Tellus SERIES B CHEMICAL AND PHYSICAL METEOROLOGY
PUBLISHED BY THE INTERNATIONAL METEOROLOGICAL INSTITUTE IN STOCKHOLM

Stable carbon isotope signatures of methane from a Finnish subarctic wetland

By S. SRISKANTHARAJAH[1], R. E. FISHER[1], D. LOWRY[1], T. AALTO[2], J. HATAKKA[2], M. AURELA[2], T. LAURILA[2], A. LOHILA[2], E. KUITUNEN[2] and E. G. NISBET[1]*, [1]*Department of Earth Sciences, Royal Holloway University of London, Egham TW20 0EX, UK;* [2]*Finnish Meteorological Institute, Climate Change Research, P.O. Box 503, FI-00101 Helsinki, Finland*

(Manuscript received 27 August 2011; in final form 17 May 2012)

ABSTRACT

Methane emissions from Lompolojänkkä, a Finnish aapa mire within the Arctic Circle, were studied by non-intrusive Keeling plot methods, to place better constraints on the seasonal variations in isotopic signature of methane ($\delta^{13}C_{CH4}$) emitted from Arctic wetland. Air samples were collected in Tedlar bags over the wetland at heights of 42 and 280 cm between May and October 2009 and in August 2008. The mixing ratio and $\delta^{13}C$ of the methane in the samples were incorporated into Keeling plot analyses to derive bulk $\delta^{13}C_{CH4}$ signatures for the methane inputs to the air above the wetland. The results show an unexpected consistence in $\delta^{13}C_{CH4}$ from early to late summer, clustered around -68.5 ± 0.7‰, but during spring thaw and autumnal freezing, $\delta^{13}C_{CH4}$ is enriched by approximately 2 and 4‰, respectively. The techniques reported in this paper are simple and economical to employ, and give a bulk source signature for the methane inputs to the air above the entire wetland that can be extrapolated to a larger regional area.

Keywords: Methane, carbon isotopes, Arctic wetland, Finland, greenhouse gas

1. Introduction

Methane from Arctic wetland is closely implicated in past rapid climate change (Nisbet and Chappellaz, 2009). Mean annual temperatures are currently rising two times faster in the Arctic than the global average temperature (Rodrigues, 2008). This change is extending the growing season significantly and is likely to increase methane emissions from northern wetlands. It is thus important to develop ways of characterising Arctic and boreal emissions so that the northern inputs to the global budget can be specifically quantified. Isotopic methods in particular offer powerful tools in characterising the signatures of northern emissions.

In 2007, after a long period of near stability, global annual methane mixing ratios rose suddenly (Rigby et al., 2008; Kaufman et al., 2009; Dlugokencky et al., 2009, 2011). The rise might partly be attributed to methane sources in the Arctic (Rigby et al., 2008; Dlugokencky et al., 2009) where summer 2007 brought spectacular sea ice retreat (Comiso et al., 2008) and an intense heatwave in the Siberian Arctic (Rodrigues, 2008). Arctic wetland is most active between the thaw in spring and the freeze in autumn, and this is the time when methane fluxes to air are highest (Christensen et al., 2003; Tokida et al., 2007; Mastepanov et al., 2008). This study was designed to characterise these emissions isotopically.

Most isotopic measurements of methane emissions depend on small-scale chamber studies. Unless the wetland is very homogenous, local microbial consortia under the chamber may differ from the wider wetland. Some parts of the wetland may experience higher fluxes at certain times than other parts (Moore et al., 1990). Even if the selected area under the chamber is fully representative of the wetland as a whole, the chamber itself may create local, disturbed microenvironments within the trapped air, where pressures and temperatures may differ from ambient conditions.

In contrast, bulk emissions from wide areas of wetland can be measured in campaigns sampling diel (24-hour period, over the day/night cycle) variations in methane in ambient air, under conditions when there is a build up of methane under nocturnal inversions (Quay et al., 1988;

*Corresponding author.
email: e.nisbet@es.rhul.ac.uk

Citation: Tellus B 2012, **64**, 18818, http://dx.doi.org/10.3402/tellusb.v64i0.18818

Levin et al., 1993; Lowry et al., 2001). These diel sampling campaigns allow the calculation of an isotopic signature that is better representative of methane from across the whole wetland. The isotopic signature of the methane source is identified from the intercept of Keeling plots, a graphical technique in which $\delta^{13}C_{CH4}$ is plotted against the reciprocal of the CH_4 mixing ratio (Keeling, 1958, 1961; Levin et al., 1993; Lowry et al., 2001; Pataki et al., 2003; Miller and Tans, 2003; Cuna et al., 2008).

