Arctic methane sources: Isotopic evidence for atmospheric inputs

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[1] By comparison of the methane mixing ratio and the carbon isotope ratio ($\delta^{13}C_{CH4}$) in Arctic air with regional background, the incremental input of CH_4 in an air parcel and the source $\delta^{13}C_{CH4}$ signature can be determined. Using this technique the bulk Arctic CH_4 source signature of air arriving at Spitsbergen in late summer 2008 and 2009 was found to be −68‰, indicative of the dominance of a biogenic CH_4 source. This is close to the source signature of CH_4 emissions from boreal wetlands. In spring, when wetland was frozen, the CH_4 source signature was more enriched in ^{13}C at −53 ± 6‰ with air mass back trajectories indicating a large influence from gas field emissions in the Ob River region. Emissions of CH_4 to the water column from the seabed on the Spitsbergen continental slope are occurring but none has yet been detected reaching the atmosphere. The measurements illustrate the significance of wetland emissions. Potentially, these may respond quickly and powerfully to meteorological variations and to sustained climate warming. **Citation:** Fisher, R. E., et al. (2011), Arctic methane sources: Isotopic evidence for atmospheric inputs, *Geophys. Res. Lett.*, *38*, L21803, doi:10.1029/2011GL049319.

1. Introduction

[2] Arctic CH_4 emissions may have played a major role both in modern CH_4 excursions [*Dlugokencky et al.*, 2011] and in past global climatic change [*Nisbet and Chappellaz*, 2009]. Arctic CH_4 comes from varied sources, most of which respond quickly to temperature change, with strong positive feedbacks such that warming feeds warming. Four of the five warmest decades of a 2000-year-long reconstruction of Arctic temperatures occurred between 1950 and 2000 [*Kaufman et al.*, 2009]. An increase in global CH_4 in 2007 following years of near stability [*Dlugokencky et al.*, 2009, 2011; *Rigby et al.*, 2008] may have been in part a response to the Siberian heatwave that summer. Northern wetland emissions are likely to increase sharply with temperature [*Bohn et al.*, 2007] and may have helped drive past global glacial/interglacial changes [*Nisbet and Chappellaz*, 2009; *Petrenko et al.*, 2009].

2. Isotopic Signature of Sources of Methane to the Arctic

[3] Arctic CH_4 sources can be identified by isotopic signature (Table 1). In the Eurasian Arctic, emissions from wetlands sampled in ambient air give a characteristic and consistent isotopic signature with $\delta^{13}C_{CH4}$ in the range −69 to −65‰. Emissions occur from May melt to October freeze-up, and may show an exponential (Arrhenius) increase with temperature [*Nisbet*, 1989; *Westermann and Ahring*, 1987]. Keeling plot experiments by our group reported elsewhere (S. Sriskantharajah, manuscript in preparation, 2011) find a relatively constant source $\delta^{13}C_{CH4}$ −68.5 ± 0.7‰ for wetland emissions from Northern Finland during the summer. Warming permafrost and thermokarst can emit CH_4, made by methanogens from organic matter. The isotopic composition of CH_4 from thermokarst lakes in E. Siberia ranges widely, from −83‰ to −58‰ [*Walter et al.*, 2006]. Fire is another CH_4 source likely to increase with warming and drought. With warm dry summers, such as in Russia in 2010, tundra fires may become more frequent [*Qiu*, 2009]. We report here new results of source studies that have been carried out to identify the isotopic source signature of CH_4 from forest fires in Canada. Source signatures were identified using Keeling plots of CH_4 measured in ambient air collected close to prescribed burns. The mean isotopic composition of CH_4 emitted by a boreal jack pine forest fire in Ontario, Canada (46°47′N, 83°20′W) in May 2007 was −27.8 ± 0.3‰. CH_4 from a mature pine fire in Northwest Territories, Canada (61°21′N, 117°40′W) in June 2010 had a mean isotopic composition of −28.7 ± 0.7‰. These results fall within the range measured for pine forest fire emissions in the United States (−30 to −21‰) [*Chanton et al.*, 2000]. Fire-sourced CH_4, $\delta^{13}C_{CH4}$ around −28‰ for northern pine forests, is isotopically very distinct from wetland CH_4. Increased burning, also fingerprinted by elevated CO, should enrich CH_4 in ^{13}C.

