d}^{-1}$ observed at MC118: 1242 out of 8496 data points exceeded this threshold.

There were broad, long lasting plumes but also extremely short ones that lasted for only 12 minutes long such as plumes (2) and (4); these short duration peaks were not controlled by weather. With regards to previous flux studies, concentration spikes such as the ones observed during this survey could have easily been missed during previous studies using Weiss equilibrators since methane can have an equilibration time of 11 to 12 minutes (Gulzow et al. 2011; Hu et al. 2012), although Kodovska Garcia-Tigreros et al. [2016] found an equilibration time of 4.53 minutes. Unfortunately even with the new technique it is impossible to know if an entire plume was captured due to the fact that the vessel can only travel in one direction at a time, and the high temporal variability in the magnitude of surface methane concentrations in a given location (fig. 3) further frustrates the task of fully capturing a methane plume’s three-dimensional extent. Nonetheless, the VES allowed for very accurate cross sections of these plumes. The accuracy of this new technique warrants that previous measurements of sea-to-air methane flux over other hydrocarbon seeps be revisited to refine the contribution these sites
make to the atmospheric methane budget, as an order of magnitude increase in the flux range was detected with this new technique.

### 4.2 3D distance versus concentration correlations

The spatial correlation results for all four plume peaks overall showed that there was no relationship between the location of the top of each plume in the water column and the surface methane concentration measured by the VES. There were no obvious concentration spikes closer to the peaks counter to what was hypothesized. In most cases, although concentrations were always elevated relative to background level, this elevated concentration stayed constant or fluctuated within a constant interval, rather than radially decreasing linearly or quadratically with 3D distance as anticipated. There were a number of factors that led to this null result which are discussed below.

What complicated a simple 3D distance-concentration correlation was that it is unknown in fine detail what happens to the methane plumes in the upper few hundred meters of the water column. It is obvious that perfect vertical transport does not occur and this reality manifests itself in the null result; in general horizontal transport in the ocean is much faster than vertical transport (Sarmiento and Gruber, 2006). If there were perfect vertical transport, there would be concentration spikes directly above the top of each plume with radially attenuated concentration. However, horizontal deflection of the water column plumes occurs, so it is possible that the elevated concentrations of methane observed at the DWH site and MC118 could have been transported from adjacent seep fields or aerobically produced in situ (Karl et al. 2008; Metcalf et al. 2012; Carini et al. 2014). If so, the bubble plumes at Gloria Dome and MC118 would be decoupled from the surface concentration observed. Thus, it is reasonable that the DWH site had such a large flux despite that it is not a seep field and flux at Gloria Dome was minimal.

Another component that precluded a strong singular relationship in the correlation was that there was high temporal variability in the surface methane concentration measured between (fig. 3a) and within days (fig. 3b), and so at a given surface location there were often values that differed significantly as the vessel made multiple passes over MC118. The lack of a one-to-one relationship between location and concentration led to bifurcating or multiple disparate trends, e.g. fig. 5 graphs A1, A2, B4, and C1, as each disparate trend shows a different pass through MC118 where concentration changed. Concentration could also change on a different side of the plume since two points could have the same radial distance from the peak but be in different locations.

### 5 Conclusion

The vacuum extraction system was able to detect localized plumes of methane at MC118 and the DWH site due to its high temporal resolution. Thus, this measurement technique is a significant improvement over the Weiss-type equilibrators. This study provides an updated and more accurate estimate of methane flux range that was larger by an order of magnitude than previous equilibrator studies. The accuracy of this new technique warrants that other seep sites be revisited so that the total contribution to the methane atmospheric budget from hydrocarbon seeps can be further constrained, and it is likely that the ocean is a greater source of methane to
the atmosphere than previously thought. The survey size of this study was relatively small compared to the entire Gulf of Mexico, but the number of localized features observed on this survey suggests that there may be many more throughout the Gulf.

It is evident that three-dimensional distance versus concentration correlations are not sufficient to analytically probe the dynamics of the water column methane plumes. There was overall no relationship between the two, which is a manifestation of the complexity of the controls on methane distribution in the water column and at the surface. There was high temporal variability within and between days in the surface water methane concentration due to complex oceanic circulation in the region, many seep sites with dynamic emission rates, as well as other dynamic factors such as microbial methane oxidation and aerobic methane production. The lack of a relationship between three-dimensional distance and concentration suggests that elevated concentrations of methane over a seep site may not be connected to the seeps below and instead may be transported from adjacent seep sites or produced in-situ. Further research is needed to rigorously explain the spatial relationship as well as determine if the particular seep sites and the dissolved methane above them at the surface are truly connected. This future research to determine the true sources of these localized areas of elevated methane concentration should incorporate a three-dimensional circulation model, the magnitude and locations of all seep sources of interest, isotopic data of the methane from the seep sources and the surface, and other factors that impact methane concentration in the water column.

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7 References


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