This method allows local inputs to a regional background to be identified and characterised and has the great advantage that it does not intervene in, or in any way disturb, the source. The method measures only the methane that is actually emitted into the air, which is of particular interest in assessing the changing contribution of wetlands to the regional methane budget. By characterising specific sources of Arctic methane emissions, it may be possible to determine if new or increased methane sources may be responding to global warming (Fisher et al., 2011).

2. Methodology

We report bulk $\delta^{13}C_{CH4}$ signatures of methane emitted from subarctic wetland, using isotopic fingerprinting by Keeling plot analysis. This study was conducted in Pallas, Finnish Lapland, which is within the Arctic Circle. Mean wetland methane emissions in the northern zone of the country are estimated at $23\,g\,m^{-2}\,yr^{-1}$. (Huttunen et al., 2003). Approximately $42\,000\,km^2$ of land in Finland is wetland (Vasander, 1996).

2.1. Location

Air samples were taken at a wetland site, Lompolojänkkä (67°59.832′N, 24°12.551′E, 269 m a.s.l.), that covers an area of approximately $12\,000\,m^2$ (Aurela et al., 2009; Lohila et al., 2010). The station is run by the Finnish Meteorological Institute (FMI) and contributes to the UN World Meteorological Organisation's *Global Atmosphere Watch* programme (Hatakka et al., 2003; Aalto et al., 2007).

The Lompolojänkkä site is an open, rich fen. The field layer, which is quite dense, is dominated by *Betula nana*, *Menyanthes trifoliata* and *Salix lapponum*. One-sided leaf area index at the peak season is about $1.3\,m^2\,m^{-2}$. Moss cover of the ground layer is patchy (57%), dominated by peat mosses (*Sphagnum angustifolium*, *Sphagnum riparium* and *Sphagnum fallax*) and some brown mosses (*Warnstorfia exannulata*) (Aurela et al., 2009).

The peat depth at the site varies up to 2 m. The mean water level is relatively high, only seldom falling to a few centimetres below the peat surface, meaning that nearly the whole peat profile is water saturated throughout the year. The long-term annual air temperature is −1.4°C and annual precipitation is 484 mm measured at the nearmost long-term weather station run by FMI (Alamuonio, 67°58′N, 23°41′E) (Drebs et al., 2002).

2.2. Sampling

Ambient air samples were collected from a fixed location near the centre of Lompolojänkkä at heights of 42 and 280 cm above the wetland throughout diel periods during which there was night-time methane build up. The campaigns were carried out at distinct points in the growing season: spring thaw, early summer, late summer and autumn (5–6 August 2008, 4–5 May 2009, 15–17 June 2009, 8–10 August 2009 and 8–9 October 2009). Samples were collected at both heights at 1-hour intervals using identical battery-operated pumps (flow rate $2\,l\,min^{-1}$). To remove contamination, connections and tubing were flushed with wetland air for 30 s before samples were collected in 5 l clear Tedlar bags. A maximum 4 l of sample was collected in each Tedlar bag to ensure that the Tedlar bags did not burst during transit. The Tedlar bags were kept in opaque boxes and were analysed in the laboratory within 2 weeks of collection. Our previous laboratory studies (RHUL) had shown that methane mixing ratio and isotopic ratio were well conserved in Tedlar under these conditions.

Air samples were also taken from stainless steel chambers for comparison with the ambient air samples. Samples were collected using battery-operated pumps (flow rate $2\,l\,min^{-1}$) that were identical to the pumps used for the ambient air sampling. Tubing and connections were flushed with sample air to remove contamination before samples were collected into 3 l clear Tedlar bags (filled to 2.5 l). Samples were taken from manual chambers (22 l) and fixed automatic chambers (240 l) in June and August, but in May and October when the automatic chambers were not in operation (due to weather conditions) only manual chambers were used. Lohila et al. (2010) describe these chambers in more detail.

The manual chambers were placed into the wetland water (10 cm below the surface) to ensure the chamber was sealed from the atmosphere. Before sampling began the chambers were left open to ensure that any gas emitted from the wetland during the placing of the chamber did not remain in the chamber. Chambers were closed for 10 min and air samples were obtained at $t = 0$ min and $t = 10$ min.

2.3. Analytical methods

Methane mixing ratios were analysed in triplicate using an HP 5890 Gas Chromatograph – Flame Ionization Detector system with a repeatability of better than ± 5ppb (quoted to 1σ as are all the uncertainties in this study) during the

analysis period. Calibration was against US National Oceanic and Atmospheric Administration (NOAA) standards. Methane was converted to CO_2 for stable carbon isotope analysis ($\delta^{13}C_{CH4}$) using a Trace Gas pre-concentrator (Micromass, Manchester, UK). The continuous flow of He carries the liberated CO_2 from the pre-concentrator to an IsoPrime mass spectrometer. Full details of the operation of the Trace Gas pre-concentrator can be found in the study of Fisher et al. (2006). Analytical repeatability for $\delta^{13}C_{CH4}$ is better than $\pm 0.05‰$.