[4] Industrial gas leaks are a major component of global anthropogenic CH_4 emissions, with many of the world's largest gas fields being north of the Arctic circle. The giant gas fields around the Ob estuary supply much of Europe's heat and electric power via long pipelines, and Arctic gas leaks may have contributed in part to the rapid rise in the global CH_4 burden in the 1980s [*Dlugokencky et al.*, 1994]. Gas can escape to the atmosphere both from leaks in wells and pipes, and from normal technical operations [*Reshetnikov et al.*, 2000]. CH_4 from the W. Siberian fields varies isotopically. W Siberian gas measured by the Uni-

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Table 1. $\delta^{13}C$ in Northern Methane Sources

Source	Reference	$\delta^{13}C$ (‰)
Wetland, N. Finland: summer spring thaw autumn freeze-up	S. Sriskantharajah (unpublished data)	−68.5 ± 0.7 −66.3 ± 0.6 −64.9 ± 4.0
Wetland, Hudson Bay Lowlands, Canada	*Kuhlmann et al.* [1998]	−60 ± 3
Tundra, Alaska	*Quay et al.* [1988]	−73 to −55
Wetland, Siberia	*Nisbet* [2005]	−67 ± 2
Ebullition from thermokarst lakes, N. Siberia	*Walter et al.* [2006]	−83 to −58
W Siberian natural gas	*Cramer et al.* [1999]	−51 ± 3
Marine clathrate, W. Spitsbergen	This work	−50 ± 5
Onshore hydrate, Mackenzie delta, Canada	*Lorenson et al.* [1999]	−48.7 to −39.6
Pine forest fires, Canada	This work	−28 ± 1

versity of Heidelberg [*Nisbet*, 2001] and leaked gas in average ambient air in the production region around Korotchaevo tower in the Ob River region measured by our group [*Nisbet*, 2005] has an isotopic signature of −51 ± 2‰, which is comparable to other measurements of W Siberian production gas [*Cramer et al.*, 1999].

[5] CH_4 emitted by decomposing Arctic gas hydrates is also isotopically variable, depending on the original source of the CH_4 trapped in hydrate, or free gas pooled below it, and also on fractionation that may occur on release to the atmosphere. Hydrate is a capacitor, trapping CH_4, not a source *per se*. Thermogenic gas from deep geological carbon stores is relatively rich in ^{13}C. In contrast, gas sourced from biological methanogenesis at shallow levels is richer in ^{12}C. Measurements of CH_4 from decomposing CH_4 hydrate show a wide isotopic range: hydrate gas with $\delta^{13}C_{CH4}$ −62 to −56‰ has previously been measured in the Norwegian Arctic [*Milkov*, 2005]; and ∼−72 to −66‰ in the gas in the Nyegga pockmarks [*Vaular et al.*, 2010]. Extensive Arctic CH_4 hydrates are vulnerable to decomposition with warming [*Nisbet*, 1989], if shallow submarine and terrestrial clathrates destabilise. There is evidence for strong CH_4 ebullition to the atmosphere in response to the warming of shallow offshore sediments of the East Siberian Arctic Shelf in the far eastern Arctic [*Shakhova et al.*, 2010a, 2010b]. In deeper water, CH_4 bubble plumes have recently been identified from the shelf edge west of Spitsbergen [*Westbrook et al.*, 2009].

[6] We report here (Table 2) $\delta^{13}C_{CH4}$ source signatures of −55 ± 2‰ and −46 ± 3‰ in samples of CH_4 hydrate in two sediment cores collected from within the gas hydrate stability zone, during a cruise along the continental slope NW of Spitsbergen in 2008 [*Westbrook et al.*, 2009]. CH_4 in any bubbles that escape from the sea-surface to the atmosphere may be further enriched in ^{13}C following partial oxidation of gas in the water column or sediments, because methanotrophs would preferentially consume the lighter carbon isotope. Isotopic fractionation of CH_4 in the water column has been observed in the nearby Spitsbergen continental shelf [*Damm et al.*, 2005].

