

Measurements of $\delta^{13}\text{C}$ in CH_4 and Using Particle Dispersion Modeling to Characterize Sources of Arctic Methane within an Air Mass

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Key Points

Northern Russian wetlands can contribute notably to methane in the remote Arctic.

Isotopic bulk signature of $^{13}\text{CH}_4$ determined in air mass with enhanced methane observed over the Arctic Sea.

Isotopic source signature for $^{13}\text{CH}_4$ bulk input from northern Russian wetlands and potential shallow shelf region offshore is < -70 ‰.

Abstract

A stratified air mass enriched in methane (CH_4) was sampled at ~600 m to ~2000 m altitude, between the north coast of Norway and Svalbard as part of the MAMM (Methane in the Arctic: Measurements and Modelling) campaign on board the UK's BAe-146-301 Atmospheric Research Aircraft (ARA). The approach used here, which combines interpretation of multiple tracers with transport modeling, enables better understanding of the emission sources that contribute to the background mixing ratios of CH_4 in the Arctic. Importantly, it allows constraints to be placed on the location and isotopic bulk signature of the emission source(s). Measurements of $\delta^{13}\text{C}$ in CH_4 in whole air samples taken whilst traversing the air mass identified that the source(s) had a strongly depleted combined $\delta^{13}\text{C}$ CH_4 isotopic signature of $-70 (\pm 2.1) \text{‰}$. Combined NAME (Numerical Atmospheric-dispersion Modelling Environment) and inventory analysis indicates that the air mass was recently in the planetary boundary layer over northwest Russia and the Barents Sea, with the dominant source of methane being from wetlands in that region.

Index Terms and Keywords

0368 Troposphere: constituent transport and chemistry

0322 Constituent sources and sinks

Emissions, arctic, wetlands, methane, fluxes

1. Introduction

Methane (CH_4) is well known to be a powerful greenhouse gas, with approximately 28 times the global warming potential of carbon dioxide over a 100 year period, and is the second most important anthropogenic greenhouse gas in terms of radiative forcing [Denman *et al.*, 2007; Myhre *et al.*, 2013]. The IPCC [Denman *et al.*, 2007] has previously highlighted that terrestrial carbon flux processes are complex with high uncertainties and that continued investigation to understand the role of CH_4 in the atmosphere is vital. It is especially important to understand CH_4 sources in the Arctic as temperatures there are rising twice as fast as global averages and are expected to continue to rise [Parmentier *et al.*, 2013]. The increasing temperatures could destabilize reservoirs of CH_4 from terrestrial and oceanic permafrost and marine hydrates [O'Connor *et al.*, 2010], as well as leading to increased fluxes from Arctic wetlands.

Sources of CH_4 to the Arctic are dominated in summer by wetland emissions [Kirschke *et al.*, 2013]. Wetlands globally provide a CH_4 flux to the atmosphere of $142\text{--}208 \text{ Tg yr}^{-1}$ out of a total of $\sim 550 \text{ Tg yr}^{-1}$ from all CH_4 sources, but for the Arctic budget it is less clear, as recent work has struggled to constrain the wetland contributions spatially due to inconsistencies comparing ground mapping and remote sensing of wetlands [Melton *et al.*, 2013]. Older estimates put the total emission from wetlands above 50°N as 10–15 % of the total global wetland contribution [Christensen *et al.*, 1996]. Other sources of CH_4 within the Arctic include the tundra permafrost melt [Wille *et al.*, 2008], sub-sea permafrost and hydrate degradation [Shakhova *et al.*, 2014; Vonk *et al.*, 2012; Westbrook *et al.*, 2009], Arctic ocean surface waters [Kort *et al.*, 2012], natural geological CH_4 seepage [Walter *et al.*, 2012] and anthropogenic emissions such as fugitive emissions from oil and gas platforms. Sources such

as CH₄ hydrates are not as yet thought to be contributing significantly to the Arctic CH₄ budget (e.g. *Kirschke et al.* [2013] attribute 6 Tg yr⁻¹ globally from hydrates), but it has been suggested that they might do so more significantly in the future with increasing temperatures [*Biastoch et al.*, 2011]. Removal of CH₄ from the atmosphere is dominated by oxidation through tropospheric OH radical interaction (~85 %) [*Lelieveld et al.*, 1998].

Recently, the global CH₄ budget has been seen to be changing with year to year increases since 2007 [*Nisbet et al.*, 2014; *Sussmann et al.*, 2012]. The cause of this increase is thought to be dominated by changes to the tropical wetland emissions [*Bousquet et al.*, 2011; *Nisbet et al.*, 2014], or agricultural activities (ruminants and rice cultivation [*Schaefer et al.*, 2016]), with the drivers for the tropical wetland growth thought to be a combination of high precipitation and high temperatures, enhancing biogenic activity [*Dlugokencky et al.*, 2009].

As many of the sources of Arctic CH₄ are at least partly temperature dependent, the projected Arctic temperature change of between 2.2 °C and 8.3 °C by 2100 [*Collins et al.*, 2013] makes an urgent case for better understanding of Arctic CH₄ and the effect of temperature rises on sources of CH₄ emissions. Recent studies have identified previously unquantified sources of atmospheric CH₄ to the Arctic, such as sub-sea permafrost degradation [*Portnov et al.*, 2014; *Portnov et al.*, 2013], CH₄ bubbling and geologically old CH₄ seepage along thaw features [*Walter et al.*, 2008; 2012], all of which have been linked to the increasing Arctic temperatures.

The ratio of ¹³C:¹²C (expressed relative to the Pee Dee Belemnite standard as δ¹³C) in CH₄ (along with the ratio of D:H) can be used to help determine the origin of detected CH₄ emissions. Light CH₄ (depleted in ¹³C) is emitted mainly during biological production and isotopically varies depending on the amount of oxidation occurring before emission (e.g.

during transport in soil or water); on the other hand, heavy CH₄ (relatively enriched in ¹³C compared to biological sources) comes from pyrogenic and thermogenic sources such as biomass burning and coal mines [Zazzeri *et al.*, 2015]. Figure 1 demonstrates how the δ¹³C value varies between differing sources of CH₄. Much work has been done at specific localities in order to determine isotopic source signatures for differing sources (e.g. Fisher *et al.* [2006]; Iverach *et al.* [2015] and Zazzeri *et al.* [2015]) and a comprehensive database has been set up to allow much more rigorous selection of δ¹³C values for use in both global and regional modelling studies [Sherwood *et al.*, 2016]. Use of the updated δ¹³C database has already demonstrated that commonly used natural gas and coal δ¹³C values in previous top down studies have been poorly constrained [Schwietzke *et al.*, 2016].

In this work, methane mixing ratios, methane isotope and supporting measurements from two flights during the MAMM field campaign are combined with air parcel trajectory modeling and previously determined emission inventories. The primary aim is to assess the use of this combination of tools in determining methane emission sources hundreds of km from the measurement location. Previous aircraft campaigns have been undertaken where CH₄ δ¹³C has been measured in order to determine source characteristics (e.g. Umezawa *et al.* [2011]). However, those flights were performed over expected CH₄ sources. This current work aims to show the value of determining δ¹³C values for air masses that have an unknown source, by using the δ¹³C signature along with particle dispersion and emission inventories modeling to identify the source(s).

2. Methods

2.1. Aircraft Measurements

The MAMM program was designed to investigate Arctic CH₄ using a combination of aircraft and ground measurement studies, and complementary modeling approaches. An initial field campaign took place during July 2012 when the FAAM (Facility for Airborne Atmospheric Measurements) modified BAe-146 Atmospheric Research Aircraft (ARA) was deployed to Kiruna, Sweden (67.850 °N, 20.216 °E). Seven flights took place over a four day period both to survey Arctic wetland areas (see *O'Shea et al.* [2014] for general details of the MAMM campaign) and to measure long range transport of CH₄. The measurements presented here are from two flights on July 21, 2012 (B718 and B719), outbound from Kiruna to and returning from Longyearbyen, Spitsbergen (78.220 °N, 15.650 °E), respectively. Flightpaths for B718 and B719 are shown in Figure 2.