$\delta^{13}C_{CH4}$ are reported relative to Vienna Pee Dee Belemnite and are calculated as follows:

$$\delta^{13}C(‰) = [(R_{sample}/R_{std}) - 1] \times 1000$$

where R_{sample} and R_{std} are the $^{13}C/^{12}C$ ratio of the sample and standard, respectively. The instrument is first calibrated for $\delta^{13}C_{CO2}$ in air close to $-8‰$ using an air standard provided by NOAA for which $\delta^{13}C_{CO2}$ has been measured by the INSTAAR Stable Isotope Laboratory, University of Colorado. A mass spectrometer scale compression correction is then applied to more depleted values based on analysis of US National Institute of Standards ad Technology (NIST) CO_2 isotopic standards.

The vertical CH_4 flux from soil to atmosphere was measured at a height of 3 m using the eddy covariance method (Baldocchi, 2003; Rinne et al., 2007). The instrumentation included a USA-1 (METEK, Meteorologische Messtechnik GmbH, Elmshorn, 25337-D) three-axis sonic anemometer/thermometer and an RMT-100 (Los Gatos Research, Mountain View, CA, USA) CH_4 gas analyser. Further details are given by Aurela et al. (2009).

3. Results and discussions

The campaigns are discussed individually below. To illustrate a typical result, Fig. 1 shows methane mixing ratio and $\delta^{13}C$ measured throughout the first diel period in 5–6 August 2008. There was an overnight build up in methane under an inversion with corresponding depletion in $\delta^{13}C_{CH4}$. The source signature derived from this event is the intercept of a geometric mean regression. Keeling plot discrimination of all diel campaign samples is shown in Fig. 2.

3.1. Summer campaign

Bulk methane emissions during early to late summer were tightly clustered. The mean $\delta^{13}C_{CH4}$ from the campaigns on 5–6 August 2008, 15–17 June 2009 and 8–10 August 2009 was $-68.5 \pm 0.7‰$. The diel campaign measurements of source signatures in August 2008 and August 2009 were essentially indistinguishable (Table 1).

This finding is close to the $-67.2‰$ result of a diel campaign in the Ob River wetlands (Lowry et al., 2004; Meth-MonitEUr, 2005), and comparable to older results in Russia around -69 to $-62‰$ (Ovsyannikov and Lebedev, 1967; Bergamaschi et al., 1998; Tarasova et al., 2006)

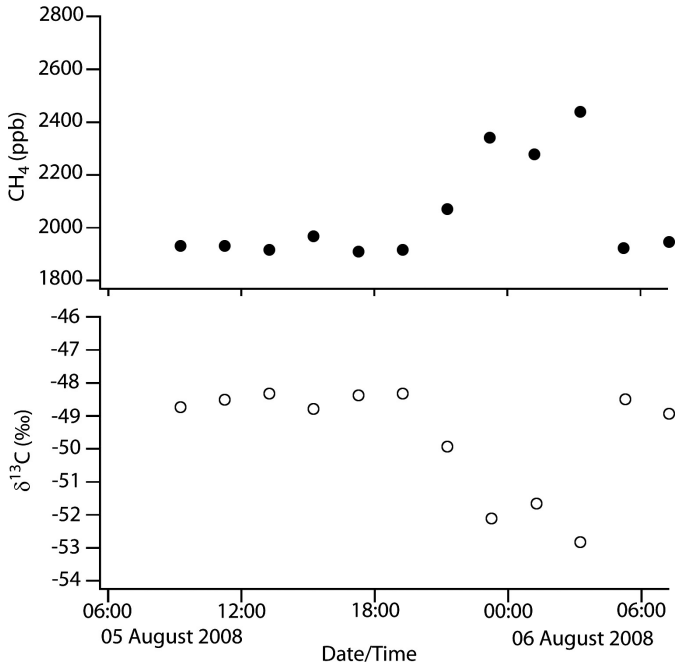

Fig. 1. Methane mixing ratio and $\delta^{13}C$ measured in air samples collected at 42 cm above ground level throughout a diel period, 5–6 August 2008.