3. Experimental Methods

[7] To identify major emissions of Arctic CH_4 and assess their relative inputs to the Arctic CH_4 budget, ambient air samples were collected daily at the Zeppelin station, Spitsbergen, during late summer/autumn 2008, spring 2009 and late summer/autumn 2009. Zeppelin (78°54′N, 11°53′E), at 475 m above sea level is a representative background site normally above the planetary boundary layer with limited influence from local CH_4 sources [*Pedersen et al.*, 2005]. Simultaneously with the summer 2008 campaign, in the nearby Fram Strait, off W. Spitsbergen, intensive air sampling was carried out on the bridge of RRS *James Clark Ross*. Shipboard sampling was repeated during two cruises with RV *Jan Mayen* over the gas plume field in the Fram Strait in July 2009 and October 2010.

[8] Air was collected by pumping into 5 litre tedlar bags. Mixing ratio and $\delta^{13}C$ of atmospheric CH_4 was measured in all air samples in the Dept. of Earth Sciences at Royal Holloway University of London. For air samples collected at Zeppelin in Autumn 2009 and shipboard samples from 2010 CH_4 mixing ratios were measured using a Picarro Cavity Ringdown spectrometer (CRDS) with a repeatability of ±0.3 ppb. For all other air samples CH_4 mixing ratios were determined using an HP 5890 gas chromatograph (GC) with a flame ionization detector (FID) with a repeatability of ±5 ppb. The GC and CRDS instruments are calibrated for CH_4 in the range 1831 to 1965 ppb using NOAA air standards and all CH_4 mixing ratio data are given on the NOAA04 scale [*Dlugokencky et al.*, 2005]. CH_4 $\delta^{13}C$ was analysed using a modified gas chromatography isotope ratio mass spectrometry (GC-IRMS) system (Trace Gas and Isoprime mass spectrometer, Isoprime Ltd.) with 0.05‰ repeatability [*Fisher et al.*, 2006]. All measurements were made in triplicate. Isotope ratios are given in δ-notation on the VPDB (Vienna Pee Dee Belemnite) scale.

4. Results and Discussion

[9] During the summer 2008 cruise, more than 250 plumes of gas bubbles were identified [*Westbrook et al.*, 2009] using a 38 kHz sonar. Plumes were identified in the same area in 2009 (Figure 1). In seawater samples collected in 2008 dissolved CH_4 concentrations were up to 20 times greater at the sea bottom than in the surface waters above the plumes. Some bubble plumes rose close to the sea surface. Despite the proximity of the plumes beneath the ship's track, air collected on the ship did not contain elevated CH_4 compared with contemporaneous samples from Zeppelin (Figure 2), which is located 70 km NW of the observed

Table 2. Hydrate Samples Collected in the Fram Strait in September 2008[a]

Core ID	Location	Seawater Depth (m)	Depth of Hydrate Below Sediment Surface (cm)	$\delta^{13}C_{CH4}$ (‰)
JR211-33-GC	Plume field 78°41.07′N, 08°16.36′E	890 m	>126 cm	−54.6 ± 1.7
JR211-26-GC	Vestnesa ridge 79°00.39′N, 06°54.26′E	1210 m	>193 cm	−45.7 ± 2.7

[a]Methane $\delta^{13}C$ was measured in 3 chips from each sample of hydrate.