On board the aircraft, and operating continuously, were a Fast Greenhouse Gas Analyzer (FGGA) and a mobile CIMS (Chemical Ionization Mass Spectrometer) whose hydrogen cyanide (HCN) measurements can be used as a tracer for biomass burning [*Tereszchuk et al.*, 2011]. The FGGA (model 907-0010, Los Gatos Research Inc., USA) measures CO₂, CH₄, and H₂O dry air molar fractions using cavity-enhanced laser absorption spectroscopy at a rate of 1 Hz, with these data available in real-time during the flight. The CIMS was used to determine formic acid (HCOOH) and HCN concentrations at a rate of 1 Hz, averaged to 30 second data. In-flight repeatability was determined using in-flight gas standards as detailed in *O'Shea et al.* [2013], for CO₂ repeatability was determined to be ±0.17 ppm; typical 1 Hz precision is ±0.66 ppm (all precisions are 1σ). CH₄ repeatability was determined to be ±1.28

ppb; 1 Hz precision is ± 2.48 ppb. For a detailed system description, see *O'Shea et al.* [2013]. In-flight calibrations of HCOOH were used to determine a relative HCN sensitivity average of $0.4 (\pm 0.01)$ ion counts s^{-1} ppt $^{-1}$, with a 3σ limit of detection for HCN of 62 ppt; (see *Le Breton*, [2013] for further details). Carbon monoxide (CO) and ozone (O₃) measurements were made at 1 Hz using an AL5002 UV fluorescence monitor [*Gerbige et al.*, 1999], and a TECO 49C UV photometer, respectively [*Real et al.*, 2007]. Wind speed was measured on board the aircraft using the five-port pressure measurement system, along with static pressure ports and the inertial navigation unit system, providing wind velocity components at 32 Hz, which have been averaged to 1 Hz for this study. For a previous campaign, *Petersen and Renfrew* [2009] estimated the overall uncertainty in horizontal wind measurements to be $< \pm 0.5$ ms $^{-1}$.

The data from the FGGA were used in real-time for decisions on changes to the flightpath of the aircraft to optimize sampling and also used to pick appropriate sampling times to fill Whole Air Sample (WAS) steel canisters for further analysis post-campaign. A total of 34 WAS samples were taken in or around the region of enhanced methane. Comparisons of WAS sample measurements in the lab and corresponding FGGA in-flight measurements show a standard deviation of 2 ppb for CH₄ and 0.9ppm for CO₂, and are normally distributed around the FGGA measurements indicating no systematic bias from the post flight sampling or storage of the WAS samples. Once it was established that the aircraft was flying within the CH₄ enhanced air mass, the altitude of the aircraft was varied in order to determine the vertical extent of the air mass and also to map the mixing ratio of CH₄ throughout. In order for the Keeling analysis method [*Keeling*, 1958; 1961; *Pataki et al.*, 2003] to give the best possible precision in determining the isotopic signature of the excess methane in the air mass, the largest possible range of mixing ratios of CH₄ within the air mass is required. Depending

upon the altitude of the aircraft the filling time had to be altered to make the total pressure in the WAS bottles ~45 psi. The WAS were filled for between 15 seconds at very low level flying at approximately 100 ft. (~30 m) above sea-level and for 40 seconds at 10,000 ft. (~3000 m) altitude. The locations where WAS samples were collected are shown in Figure 2a and marked with a red star.

The WAS bottles were returned to the Royal Holloway, University of London (RHUL) greenhouse gas laboratory for post-campaign analysis. CO₂ and CH₄ mixing ratios in each WAS sample were measured using a Picarro 1301 cavity ringdown spectroscopic greenhouse gas analyzer for 360 seconds, with a 180 second flush and 180 second measurement period. During the measurement period the sample was analyzed every 5 seconds, with an average value determined for the 3 minute period. The 1 σ precision on the measurements was better than ± 0.3 ppb for CH₄, with small variations between samples. The resulting mixing ratios were corrected for water vapor using the adjustment shown in Equation (1).

$$\text{CH}_4_{dry} = \text{CH}_4_{wet} \times (1 + (0.01010244 \times \text{H}_2\text{O}(\%))) \quad (1).$$

This water vapor correction, which is valid for up to 1.5 % H₂O, was determined using a similar method to that described in *Chen et al.* [2010]. The Picarro 1301 greenhouse gas analyzer is calibrated weekly to the National Oceanic and Atmospheric Administration (NOAA) scale using air standards supplied by MPI-Jena as part of the IMECC project. The Picarro measurements use approximately 1.5 liters of air for each WAS bottle measurement routine.

Subsequently, the remaining air in each WAS bottle was analyzed for $\delta^{13}\text{C}$ in CH_4 using the Continuous Flow Gas Chromatography/Isotope-Ratio Mass Spectrometry (CF-GC/IRMS) method outlined in *Fisher et al.* [2006]. Each WAS bottle was analyzed at least 3 times with a mean repeatability (1σ) of 0.05 ‰ for $\delta^{13}\text{C}$ in CH_4 .

2.2. Particle Dispersion Modeling

The Numerical Atmospheric-dispersion Modeling Environment (NAME) is a 3D Lagrangian particle dispersion model [*Jones et al.*, 2007; *Ryall and Maryon*, 1998], which is run here using the UK Meteorological Office's Unified Model meteorological fields [*Cullen*, 1993]. In this study, particles are released from the locations of the WAS samples along flights B718 and B719, with the model then calculating the trajectories of the particles backwards in time. The particle motions are calculated based on the large-scale winds, wind meander and sub-grid scale turbulence. NAME has previously been used to identify CH_4 sources from measurements at Mace Head [*Manning et al.*, 2011], and to identify the long range transport of biomass burning emissions from Russia to the UK [*Witham and Manning*, 2007], over similar distance scales as those presented here.

To model the back trajectories from each WAS, 33,333 particles were released at the time and location of the aircraft at the start of each WAS sample. To account for some uncertainty in the model, the particles were released not from a point, but from a cube of side 100 m and for two minutes in time (centered on the WAS location). The particles were tracked for 10 days back in time, and the time that the particles spent in the planetary boundary layer of the model was recorded. This information was used to construct the “footprint” maps, which

indicate where, during the previous 10 days, air from the surface could have been incorporated into the measured air mass.

3. Results and Discussions

3.1 Aircraft Observations

The flight tracks for the two flights, B718 and B719, are shown geographically in Figure 2. Figure 3 contains the combined flight tracks with respect to latitude and elevation so that the profiles of the two flights can be seen. The air mass containing elevated CH₄ mixing ratios can clearly be visualized by creating a linearly interpolated matrix of continuous CH₄ mixing ratio measurements plotted against the latitude and altitude as shown in Figure 3. The elevated mixing ratios of CH₄ were observed between 71.1 °N, 17.9 °E and 76.5 °N, 12.4 °E, a distance of ~600 km. A maximum mixing ratio of CH₄ of ~1920 ppb was observed in the core of the air mass with enhanced methane. The wind speed averaged 8.5 ms⁻¹ during the outbound flight and 10 ms⁻¹ on the return flight with a predominant easterly/east-north-easterly wind direction through the sampled region (Figure S1).

CO and CO₂ mixing ratios, both made at 1 Hz frequency, are shown in Figures 2b and 2c, respectively, along with scatter plots shown in Figure S2. The CO₂ measurements display anti-correlation to CH₄ with minimum CO₂ associated with high CH₄, but show very little variation with only a few ppm change across hundreds of km. The CO measurements are bimodal when plotted against the corresponding CH₄ measurements, with very low CO mixing ratios associated with the background air and some enhancement of CO at altitudes higher than a few hundred meters above sea level associated with enhanced CH₄. The

presence of higher CO with enhanced CH₄ could be indicative of a mixed source, or simply transportation of long lived CO enhanced air from lower latitudes. Polluted air masses from Europe with clear enhancements in both CO₂ and CO have previously been recorded at Zeppelin Observatory, Svalbard [Stohl *et al.*, 2007].