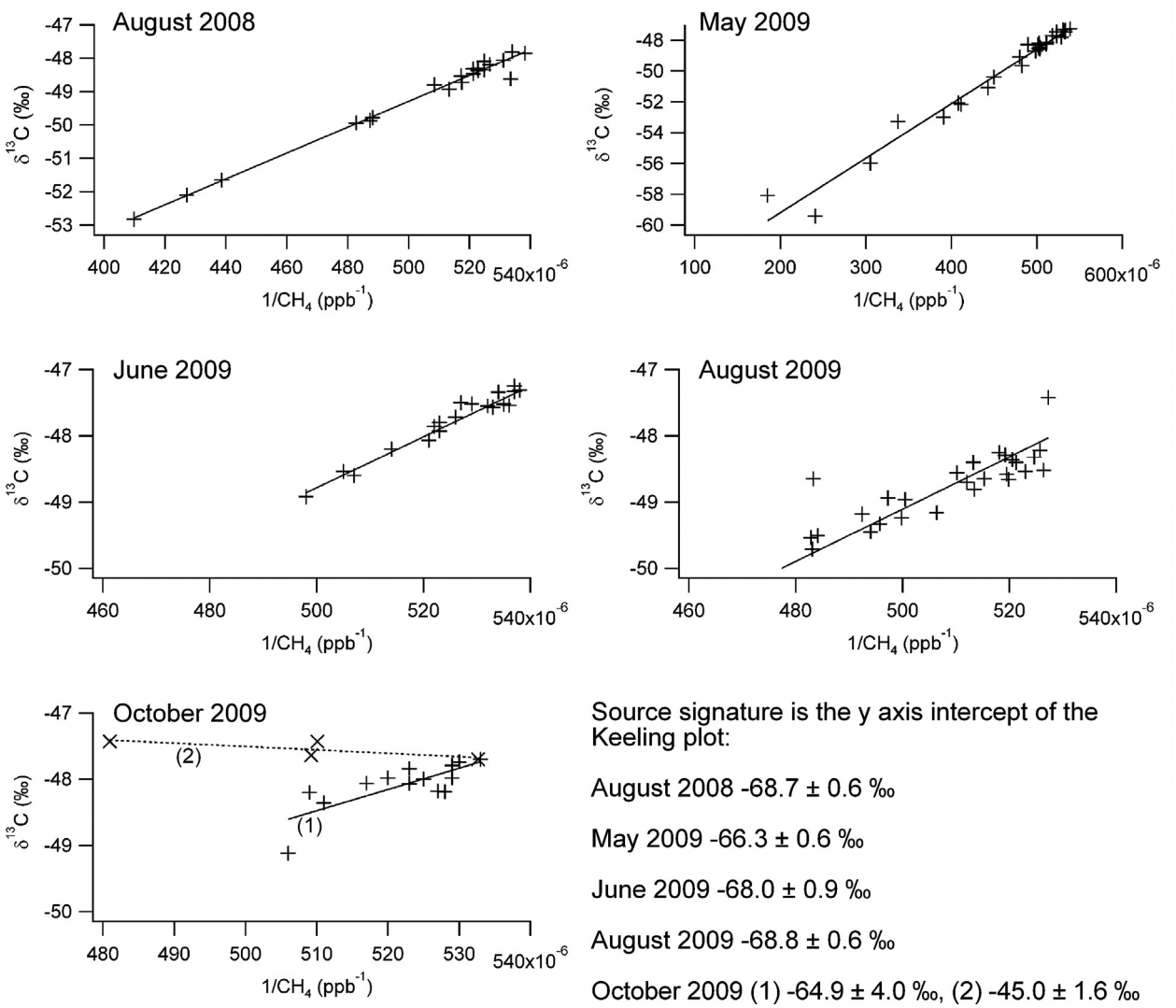

Fig. 2. Keeling plots showing the source signature of methane from Lompolojänkkä from spring thaw to autumn freeze in 2009. Also included is the Keeling plot for the sampling in August 2008, showing that the summer source signature did not change between 2008 and 2009. The source signature in each case is the intercept of a geometric mean regression. The uncertainty given is the *SE* in the intercept from the regression.

and $-64 \pm 5‰$ in Alaska (Quay et al., 1988). This pan-Arctic uniformity, though surprising, may reflect the similar conditions of temperature and moisture across the Arctic. Interestingly, warmer Minnesota wetland in summer also emitted methane with $\delta^{13}C_{CH4} -67.2 \pm 1‰$ (Stevens and Engelkemeir, 1988). Also in Minnesota, Quay et al. (1988) found very similar values of $\delta^{13}C_{CH4}$ around $-66 \pm 5‰$.

3.2. Spring thaw

The bulk $\delta^{13}C_{CH4}$ signature during the spring thaw was measured in the diel experiment of 4–5 May 2009. For this campaign, $\delta^{13}C_{CH4}$ was $-66.3 \pm 0.6‰$, an approximate 2‰ increase relative to the summer signature. The enrichment of the May signature compared with the summer signature is small but is statistically significant (Table 1).