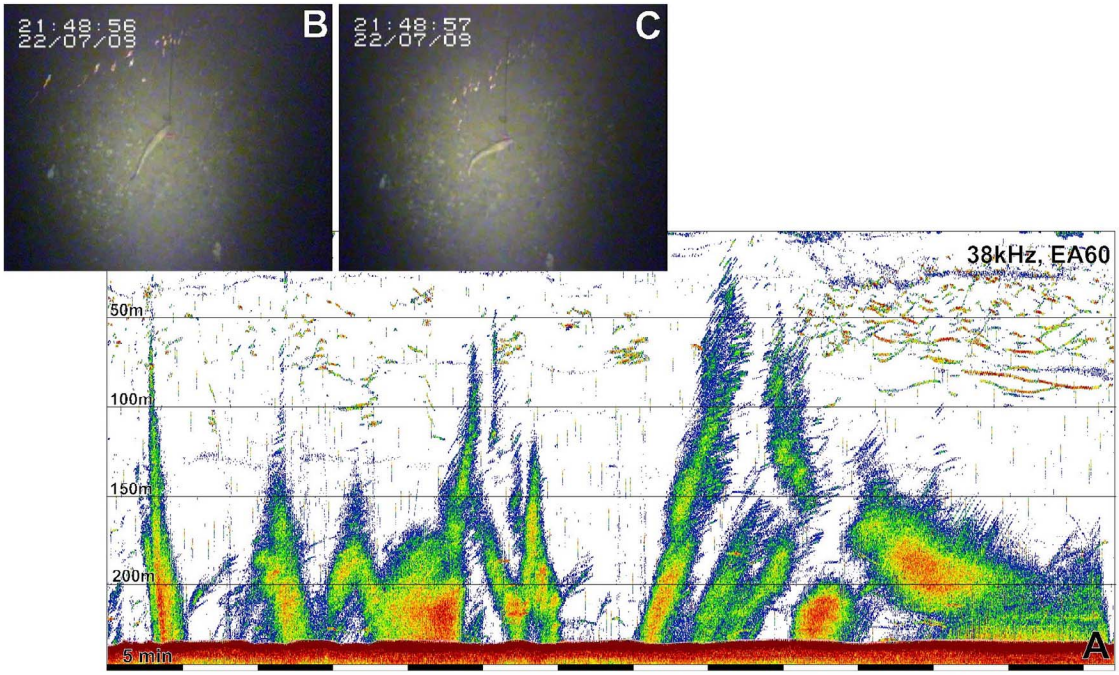

Figure 1. (a) Simrad ER 60 echosounder (38 kHz) showing several flares at an active seep site on the west Spitsbergen slope in 240 m water depth. Horizontal axis shows bars for 5 minute intervals during positioning of the ship for CTD sampling. Distance along the x axis is non-linear as the ship was drifting: for a transect through the plume field on the W. Spitsbergen continental margin see *Westbrook et al.* [2009]. (b and c) Frame grabs of the video survey at the sea floor around this seep and the larger bubbles that contribute to the flares in the echogram. Bubbles visible above the fish in Figures 1b and 1c are about 8 to 10 mm diameter.

plume field. Nor were the shipboard results significantly different isotopically from Zeppelin samples. Probably, complete CH_4 dissolution and gas stripping [*McGinnis et al.*, 2006; *Rehder et al.*, 2009] or methanotrophic oxidation occur as the bubbles rise. Oceanic CH_4 and oxygen measurements following the 2010 Deepwater Horizon oil spill in the Gulf of Mexico [*Kessler et al.*, 2011] showed that rapid methanotrophic oxidation of released CH_4 occurred in the water column. Our results show that seabed CH_4 emissions from much shallower waters, though demonstrably present in the sonar records and water column measurements, did not reach the atmosphere.

[10] Bulk CH_4 inputs to Arctic air may be assessed by sampling air masses from a range of directions, using high precision $\delta^{13}C_{CH4}$ measurement, if isotopic signatures of regional sources are known. The y-intercept of a Keeling plot of $\delta^{13}C_{CH4}$ against $1/CH_4$ mixing ratio in the shipboard and Zeppelin air samples during the period 23 August to 20 September 2008 gives the bulk source input of $\delta^{13}C_{CH4}$ −67.5 ± 1.1‰. This bulk result is strikingly similar to typical wetland emissions, though with the caution that it may record a mix of disparate sources. Additional shipboard campaigns in summer and autumn 2009 and autumn 2010 produced similar results, with CH_4 mixing ratios measured in the gas plume area no higher than those measured at the Zeppelin station. The source signature of CH_4 in these samples was $\delta^{13}C_{CH4}$ −68.6 ± 4.5‰ in July 2009 and −68.7 ± 4.4‰ in October 2010. CH_4 in air sampled daily at the Zeppelin station in September to October 2009 had a $\delta^{13}C_{CH4}$ source signature of −67.4 ± 3.1‰ (Table 3). Destruction of CH_4 by OH is small in the Arctic where OH concentrations are low so there is little isotopic enrichment by reaction with OH over the periods considered. The large observed variations in CH_4 concentration are related to meteorological dynamics in the surface boundary layer with a timescale much shorter than the lifetime of tropospheric CH_4 and the bulk isotopic signature reflects the CH_4 source mix.