HCN was measured at 1 Hz frequency for flights B718 and B719, as illustrated in Figure S3. HCN is an effective tracer for biomass burning due to its limited sources and its relatively long atmospheric lifetime [Le Breton *et al.*, 2013; Lobert *et al.*, 1990]. Average HCN mixing ratios were relatively low for flights B718 and B719 at 36.0 (± 12.7) ppt and 86.9 (± 15.3) ppt respectively which are characteristic of expected background concentrations for this region. Furthermore, the observed HCN concentrations display no correlation with measured CH₄ enhancements, adding evidence that biomass burning did not contribute to the air mass.

The near surface O₃ measured during the two flights shows concentrations in line with those expected from background Arctic surface O₃ of ~30 ppb, with a gradual increase in concentration with altitude, consistent with a descending and stably stratified free tropospheric air mass. The measurements suggest a lack of recent O₃ formation above background levels and therefore little input from anthropogenic sources into the air mass.

3.2 Associated Measurements from Zeppelin Observatory

Supplementary observations from the Zeppelin Observatory have been explored. The Zeppelin Observatory is a comprehensive atmospheric measurement site located on the west coast of Norway at 78.90 °N, 11.88 °E on the Zeppelin Mountain, 478 m.a.s.l. At the Zeppelin Observatory more than 25 greenhouse gases are measured continuously in addition

to aerosol variables (optical, physical, chemical properties) and other atmospheric components (as reactive trace gases). Methane has been measured continuously since 2001 with high time resolution [Myhre *et al.*, 2014]. Since 2007 the standard measurement program has been supplemented by taking air samples for $\delta^{13}\text{C}$ in CH_4 as a part of various research projects, and 5 days per week since summer 2012. At Zeppelin, CH_4 showed elevated levels over a relatively long period during summer 2012 from July 17 – August 8, but for the days around July 21, CO, ozone, CO_2 , and sulfate showed mixing ratios typical of Arctic background air.

3.3 Using NAME to Identify Potential CH_4 Source Regions

Air mass histories for each of the WAS locations in B718 and B719 have been calculated using the NAME model, as described in section 2.2. Two examples of footprint maps (Figure 4), show where the particles, run backwards from a particular measurement, passed through the modeled planetary boundary layer. Assuming that the source of the additional CH_4 in the air mass is emitted from the surface, and that the CH_4 originated from emissions in the previous 10 days, then the footprint map indicates the weighted source location of the air mass (note that the scale is logarithmic).

The left panel of Figure 4 shows the footprint map generated from particles released at the location of WAS flask 4 during B718 (10:22 UTC, 71.1914 °N, 18.5343 °E, 963 hPa), where CH_4 in the flask was 1877 ppb. This is characteristic of background Arctic air, which is supported by the footprint map that shows the air has come from further north, with the measured air parcel not having been influenced by significant source regions.

The right panel of Figure 4 shows the footprint map from particles released at the location of WAS flask 8 from the same flight (10:58 UTC, 73.1077 °N, 16.6945 °E, 909 hPa), where CH₄ was about 35 ppb higher at 1911 ppb. It is clear that, in this case, there is some influence from parts of northern Russia and Europe, including the Pechora River Delta and associated methane-emitting wetlands. Up to 20% of this region is classified as wetland based on MODIS (Moderate Resolution Imaging Spectroradiometer) land cover maps [Friedl *et al.*, 2010]. The measurements could also have been influenced by transport from a large region of the Pechora Sea, Barents Sea and Kara Sea. The West Yamal Shelf in the Kara Sea has recently been shown to be a likely (and large) source of methane [Portnov *et al.*, 2014].

3.4 $\delta^{13}\text{CH}_4$ Analysis

The principle behind Keeling plots [Keeling, 1958; 1960; 1961] is that the conservation of mass can be applied to an atmospheric system in order to determine source characteristics of a mixed air mass consisting of background air and an added component. If an extra source of CH₄ is added to a background air mass with a different $\delta^{13}\text{C}$ value, then the overall $\delta^{13}\text{C}$ signature will become a linear combination of the background and the added $\delta^{13}\text{C}$. At the limit of possibility where the added CH₄ is effectively infinitely larger than the original concentration then the $\delta^{13}\text{C}$ signature will be entirely from the added CH₄. The linear extrapolation to the y-axis of $\delta^{13}\text{C}$ against $1/[\text{CH}_4]$ will represent the $\delta^{13}\text{C}$ of this infinite mixing ratio of CH₄, and therefore represents the $\delta^{13}\text{C}$ of the “added (X)” CH₄ component. This is shown mathematically in Equations (2) and (3).

$$\delta^{13}\text{C}_{\text{measured}} \times [\text{measured}] = \delta^{13}\text{C}_{\text{background}} \times [B] + \delta^{13}\text{C}_{\text{added}} \times [X] \quad (2)$$

$$\delta^{13}\text{C}_{\text{measured}} = [B](\delta^{13}\text{C}_{\text{background}} - \delta^{13}\text{C}_{\text{added}})\left(\frac{1}{[\text{measured}]}\right) + \delta^{13}\text{C}_{\text{added}} \quad (3)$$

Equations 2 and 3 are modified from *Pataki et al.* (2003). [B] is the mixing ratio of the background CH₄, [X] is the mixing ratio of the added CH₄, and [measured] is the measured mixing ratio, or the sum of [B] and [X]. The intercept on the y-axis in Eqn. (3) can be seen to be equal to $\delta^{13}\text{C}_{\text{added}}$.

The intercept, and hence the isotopic signature, is found using a linear regression method accounting for individual sample errors and intrinsic scatter in the data using an orthogonal distance regression method to account for errors in both the x and y axes [*Akritas and Bershadsky*, 1996].

Measurements of the $\delta^{13}\text{C}_{\text{CH}_4}$ isotopic signature of CH₄ provide a powerful constraint in determining emission sources, as discussed earlier and shown in Figure 1. Figure 5 shows the Keeling plot analysis performed on all the WAS samples taken during the two flights in and around the CH₄ enhanced air mass. The excess CH₄ over background has a source $\delta^{13}\text{C}$ signature of $-70.1 (\pm 2.1) \text{‰}$ to 1σ , which is in the range of previously measured $\delta^{13}\text{C}$ signatures of wetland ($-68.5 (\pm 0.7) \text{‰}$ [*Sriskantharajah et al.*, 2012]), Eurasian thermokarst lakes emissions (-70.3‰ [*Walter et al.*, 2008]) and C3 plant digesting ruminants ($-70 (\pm 4) \text{‰}$ [*Dlugokencky et al.*, 2011]). The $\delta^{13}\text{C}$ value of $-70.1 (\pm 2.1) \text{‰}$ is also consistent with the isotopic signature from other MAMM project flights of based wetland areas in Fennoscandia during the MAMM campaign (*O'Shea et al.*, 2014) where values of $-70 (\pm 3) \text{‰}$ were observed at low level above wetlands. However, the regression shown in Figure 5 does in fact display several points slightly offset from the best fit regression line, suggesting that whilst there is a dominant CH₄ source there are also some minor and variable additions of CH₄ from

other sources which are only partially well mixed into the air mass. Given the distance travelled and variable potential sources from the footprint maps in Figure 4, a combination approach using the isotopic information, particle dispersion modeling and inventory analysis was used to test this hypothesis of multiple sources within the air mass.

3.5 NAME Inventory Analysis

The NAME model results show that the air mass histories from the flight track are varied, with influence from both the continent and from polar and oceanic regions. Note that the footprint maps do not include information about where emissions are located, only where the air mass has been within the boundary layer. Whilst sections 3.3 and 3.4 point to the likely dominant source of methane in the air mass measured on July 21 being from Russian wetlands, the NAME analysis on its own does not constrain the emission strength. In this section we explore a further approach to quantification by combining a global CH₄ emission inventory with the NAME back trajectory analysis.