High spring fluxes have been observed at Stordalen mire in Sweden (Friborg et al., 1997), which is at a comparable latitude to Lompolojänkkä. Neither Stordalen nor Lompolojänkkä has permafrost, and there may be some modest winter methane production within lower Arctic latitude wetlands. This winter-accumulated methane could give rise to the isotopic shift, if it reflects a burst of methane emissions seen during the spring thaw. One possibility is

Table 1. Comparison of wetland methane source signatures calculated from diel and chamber samples in 2009 and some examples from other studies

Study period	*$\delta^{13}C_{CH4}$ calculated from diel campaign (‰)*	*Average $\delta^{13}C_{CH4}$ calculated from all chambers (‰)*	*Range of $\delta^{13}C_{CH4}$ calculated from chambers (‰)*
5–6 August 2008	−68.7 ± 0.6	−65.8 ± 0.7	−66.5 to −65.1 (n = 6)
4–5 May 2009	−66.3 ± 0.6	−67.4 ± 0.5	−67.7 to −66.7 (n = 15)
15–17 June 2009	−68.0 ± 0.9	−68.7 ± 3.8	−76.8 to −61.9 (n = 13)
8–10 August 2009	−68.8 ± 0.6	−64.5 ± 1.8	−68.1 to −61.0 (n = 23)
8–9 October 2009	−64.9 ± 4.0	−66.1 ± 1.7	−67.9 to −62.7 (n = 8)
Location	*$\delta^{13}C_{CH4}$ (‰)*	*References*	
Ob River Wetlands: Meth-MonitEUr study	−67.2	Lowry et al. (2004) and Meth-MonitEUr (2005)	
Russia – various	−69 to −62	Ovsyannikov and Lebedev (1967), Bergamaschi et al. (1998) and Tarasova et al. (2006)	
Alaska	−64 ± 5	Quay (1988)	
Minnesota wetland	−67.2 ± 1	Stevens and Engelkemeir (1988)	
	−66 ± 5	Quay et al. (1988)	

Numbers in parentheses denote the number of individual chamber experiments.

that winter-produced methane may be isotopically similar to summer methane, but that methanotrophy may occur during winter and early spring, which may selectively consume $^{12}CH_4$, leaving an enriched remnant for emission during spring thaw.

3.3. *Autumn freeze*

During the campaign of 8–9 October 2009, we did not observe a strong night-time build-up of methane, possibly because of the lack of development of a stable nocturnal boundary layer. Flux measurements (Fig. 4) do show small peaks though they are not obviously correlated with temperature. The assessed bulk signature, $\delta^{13}C_{CH4}$ −64.9‰, therefore has a large *SE* of ±4.0‰ and is comparable to the summer results.

Interestingly during the freeze-up campaign, once the main wetland had been frozen over for some hours and the wind speeds were low, the low methane flux from the local wetland allowed a second methane input to be detected, with a bulk $\delta^{13}C_{CH4}$ signature of −45.0 ± 1.6‰. This input was most noticeable at the 280 cm sampling height, implying that it was from a remote source. This ^{13}C enriched signature may reflect an influence from fossil fuel or other fuel burning sources in the regional source mix.

In Greenland, spring thaw emissions were less pronounced than emissions during the autumn freeze (Mastepanov et al., 2008). We found the opposite: methane fluxes during the spring thaw were higher than during the autumn freeze (Figs. 3 and 4). It may be that our observation of stronger spring emissions reflect release

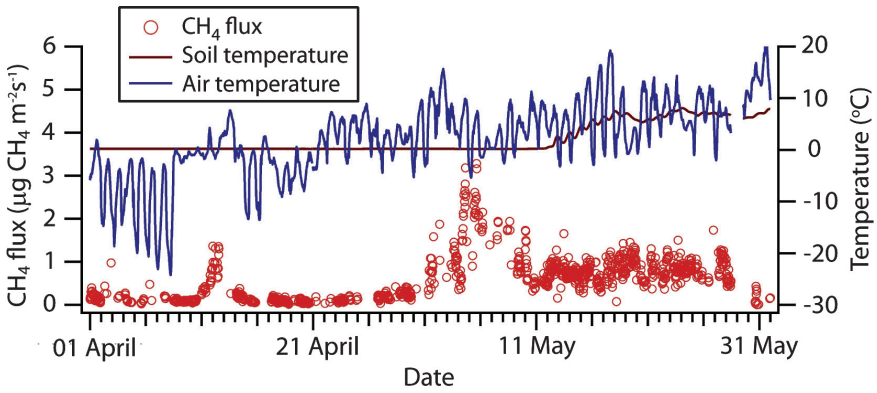

Fig. 3. Methane fluxes, air and soil temperatures (at 7 cm below the surface) observed at Lompolojänkkä during the spring thaw in May 2009. The methane flux is derived on site using the eddy covariance technique. The methane flux increases rapidly between 4 and 5 May.