[11] The measured bulk input signature at Spitsbergen of ~−68‰ for 2008–10 shows the late summer CH_4 input is dominantly from $\delta^{13}C$ depleted sources such as wetland ($\delta^{13}C_{CH4}$ typically −69‰), or thermokarst (−83 to −58‰) (Table 1). If the mean biogenic source signature is −69 or −70‰, then a simple mass balance equation implies no more than 10% of the −68‰ Arctic summer input to Spitsbergen air can be from isotopically heavier inputs such as gas leaks (circa −51‰), fires, or local clathrate identified on the W Spitsbergen slope (−55 to −46‰).

[12] Any isotopically heavy CH_4 input from boreal fires was small as no large CO excursions were observed during the period. CO mixing ratio measured semi-continuously at the Zeppelin station by the Norwegian Institute for Air Research (NILU) using an in situ RGA3 (Reduction Gas Analyser, Trace Analytical) was compared with the CH_4 mixing ratio measured in the bags collected at the Zeppelin station at the same time. There is a weak correlation (R^2 = 0.49) between excess CO and CH_4 at Zeppelin during the period 09 to 20 September 2008, with a CO:CH_4 ratio of 0.3 ppb(CO)/ppb(CH_4). This is much smaller than the ratio expected from boreal forest fires which would produce

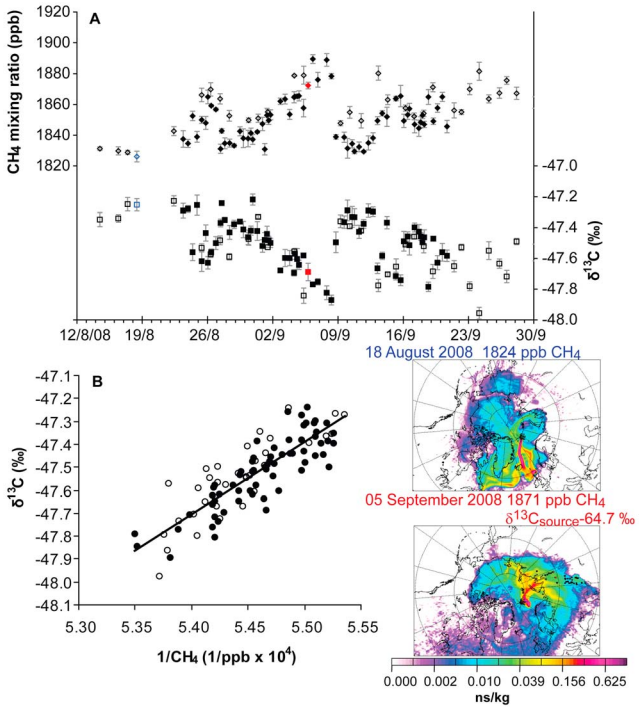

Figure 2. (a) Summer 2008 time series of CH_4 mixing ratio (diamonds) and $\delta^{13}C_{CH4}$ (squares) in ambient air at the Zeppelin station (hollow) and on the RRS James Clark Ross in the Fram Strait (filled). Error bars denote one standard deviation in triplicate measurements of each air sample. (b) Corresponding Keeling plot. The y axis intercept of the Keeling plot is −67.5 ± 1.1‰. FLEXPART footprint emission sensitivity plots using ECMWF wind fields are shown for air arriving at Zeppelin from the Atlantic on 18 August (blue points on Figure 2a) and from Northern Siberia on 05 September (red points on Figure 2a).

CO and CH_4 with a CO:CH_4 ratio of between 12 and 38 ppb/ppb [*Cofer et al.*, 1998]. Given the proximity of giant Russian Ob River gasfields, which are known to emit at least some leakage in summer [*Reshetnikov et al.*, 2000], some part of the isotopically heavier contribution to the bulk mix must come from gas fields.