“Pseudo-observations” have been calculated to assess the contributions from different CH₄ emission sources in the WAS measurements, using an emissions inventory and a transport model. Back trajectories from each of the WAS locations in flights B718 and B719 from the NAME model were used for the transport. The CH₄ emission inventory published in Bousquet *et al.* [2011] was used in combination with the atmospheric transport to calculate contributions from different emission sources during the previous 10 days, to the CH₄ mixing ratio at the WAS measurement points. These contributions, modeled as increments above the background, we call “pseudo observations”, and have been calculated using Equation (4):

$$\text{Increment above background [g m}^{-3}] = \text{Emission [g m}^{-2} \text{ s}^{-1}] \times \text{Dilution [s m}^{-1}], \quad (4)$$

where the dilution is calculated from the NAME footprint maps. This method is described in more detail in *Ashfold et al.* [2014].

The emissions inventory used here (henceforth referred to as the modeled emissions) was created by *Bousquet et al.* [2011] and was generated using a top-down inversion method, based on global surface measurements and a transport model. Their CH₄ emissions have been divided into different source sectors: agriculture and waste; fossil fuel related; biomass burning; natural wetlands; all other sources e.g. oceans and termites; soil uptake (equivalent to a negative source). The inventory contains monthly mean emissions on a regular 1x1 degree grid between 1984 and 2009. Here, the calculations were performed using each individual July monthly mean emission between 2005 and 2009, as well as the average of all of those months. The average of July 2005 to 2009 is referred to henceforth as the July emissions climatology.

The wetland methane emissions from *Bousquet et al.* [2011] are similar to other inventories in recent literature. In the Scandinavian region, they fall within the range of the models in the Melton *et al.*, [2013] intercomparison of wetland methane models. The total emissions north of 35 °N, averaged over 1993 to 2004, in *Bousquet et al.* [2011] is 43 (±4) Tg CH₄ yr⁻¹, and is 51 (±15) Tg CH₄ yr⁻¹ in the models taking part in the intercomparison. *Bruhwiller et al.* [2014] have compared their methane emissions from the CarbonTracker-CH₄ assimilation system, and conclude that for 2007 and 2008, their results are similar to *Bousquet et al.* [2011]. Although *Bousquet et al.* [2011] is not an outlier, there is a degree of variation between the different datasets.

To quantify the contributions from the different source sectors, the modeled emissions are combined with the NAME air mass histories as described above. Figure 6 shows the contributions from each of the emissions sectors considered by *Bousquet et al.* [2011] for each of the WAS locations along flight B718 (upper panel) and B719 (lower panel), using the July emissions climatology. We emphasize that the CH₄ shown represents the increment above the background that the model suggests would have been emitted from each of the source sectors. If the bar shows zero (e.g. for several WAS flasks in B719), then the CH₄ at that location is likely to be at a background level, as the modeling suggests it has not been influenced by surface emissions in the last 10 days. Red squares show the measured CH₄ from the WAS with an assumed background mixing ratio deducted. Red squares show the measured CH₄ from the WAS with an assumed background mixing ratio deducted. The background mole fraction for each particle, dependent on its end point time and location, is taken from the MACC III CH₄ inversion reanalysis, which has been optimized using NOAA surface observations [*Bergamaschi et al.*, 2007; *Bergamaschi et al.*, 2009; *Bergamaschi et al.*, 2013]. The average background mole fraction of all the particles released from each WAS location was averaged to give the background value for that WAS. The WAS background values ranged between 1857 and 1866 ppb, with a mean of 1862 ppb.

The total calculated contribution to each WAS is generally greater than the observed increment above background, suggesting that either the magnitude of the modeled emission fluxes or the extent of the influence from the surface is too high at this specific time. As wetland emissions (the largest contributor, shown in dark blue) are highly interannually variable, and this calculation uses the average emission for the month of July between 2005 and 2009, it is possible that the actual emission in July 2012 was lower than this average.

The *Bousquet et al.* [2011] study only extended as far as 2009 so we cannot repeat our calculations using 2012 emissions. Instead, to assess the possible role of the interannual variability of the emissions, the calculation was repeated with emissions from each July between 2005 and 2009. Figure 7 shows a scatter plot of the CH₄ measured from each WAS, against the calculated value (assuming a background from the MACC III reanalysis, as before). The circles show the value using the July emissions climatology. The whiskers show the range between the minimum and maximum values generated using each individual month (July averages for each year between 2005 and 2009 inclusive). Consistently, July 2009 emissions show the closest agreement with the measurements, however, even they overestimate the CH₄ increment.

Figure 6 shows that the wetland emissions alone (dark blue bars) would often overestimate the observed CH₄ levels. Additionally, non-wetland emissions alone would in some cases also overestimate the CH₄. This suggests that both the modeled wetland and non-wetland CH₄ contributions are too high for this day. This could be because of uncertainties in the modeled transport and dilution, or because the daily variability of the emissions is also uncertain, or both.

The whiskers in Figure 7 show a large interannual variability, but any within month variability is not represented in the emission inventory. Day-to-day variation in wetland emissions flux has been reported by *Heikkinen et al.* [2004] in a region of Russian tundra close to the Pechora River Delta. Depending on the vegetation type, their chamber measurements showed mean (standard deviation) fluxes over the season (June 6 to September 10, 2001) ranging between 0.2 (± 0.2) and 5.7 (± 2.9) mg/m²/h. The range in the modeled

wetland emissions used here (for monthly mean July 2005-2009) in the region of influence is approximately 1 to 2 mg/m²/h. The modeled CH₄ emissions for the source region are therefore within the *Heikennen et al.* [2004] range of observations. It could be that for this particular day, the modeled monthly mean July flux is either too high compared with the actual day's flux in magnitude, or covers too widespread an area, or both. To obtain a more certain result, it would be necessary to use a methane emission inventory for the specific date under investigation, to take into account the meteorological influences on magnitudes of the wetland emissions. This would be beyond the scope of this study, which aims to demonstrate the application of this method using the data that is currently available to the authors.

Despite the evident overestimation, Figure 6 clearly shows that for the majority of the WAS locations, wetlands are likely the largest contributor to the CH₄ increment, with smaller contributions from fossil fuels and agriculture and waste. This is consistent with the isotopic measurements from the WAS. In Figure 5, the Keeling plot indicates a bulk source contribution to the air mass at -70.1 ‰, by assigning best estimate emission $\delta^{13}\text{C}$ signatures to each of the other significant sources, a value for the wetland source signature can be calculated. For the purpose of this analysis we assume that the relative contribution from the different sources in *Bousquet et al.* [2011] are robust, (even though the magnitudes are overestimated compared with our observations) then the wetland isotopic contribution can be estimated using Equation (5).

$$\delta^{13}\text{C}_{\text{source}} = \delta^{13}\text{C}_x[\text{X}\%] + \delta^{13}\text{C}_y[\text{Y}\%] + \delta^{13}\text{C}_z[\text{Z}\%] \quad (5)$$

Where X, Y and Z represent the different contributing sources of CH₄, such as wetland, fossil fuels and agriculture.

The overall isotopic source signature ($\delta^{13}\text{C}_{\text{source}}$) is -70.1‰ . We assume a Russian fossil fuel input of $-46.4 (\pm 9)\text{‰}$ [Sherwood *et al.*, 2016], a combined agriculture-waste $\delta^{13}\text{C}$ signature of $-65 (\pm 5)\text{‰}$ is estimated from Russian landfill data and ruminants with a C3 plant diet [Dlugokencky *et al.*, 2011; Nozhevnikova *et al.*, 1993] and we assume the other sources insignificant (Figure 6). An isotopic contribution from the wetland contribution can be calculated using Equation (5) to be $-78.4 (\pm 9)\text{‰}$, where uncertainties in the calculation were propagated using monte-carlo analysis. All uncertainties are quoted to 1 sd.