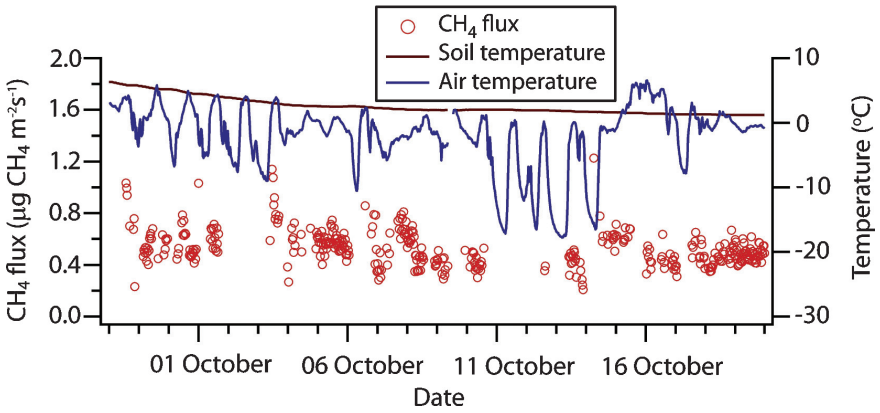

Fig. 4. Methane fluxes seen during the freezing of Lompolojänkkä wetland during autumn 2009. The decreasing flux correlates with the decreasing soil temperature (measured at 7 cm below the surface).

of winter-produced methane (see above), while the presence of permafrost would restrict winter methane production in Greenland. However, we note the burst observed by Mastepanov et al. (2008) was not found in subsequent years, which would imply significant year-on-year variations as would be expected intuitively.

4. Comparison of diel and chamber sampling techniques

In this study, the *SD*s using the chamber technique are mostly greater than those obtained through the diel technique (Table 1). It has been observed that spatial and temporal variations in results occur when using chambers to calculate source signatures (Kuhlmann et al., 1998). This could be the reason for both the bigger range and enrichment of the source signature calculated from chamber measurements in our study. Closure of a chamber for 10 min is an intervention in the normal functioning of the wetland, but it is essential to allow a long enough closure to ensure a significant build up of methane during the sampling period.

The diel technique has the great advantage of being non-intrusive. It allows measurement of an integrated signature over a wide wetland area. Though chamber methods are suited for local studies, for assessment of bulk emissions to air in the study of Arctic greenhouse gas inputs, the diel methodology is superior.

5. Conclusions

The data show that methane from Finnish Arctic wetlands, with $\delta^{13}C_{CH4}$ around -69 to $-68‰$, is isotopically recognisable from other Arctic methane sources. As discussed above (Section 3.1), our $\delta^{13}C_{CH4}$ results are closely comparable to the $-67 \pm 2‰$ measurement in W. Siberian wetland during the Meth-MonitEUr project (Meth-MonitEUr, 2005), and to other measurements of summer wetland emissions in Russia, Alaska and Minnesota. Slight enrichment of the bulk source signature was seen during spring and autumn, unrelated to flux. This isotopic enrichment is likely to reflect release of methane made during periods of reduced substrate availability for methanogenesis, at lower temperatures or under near-frozen conditions.

The characteristic summer $\delta^{13}C_{CH4}$ signature of methane from boreal wetland worldwide thus appears to be in the range of -69 to $-65‰$. Therefore, it is possible (Fisher et al., 2011) by sampling at remote stations such as Zeppelin (Spitsbergen), and by using Lagrangian back-trajectory analysis, to identify and distinguish northern wetland methane emissions from other sources such as Russian Siberian Arctic gas emissions, approximately $-50‰$ (Lowry et al., 2004) and clathrate emissions in the Arctic Ocean which vary from $-60‰$ to about $-45‰$ (Milkov, 2005; Fisher et al., 2011). Routine isotopic characterisation of air collected at remote stations, coupled with trajectory study, thus provides a powerful method of monitoring Arctic and boreal methane emissions as they respond to global change, and assessing the relative importance of inputs, source type by source type, as they change.

The results also constrain interpretation of $\delta^{13}C_{CH4}$ records in ice core studies of glacial and post-glacial changes. Wetland is strongly implicated in the rapid changes in methane mixing ratio at the end of the Younger Dryas (Nisbet and Chapellaz, 2009). Given this past history and the concern over present change, there is now a strong case for continuous monitoring of $\delta^{13}C_{CH4}$ in Arctic air.