[13] In contributing to the $\delta^{13}C_{CH4}$ −68‰ signature of the bulk CH_4 increment measured at Zeppelin, the total local clathrate input during the sampling period is likely to have been very small. Note however this does not exclude inputs from isotopically lighter shallow-sourced CH_4 emitted from clathrates further afield such as in the eastern Arctic. Our results from the high Arctic are consistent with the finding in 1999 in mid-latitude boreal wetland along the Trans-Siberian railroad and Ob river, that $\delta^{13}C_{source}$ = −62.9 ± 0.7‰, which suggested CH_4 from wetlands dominated the substantial CH_4 excess in western Siberia [*Tarasova et al.*, 2006].

[14] In spring, when Arctic wetland is still frozen, the CH_4 in air samples is significantly more enriched in ^{13}C (Figure 3). In March to May, the bulk Arctic source signature, calculated from measurements in air samples collected daily at the Zeppelin station, gives an Arctic springtime source with $\delta^{13}C_{CH4}$ −52.6 ± 6.4‰. This difference from summer is consistent with observations in the Hudson Bay Lowlands where boreal wetland has a sharp seasonal onset of emissions in June and a seasonal switch-off in September [*Pickett-Heaps et al.*, 2010]. Most likely the dominant Arctic sources in winter and spring are gas field emissions. Some (aseasonal) clathrate-derived contribution to this relatively heavy springtime signature is also possible, but given the summer result, local clathrate sources are likely to be small. More remote clathrate sources may contribute if flaw polynas (ice free regions) allow release of CH_4 from shallow clathrate to the Arctic atmosphere during the winter. However, in this spring study very few air masses arrived at Zeppelin with trajectories from known emission areas on the East Siberian Arctic Shelf region [*Shakhova et al.*, 2010a, 2010b].

[15] Footprint emission sensitivities for air arriving at Zeppelin and at the ship were calculated using the Lagrangian particle dispersion model, FLEXPART [*Stohl et al.*, 1998]. The highest CH_4 mixing ratios were measured in air masses from Siberia. The atmospheric transport on a twenty-day timescale shows that the Zeppelin observatory is highly sensitive to surface emissions in the Arctic and particularly to emissions in high latitude Eurasia in winter [*Hirdman et al.*, 2010]. Emissions that led to the highest observed CH_4 mixing ratios in the summer 2008 study period (04–08 September) were from northern Siberia, crossing a large area from the Ob River to Eastern Siberia, including the East Siberian Arctic Shelf. The mean source signature, $\delta^{13}C_{CH4}$, for these specific days was −65 ± 3‰. Assuming only wetland (−69‰) and gas leaks (−51‰) are responsible for this CH_4, then this signature may be apportioned to 78% wetlands and 22% gas leak, but there may also be significant input from East Siberian Arctic Shelf emissions [*Shakhova et al.*, 2010b] with variable $\delta^{13}C$. Air from Canada and Greenland also had high CH_4 content (19th to 20th September) with an isotopic source signature of −69‰, indicating Canadian wetland sources dominated [*Kuhlmann et al.*, 1998].

5. Summary and Conclusions

[16] The results imply the dominant Arctic summer CH_4 source in 2008 and 2009 was biogenic, from wetland. This is consistent with evidence from Siberia of the importance of wetland CH_4 [*Tarasova et al.*, 2009]. In winter, gas emissions dominate the CH_4 input. Submarine emissions along the West Spitsbergen slope currently input negligible CH_4 to the air in summer, despite the clear evidence for gas plumes in the water column. However, this could change rapidly if a warming Atlantic warms the West Spitsbergen

Table 3. Methane Source Signatures Calculated From Daily or Twice Daily Sampling at the Zeppelin Station (Ny-Ålesund, Spitsbergen) and in the Fram Strait[a]

Sampling Site	Dates	$\delta^{13}C_{CH4}$ (‰)
Zeppelin	14th August–14th October 2008	−68.7 ± 2.4
Zeppelin	6th March–9th May 2009	−52.6 ± 6.4
Zeppelin	5th September–4th October 2009	−67.4 ± 3.1
Fram Strait	23rd August–20th September 2008	−66.9 ± 1.3
Fram Strait	21st July–26th July 2009	−68.6 ± 4.5
Fram Strait	9th October–28th October 2010	−68.7 ± 4.4

[a]The source signatures were given by the y-axis intercept of a Keeling plot of the data from each period listed, using a geometric mean regression.