3.6 Discussion and Implications

Emission fluxes determined from mixing ratio measurements involve some kind of transport and flux inversion. Any inversion (without perfect and ubiquitous knowledge of atmospheric state) cannot deliver a unique answer, and so additional constraints need to be applied if possible. Here we have explored whether a combination of aircraft observations, Keeling analysis and particle dispersion modeling is sufficient to determine a source region and likely source strength. Such an approach might be especially useful when the isotopic source signature suggests that measurements could have been influenced by several different sources.

For the particular case studies here, there is very little doubt that the source of the elevated CH_4 is biogenic, with a bulk Keeling analysis $\delta^{13}\text{C}$ signature of $\sim -70\text{‰}$. Given the wetland contribution signature of $-78 (\pm 9)\text{‰}$ is within the range reported from Fennoscandian wetlands $\delta^{13}\text{C}$ source signatures [O'Shea *et al.*, 2014], it is likely to be mainly derived from a comparable wetland source. The NAME modeling indicates that a large fraction of the back trajectories at the heart of the enhanced CH_4 air mass pass through the boundary layer over an

area of north-west Russia which is up to 20 % wetland according to MODIS land use [Friedl *et al.*, 2010]. However, the right panel of Figure 4 also shows that some of the back trajectories pass over the Barents Sea and Kara Sea, which could potentially be source regions for the enhanced CH₄, which are not accounted for in the modeled emissions. The modeled emissions inventory used to calculate the pseudo-observations includes only a small oceanic source from the Barents Sea, but the flux is so small that the contribution is negligible in this case (it is a component of the ‘others’ emissions source in Figure 6). Recent work has demonstrated that large areas of the Laptev Sea and Kara Sea are emitting significant amounts of CH₄ (especially in summer months) from the thawing permafrost, with possible enhanced release from the sea to the atmosphere following storm events [Shakhova *et al.*, 2014]. The Barents Sea is also shallow, largely less than 300 m in depth, and potentially could drive a similar emission system. The wind and air pressure forecast for 24 hours before the flights are given in Figure S4 and show high winds in the eastern Barents Sea, which is similar to the conditions experienced by Shakhova *et al.* [2014], which resulted in the ocean CH₄ being overturned and released to the atmosphere. It is therefore possible that the air mass seen here in this work is representative of a storm induced CH₄ emission from the shallow Barents Sea, but there is currently no isotopic evidence from the Laptev Sea emissions to verify whether this has a comparable $\delta^{13}\text{C}$ signature to that seen here. Methane in the seawater has been characterized near to Svalbard with $\delta^{13}\text{C}$ measurements ranging from -53 to -20 ‰ [Damm *et al.*, 2005]. Oxidation in the water column serves to enrich the heavier CH₄ isotopes, therefore CH₄ in the surface waters would be heavier prior to release to the atmosphere and -53 ‰ would be the lightest anticipated isotopic signature from ocean sources given currently available data. If the model attribution ratios from the NAME and inventory modelling are correct, it is difficult to reconcile an isotopically heavy fossil fuel source and a large source from surface waters whilst maintaining a sensible estimate for the

wetland source. Therefore, the most likely main source is Russian wetlands – including land based or very shallow shelf permafrost degradation, essentially re-activating previously frozen wetland environments with no or little water column oxidation to drive the isotopic signature less negative. There is a clear need for greater constraints on the $\delta^{13}\text{C}$ signatures of biogenic sources of CH_4 such as thermokarst, permafrost and hydrates, with respect to location, so that distinctive CH_4 plumes can be traced back to their emission sources with much less uncertainty by isotope transport modeling.

Methane isotopic signatures are being increasingly used in global source and sink models to interpret trends in regional CH_4 growth (e.g. *Monteil et al.* [2011]) but, as we suggest above, regionally resolved information on the pattern of $\delta^{13}\text{C}$ emission signatures is poorly constrained. For example, in many instances the “generic wetland” $\delta^{13}\text{C}$ signature used is above -60‰ (e.g. -59‰ *Monteil et al.* [2011]), which is considerably heavier than the wetland inputs measured here and also during the rest of MAMM and other campaigns in Fennoscandia; a bulk signature closer to -70‰ , or even lighter given the wetland component determined here ($-78 (\pm 9)\text{‰}$), would seem more appropriate based on this work and others (e.g. *O'Shea et al.* [2014]) and importantly makes wetland CH_4 emissions essentially indeterminate from thermokarst lake emissions using $\delta^{13}\text{C}\text{‰}$ [*Walter et al.*, 2008]. Recommendations to improve the $\delta^{13}\text{C}$ inventory for global wetlands are in line with recent work making similar revisions to the fossil fuel $\delta^{13}\text{C}$ inventory [*Schwietzke et al.*, 2016]. Both this work and *Schwietzke et al.* [2016] demonstrate the importance of maintaining an isotopic database for global emissions studies and refining and filling in gaps in the knowledge base.

Elevated CH_4 was also measured during sampling at the Zeppelin Observatory on Svalbard from late summer 2012, where an increase of 70 ppb CH_4 was seen in a one-off measurement

of CH₄ mixing ratio and isotopic composition on September 17, 2012. Although only a single sample and background is available to create a Keeling plot from the 2012 enhancement, the resulting isotopic source signature was -68 ‰ and a HYSPLIT back trajectory analysis shows a north-western Russian/south Barents Sea source (Figure S5). Increasing the frequency of isotopic sampling of methane at Zeppelin, especially during periods of enhanced CH₄, may resolve how frequently highly isotopically depleted emissions from Russia can reach the high Arctic.

A minimum summer bulk CH₄ wetland (including degrading permafrost) isotopic source signature for northern Russia of $-78 (\pm 9)\text{ ‰}$ as reported here, is slightly lighter than previous work focused on the Siberian wetlands, possibly indicating that other lighter sources such as permafrost degradation are playing a role in this emission. *Tarasova et al.* [2006] reports wetland source signatures of $-67.4 (\pm 1.6)\text{ ‰}$ for western Siberia away from industrial sources, and *Yamada et al.* [2005] report -69.8 ‰ for the Plotnikovo region. It is clear that the Russian wetland regions are a major atmospheric source of CH₄, with model simulations suggesting that the Siberian wetland CH₄ contribution to the Arctic may be considerably underestimated [*Tarasova et al.*, 2009] compared to areas such as Finland. With CH₄ mixing ratios of 2000 ppb commonly recorded north of 59 °N during the daytime [*Tarasova et al.*, 2006], it is easy to see how air parcels from Russia could provide large volumes of isotopically depleted CH₄ to the Arctic troposphere.

4. Conclusions

We have used precision measurements of methane mixing ratios and carbon isotopes in CH₄, together with back trajectories to determine likely emission regions for an air mass with elevated CH₄ observed during aircraft flights in the Arctic. The signature of the total CH₄ enhancement observed on 21 July 2012 had a $\delta^{13}\text{C}$ value of $-70 (\pm 2.1) \text{‰}$, with NAME back trajectories showing that the most likely source(s) are the north-western Russian wetlands (including lake emissions) and coastal shelf emissions. The $-70 (\pm 2.1) \text{‰}$ can be treated as a maximum (least depleted) value for $\delta^{13}\text{C}$ in CH₄ for bulk Russian natural input from this region, as any other small inputs creating a mixed signature such as burning and anthropogenic emissions (as seen in the combined NAME and inventory approach) drive the required isotopic contribution from the wetlands and coastal regions even more negative. Using the inventory and NAME modeling coupled with the isotopic data, the bulk Russian wetlands and coastal input $\delta^{13}\text{C}$ signature could be as isotopically light as $-78 (\pm 9) \text{‰}$. Although only a single air mass was studied, it demonstrates that large scale regional sources of methane are being transported over long distances to the Arctic and that the Arctic methane budget (and isotopic bulk composition) is influenced by sources thousands of kilometers away. Therefore, such extraneous sources should always be considered when interpreting Arctic methane measurements. Higher frequency isotopic methane sampling at stations in the European Arctic, such as at Zeppelin, would be welcome in helping to constrain the frequency and duration of such events.