6. Acknowledgements

This study was supported by the European Union's IMECC, GEOmon and NITROEUROPE programmes, NERC-UK awards NE/F020937/1 and NE/I014683/1 and the Finnish Meteorological Institute. We particularly thank the referees for very helpful and constructive comments that have been much appreciated for their detailed technical insight (and for pointing out the difference between diel and diurnal). Their careful help has greatly improved the work.

References

Aalto, T., Hatakka, J. and Lallo, M. 2007. Tropospheric methane in Northern Finland: seasonal variations, transport patterns and correlations with other trace gases. *Tellus Ser. B* **59**, 251–259.

Aurela, M., Lohila, A., Tuovinen, J.-P., Hatakka, J., Riutta, T. and co-authors. 2009. Carbon dioxide exchange on a northern boreal fen. *Bor. Environ. Res.* **14**, 699–710.

Baldocchi, D. 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future. Glob. *Change Biol.* **9**, 479–492.

Bergamaschi, P., Brenninkmeijer, C., Hahn, M., Röckmann, T., Scharffe, D. and co-authors. 1998. Isotopic analyses based source identification for atmospheric CH_4 and CO sampled across Russia using the Trans-Siberian railroad. *J. Geophys. Res.* **103**, 8227–8235.

Christensen, T. R., Ekborg, A., Ström, L., Mastepanov, M., Panikov, N. and co-authors. 2003. Factors controlling large scale variations in methane emissions from wetlands. *Geophys. Res. Lett.* **30**(7), 10–13.

Comiso, J. C., Parkinson, C. L., Gersten, R. and Stock, L. 2008. Accelerated decline in the Arctic sea ice cover. *Geophys. Res Lett.* **35**, L01703.

Cuna, S., Pendall, E., Miller, J. B., Tans, P. P., Dlugokencky, E. and co-authors. 2008. Separating contributions from natural and anthropogenic sources in atmospheric methane from the Black Sea region, Romania. *Appl. Geochem.* **23**, 2871–2879.

Dlugokencky, E. J., Bruhwiler, L., White, J. C. W., Emmons, L. K, Novelli, P. C. and co-authors. 2009. Observational constraints on recent increases in the atmospheric CH_4 burden. *Geophys. Res. Lett.* **36**, L18803.

Dlugokencky, E. J., Nisbet, E. G., Fisher, R. and Lowry, D. 2011. Global atmospheric methane in 2010: budget, changes and dangers. *Phil. Trans. R. Soc. A* **369**, 2058–2072.

Drebs, A., Nordlund, A., Karlsson, P., Helminen, J. and Rissanen, P. 2002. Tilastoja suomen ilmastosta 1971–2000 (Climatological statistics of Finland 1971–2000). Helsinki: Finnish Meteorological Institute.

Fisher, R., Lowry, D., Wilkin, O., Sriskantharajah, S. and Nisbet, E. G. 2006. High precision, automated stable isotopic analysis of atmospheric methane and carbon dioxide using continuous-flow isotope-ratio mass spectrometry. *Rapid Commun. Mass Spectrom.* **20**, 200–208.

Fisher, R. E., Sriskantharajah, S., Lowry, D., Lanoisellé, M., Fowler, C. M. R. and co-authors. 2011. Arctic methane sources: isotopic evidence for atmospheric inputs. *Geophys. Res. Lett.* **38**, L21803. DOI: 10.1029/2011GL049319.

Friborg, T., Christensen, T. R. and Soegaard, H. 1997. Rapid response of greenhouse gas emission to early spring thaw in a subarctic mire as shown by micrometeorological techniques. *Geophys. Res. Lett.* **24**, 3061–3064.

Hatakka, J., Aalto, T., Aaltonen, V., Aurela, M., Hakola, H. and co-authors. 2003. Overview of the atmospheric research activities and results at Pallas GAW station. *Bor. Environ. Res.* **8**, 365–383.

Huttunen, J. T., Nykänen, H., Turunen, J. and Martikainen, P. J. 2003. Methane emissions from natural peatlands in the northern boreal zone in Finland, Fennoscandia. *Atmos. Environ.* **37**, 147–151.

Kaufman, D. S., Schneider, D. P., McKay, N. P., Ammann, C. M., Bradley, R. S. and co-authors. 2009. Recent warming reverses long-term Arctic cooling. *Science* **325**, 1236–1239.

Keeling, C. D. 1958. The concentration and isotopic abundance of atmospheric carbon dioxide in rural areas. *Geochim. Cosmochim. Ac.* **13**, 322–334.

Keeling, C. D. 1961. The concentration and isotopic abundances of carbon dioxide in rural and marine air. *Geochim. Cosmochim. Ac.* **24**, 277–298.

Kuhlmann, A. J., Worthy, D. E. J., Worthy, N. B. A. and Levin, I. 1998. Methane emissions from a wetland region within the Hudson Bay lowland: an atmospheric approach. *J. Geophys. Res.* **103**, 16009–16016.