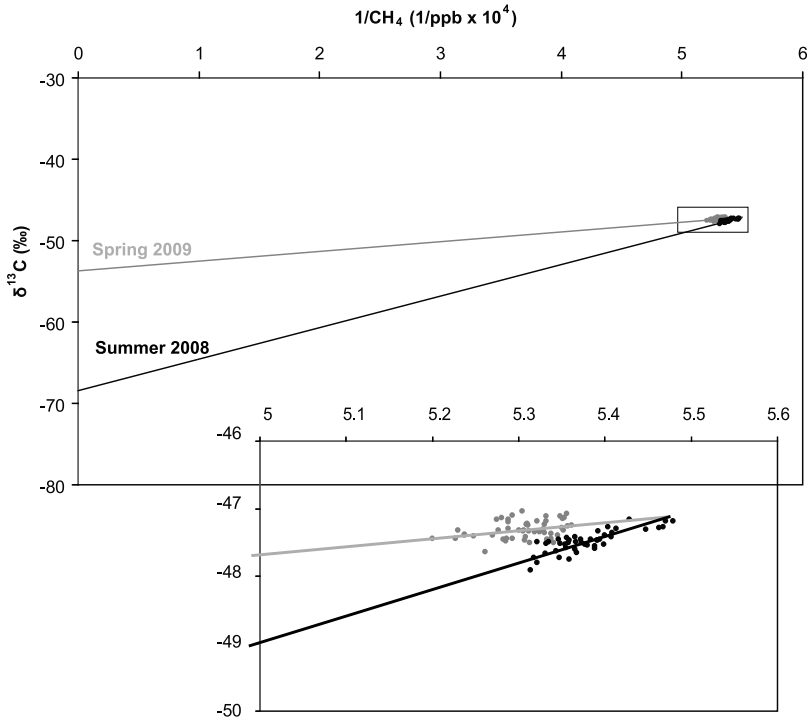

Figure 3. Keeling plot of methane mixing ratio and $\delta^{13}C$ in ambient air sampled at the Zeppelin station during August to October 2008 (black) and March to May 2009 (grey). Y axis intercepts are −68.7 ± 2.4‰ (R^2 = 0.65) in summer/autumn 2008 and −52.6 ± 6.4‰ (low correlation, R^2 = 0.14) in spring 2009.

current [*Westbrook et al.*, 2009]. Gas hydrates are widespread in thick sediments in the Fram Strait between Spitsbergen and Greenland. If the sea bottom warms, the gas hydrate stability zone will move further down the continental slope. Given the steep slopes, earthquakes triggered by ice-melt unloading could produce submarine landslides, triggering further emissions [*Berndt et al.*, 2009].

[17] Wetland CH_4 emissions respond rapidly to warming, such that the warming can feed the warming [*Nisbet and Ingham*, 1995], as evidenced by their importance in glacial terminations [*Nisbet and Chappellaz*, 2009]. In particular, Arctic and boreal wetlands are likely to respond immediately to sustained heatwaves and increases in precipitation. Fire CH_4 is also more likely with elevated temperatures. There is a strong need for more regular CH_4 isotopic measurements in the high Arctic and intercomparison with the isotopic data from flasks currently collected at Barrow [*Miller et al.*, 2002], Alert [*Dlugokencky et al.*, 2009; *Nisbet*, 2005] and Zeppelin to measure bulk inputs of CH_4 to the Arctic. Isotopic data can then be used to constrain emissions in both regional and global inversion models [*Bousquet et al.*, 2006]. High frequency, ideally continuous, monitoring of CH_4 $\delta^{13}C_{CH4}$ from a number of Arctic sites, onshore and offshore, will be important if future changes in Arctic sources are to be quantified.

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