Using combination techniques such as isotopes and particle dispersion modeling in tandem to sample air masses from sources that would otherwise be inaccessible demonstrates that sampling such mid to long range air parcels in high latitude regions with targeted campaigns

is a powerful technique to determine the influence of regional scale inputs. The resolution now available in particle dispersion models and inventory models, along with the ability to measure CH_4 isotopes to high precision will be vital to untangle not only the sources of Arctic CH_4 , but also build a larger scale picture of $\delta^{13}\text{C}$ in CH_4 for bulk regional emissions.

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Data will be available through <http://catalogue.ceda.ac.uk/uuid/03b040a422a4b694a90252410613282e> or requested through direct contact with the corresponding author.

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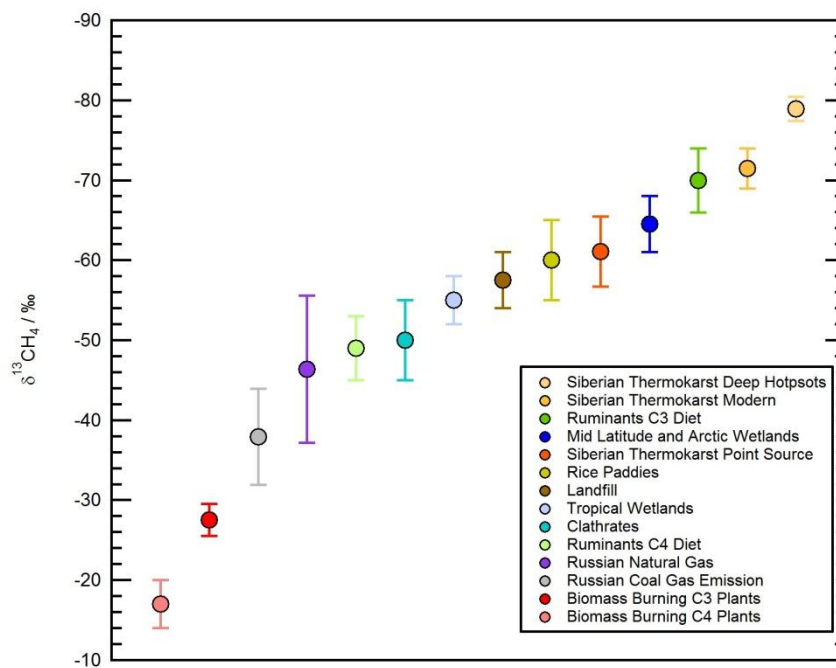


Figure 1. Isotopic ranges of $\delta^{13}\text{C}$ for CH_4 for a variety of CH_4 sources. The data for the graph and the corresponding uncertainties use data from: [Bergamaschi *et al.*, 1998; Cramer *et al.*, 1999; Dlugokencky *et al.*, 2011; Fisher *et al.*, 2011; Lowry *et al.*, 2001; Monteil *et al.*, 2011; Sherwood *et al.*, 2016; Sriskantharajah *et al.*, 2012; Umezawa *et al.*, 2011; Walter *et al.*, 2008; Zhang *et al.*, 2013].

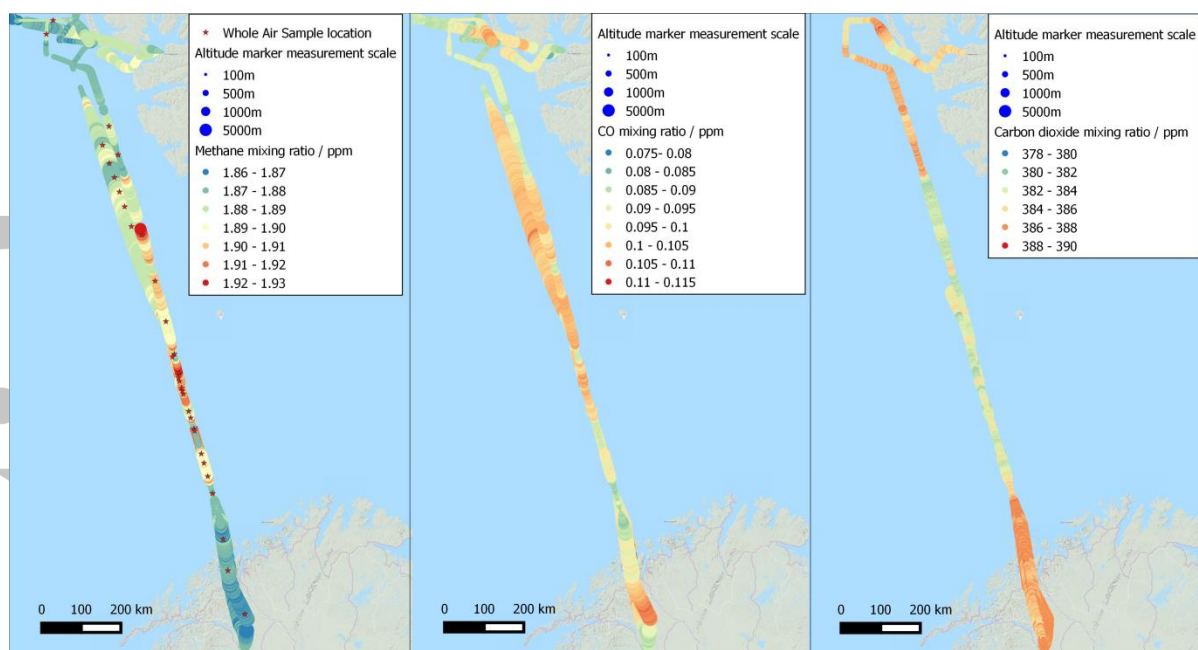


Figure 2a (Left) Flightpaths and CH₄ continuous mixing ratio measurements of tropospheric air from the fast greenhouse gas analyzer (FGGA) and WAS (Whole Air Samples) sampling locations (red stars) for both flights B718 and B719 during the MAMM campaign on July 21st, 2012. 2b (Center) CO continuous mixing ratio measurements of tropospheric air from the AL5002 UV fluorescence monitor. 2c (Right) CO₂ continuous mixing ratio measurements of tropospheric air from the FGGA. For all panels the variable size of the mixing ratio markers is a reflection of the altitude of the aircraft.