Levin, I., Bergamaschi, P., Dörr, H. and Trapp, D. 1993. Stable isotopic signature of methane from major sources in Germany. *Chemosphere* **26**, 161–177.

Lohila, A., Aurela, M., Hatakka, J., Pihlatie, M., Minkkinen, K. and co-authors. 2010. Responses of N_2O fluxes to temperature, water table and N deposition in a northern boreal fen. *Eur. J. Soil Sci.* **61**, 651–661.

Lowry, D., Fisher, R., Levin, I., Privalov, S. and Nisbet, E. G. 2004. Insight into West Siberian gas and wetland methane emissions from $\delta^{13}C$ studies of ambient air. AGU Fall Meeting, San Francisco. *EOS Suppl.* **85**, F385.

Lowry, D., Holmes, C. W., Rata, N. D., O'Brien, P. and Nisbet, E. G. 2001. London methane emissions: use of diurnal changes in concentration and the $\delta^{13}C$ to identify urban sources and verify inventories. *J. Geophys. Res.* **106**, 7427–7448.

Mastepanov, M., Sigsgaard, C., Dlugokencky, E. J., Houweling, S., Ström, L. and co-authors. 2008. Large tundra methane burst during onset of freezing. *Nature* **456**, 628–631.

Meth-MonitEUr. 2005. Meth-MonitEUr: methane monitoring in the European Union and Russia, Final Report, Sect. 6, EC Contract EVK2-CT-2002-00175 (ed. E. G. Nisbet). European Commission, Brussels. DOI: 10.1021/es100460d. Online at: http://www.rhul.ac.uk/earthsciences/labs/greengaslab.aspx

Milkov, A. V. 2005. Molecular and stable isotope compositions of natural gas hydrates. *Org.Geochem.* **36**, 681–702.

Miller, J. B. and Tans, P. 2003. Calculating isotopic fractionation from atmospheric measurements at various scales. *Tellus Ser. B* **55**, 207–214.

Moore, T., Roulet, N. and Knowles, R. 1990. Spatial and temporal variation of methane flux from subarctic/northern boreal fens. *Glob. Biogeochem. Cy.* **4**, 29–46.

Nisbet, E. G. 1989. Some northern sources of atmospheric methane: production, history, and future implications. *Can. J. Earth Sci.* **27**, 148–157.

Nisbet, E. G. and Chappellaz, J. 2009. Shifting gear, quickly. *Science* **324**, 477–478.

Ovsyannikov, V. M. and Lebedev, V. S. 1967. Isotopic composition of carbon in gases of biogenic origin. *Geochem. Int.* **4**, 453–458.

Pataki, D. E., Ehleringer, J. R., Flanagan, L. B., Yakir, D., Bowling, D. R. and co-authors. 2003. The application and interpretation of Keeling plots in terrestrial carbon cycle research. *Glob. Biogeochem. Cy.* **17**(1), 1022. DOI: 10.1029/2001GB001850.

Quay, P. D., King, S. L., Lansdown, J. M. and Wilbur, D. O. 1988. Isotopic composition of methane released from wetlands: implications for the increase in atmospheric methane. *Glob. Biogeochem. Cy.* **2**, 385–397.

Rigby, M., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Langenfelds, R. L. and co-authors. 2008. Renewed growth of atmospheric methane. *Geophys. Res. Lett.* **35**, L22085.

Rinne, J., Riutta, T., Pihlatie, M., Aurela, M., Haapanala, S. and co-authors. 2007. Annual cycle of methane emission from a boreal fen measured by the eddy covariance technique. *Tellus* **59B**, 449–457.

Rodrigues, J. 2008. The rapid decline of the sea ice in the Russian Arctic. *Cold Reg. Sci. Technol.* **54**, 124–142.

Stevens, C. M. and Engelkemeir, A. 1988. Stable carbon isotopic composition of methane from natural and anthropogenic sources. *J. Geophys. Res.* **93**, 725–733.

Tarasova, O. A., Brenninkmeijer, C. A. M., Assonov, S. S., Elansky, N. F., Röckmann, T. and co-authors. 2006. Atmospheric CH_4 along the Trans-Siberian railroad (TROICA) and river Ob: source identification using stable isotope analysis. *Atmos. Environ.* **40**, 5617–5628.

Tokida, T., Mizoguchi, M., Miyazaki, T., Kagemoto, A., Nagata, O. and co-authors. 2007. Episodic release of methane bubbles from peatland during spring thaw. *Chemosphere* **70**, 165–171.

Vasander, H. 1996. *Peatlands in Finland*. Finnish Peatland Society, Helsinki.