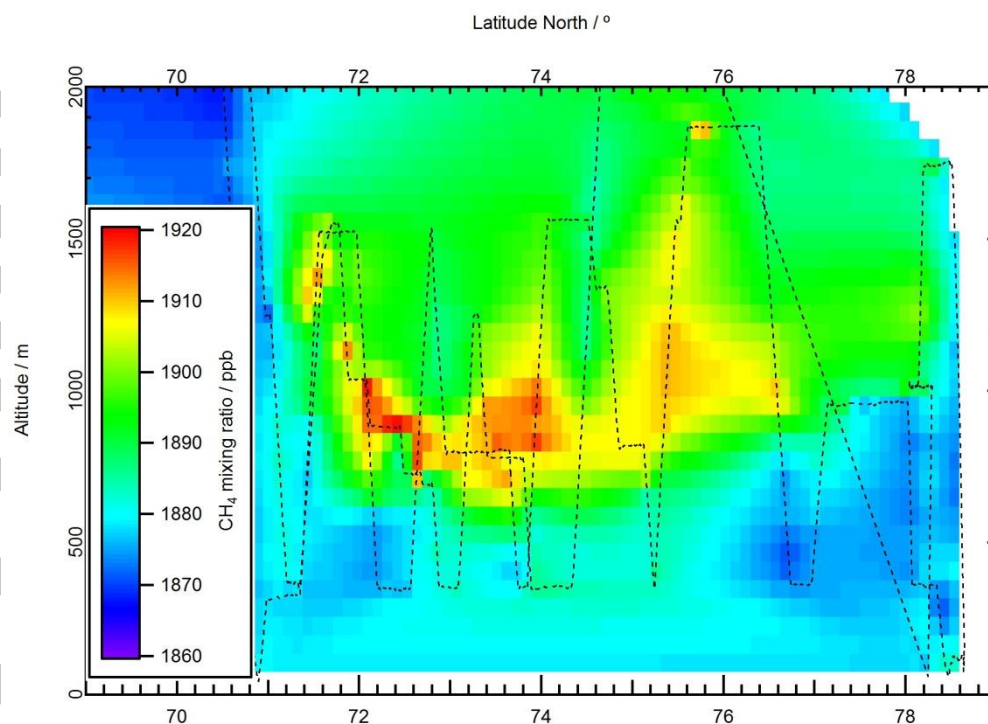


Figure 3. Matrix of linearly interpolated mixing ratios of CH_4 using the combination of all 1 Hz FGGA data from flights B718 and B719. The flight track is shown in black dashed lines and the stability of the CH_4 enriched air mass can be inferred from the continuity of the interpolated plot at repeated measurement points. The first point of contact with enhanced methane was at 10:15 local time and the final contact at 18:00.

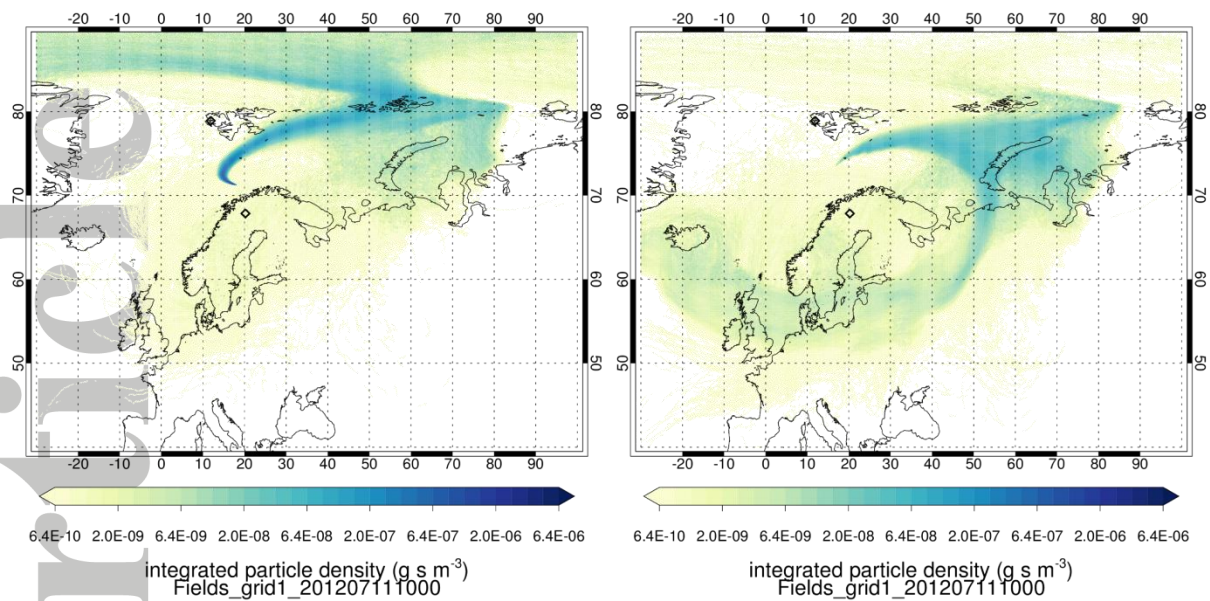


Figure 4. Examples of NAME modeling for flight B718, showing footprint maps from 10 day backward trajectories released from two WAS locations. This shows the modeled interaction with the boundary layer prior to being sampled on board the BAe-146. Left panel: WAS flask 4, where CH_4 was 1877 ppb. Flask 4 shows background Arctic air, in contrast to the higher CH_4 in flask 8 (Right panel), which is coming from parts of Russia and Europe. Diamonds mark the start and end points of B718/B719 at Kiruna and Longyearbyen. Right panel: Particles have been released from WAS flask 8, where CH_4 was measured at 1912 ppb.

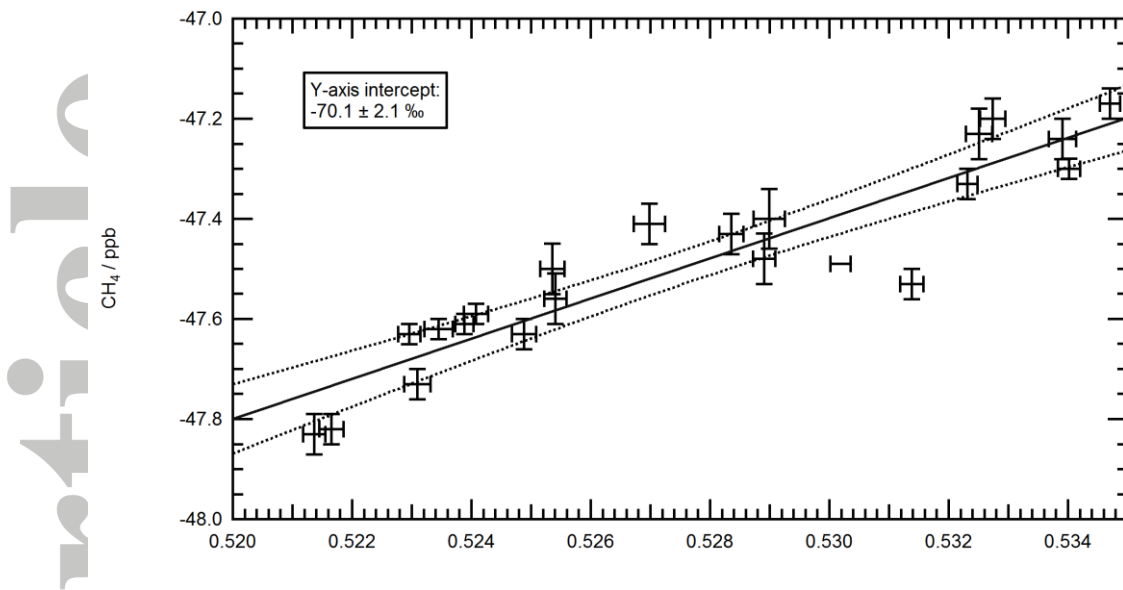


Figure 5. Keeling plot to derive isotopic source signature of the excess CH₄ over the background mixing ratios. Each point represents a Single WAS bottle sample taken during either B718 or B719 flightpaths on 21 July 2012. The fitted line is a linear orthogonal regression with fitting errors calculated using variable errors as calculated for each WAS sample. The fitting procedure and error calculation is described in *Akritas and Bershadsky* [1996].

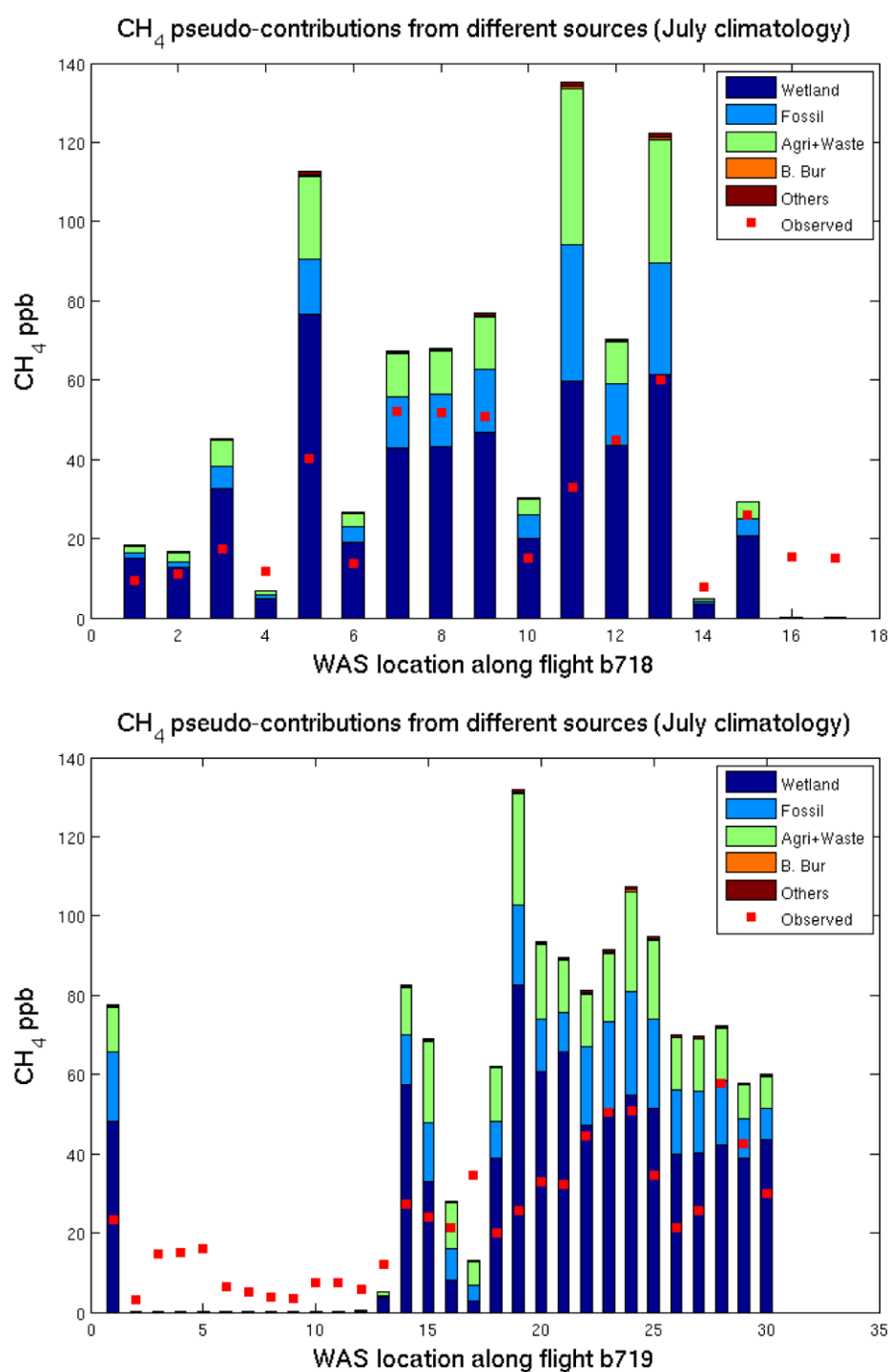
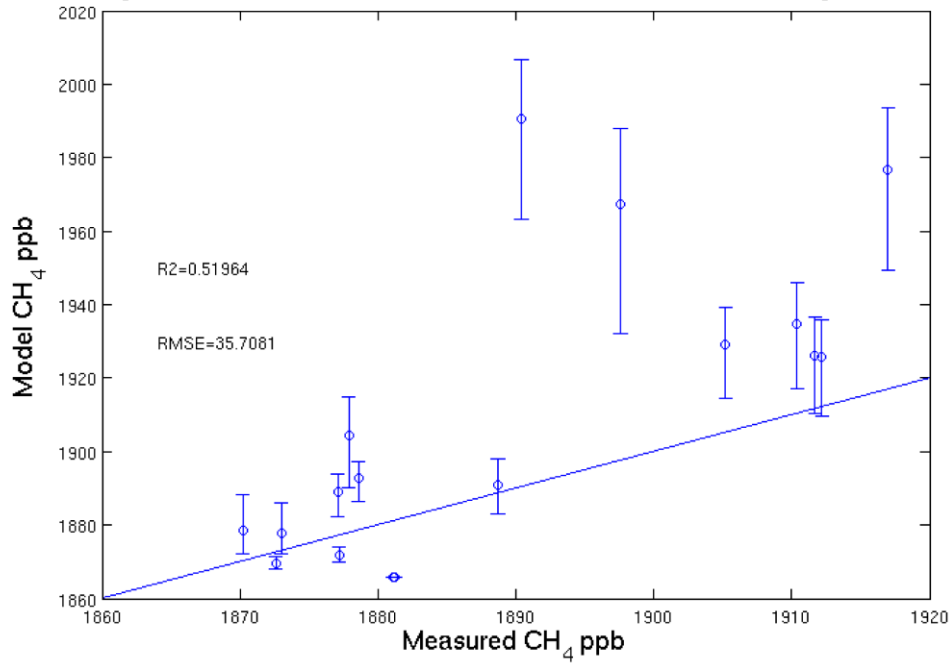


Figure 6: Contributions from different emissions sources to CH₄ at the WAS locations. Each bar represents a WAS location in B718 (upper) and B719 (lower). The bars are calculated by combining the July emissions climatology from each source sector (wetlands, fossil fuel related, agriculture and waste, biomass burning and others) with transport from the NAME dispersion model. Red squares show the mixing ratio from each WAS, with a background value deducted.

Model using July 2005-2009 mean emissions. Error bars show min/max from using individual months.



Model using July 2005-2009 mean emissions. Error bars show min/max from using individual months.

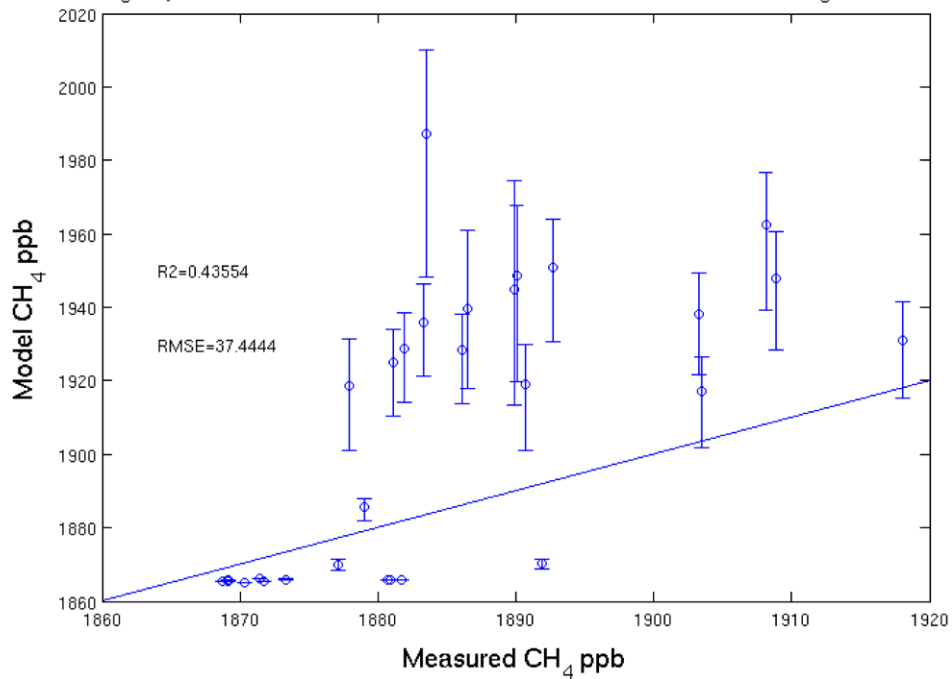


Figure 7: Scatter plots of the CH₄ modeled mixing ratio (pseudo-observation) against the corresponding CH₄ mixing ratio measured in each WAS flask for flights B718 and B719.

Circles show the pseudo-observation using the July emissions climatology. Whiskers show the range of values obtained by using each individual July mean emission (between 2005 and 2009). The one-to-one line is shown as the solid line.