Development and use of CF-GC-IRMS and small airbag sample techniques to investigate Arctic methane sources 2008-9: Wetland, clathrates and gas leaks - the isotopic picture

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Outline

- Use of CF-GC-IRMS for methane $\delta^{13}C$ measurements
- Small volume sampling using Tedlar bags
- Use of diurnal studies in source areas to identify source signatures
- Use of back trajectory analysis of daily sampling from remote sites to consider regional $\delta^{13}C$ signatures
- Linking between source and ambient air measurements

Methane $\delta^{13}C$ Analysis at Royal Holloway

Methane $\delta^{13}C$ measured by continuous flow GC-IRMS using a Trace Gas and Isoprime mass spectrometer (Isoprime Ltd.)

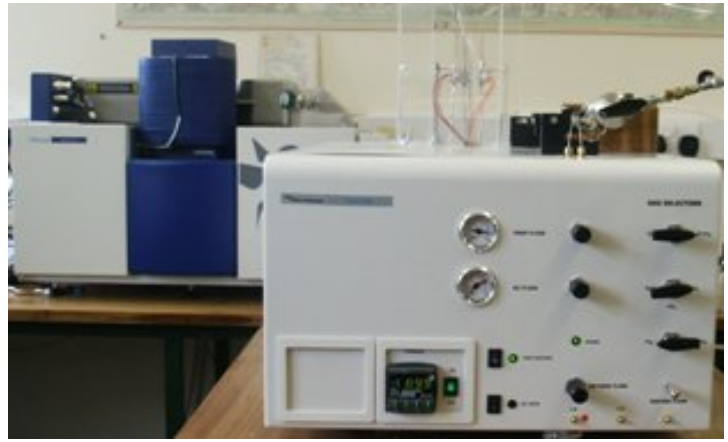
Changes have been made to automate inlet and improve precision (repeatability) to 0.05‰ for CH_4 $\delta^{13}C$ analysis. *

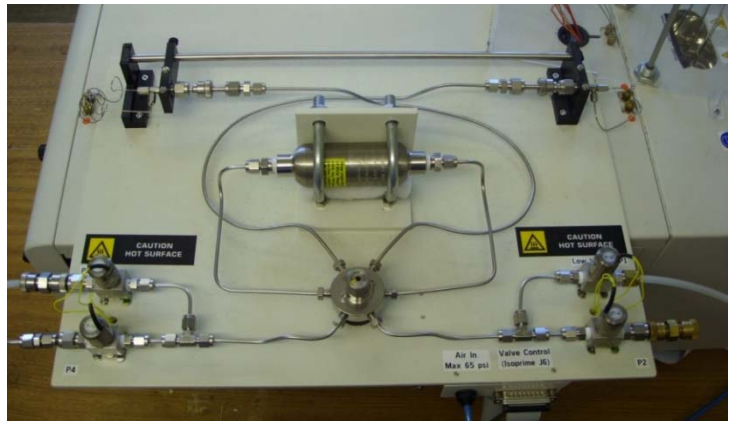
Small sample volume (75 mL for ambient air) and fast analysis time (16 minutes per analysis) allows high throughput of air samples.

Instrument has been run since 2003 with no deterioration in efficiency of the palladium catalyst.

Typically 150 analyses per week

A second Trace Gas instrument has been ordered to allow more samples to be analysed, and more continuous London diurnal work.

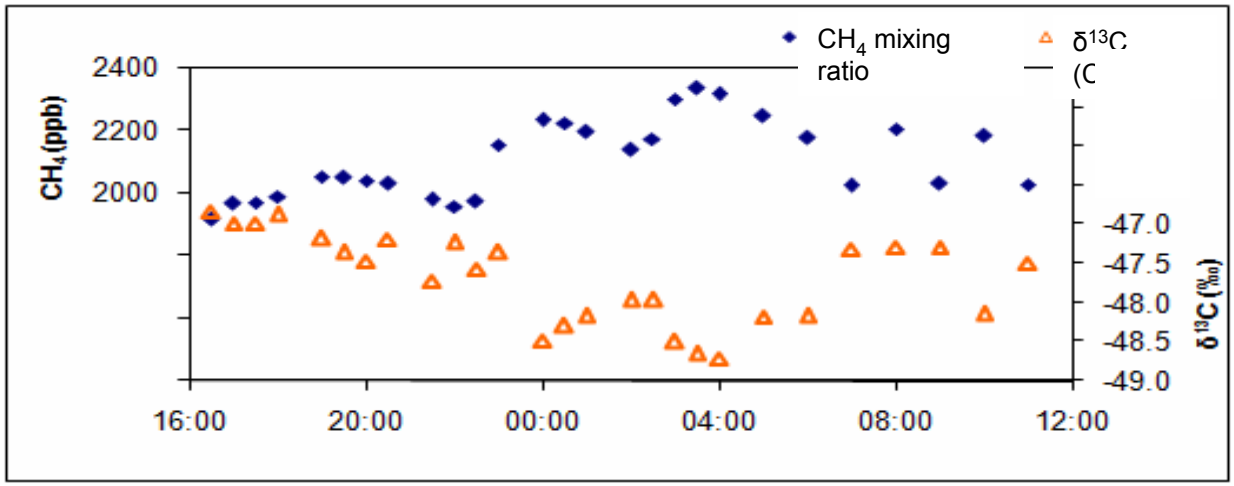




*Fisher *et al.*, Rapid Communications in Mass Spectrometry, 2006.

Methane $\delta^{13}C$ diurnal measurements from the Royal Holloway site, Egham (near London)

- Automated to make half hourly measurements through diurnal cycle



- Can be used to calculate relative amounts of methane from landfill at -53‰ and gas distribution leaks at -37‰ in the London region.

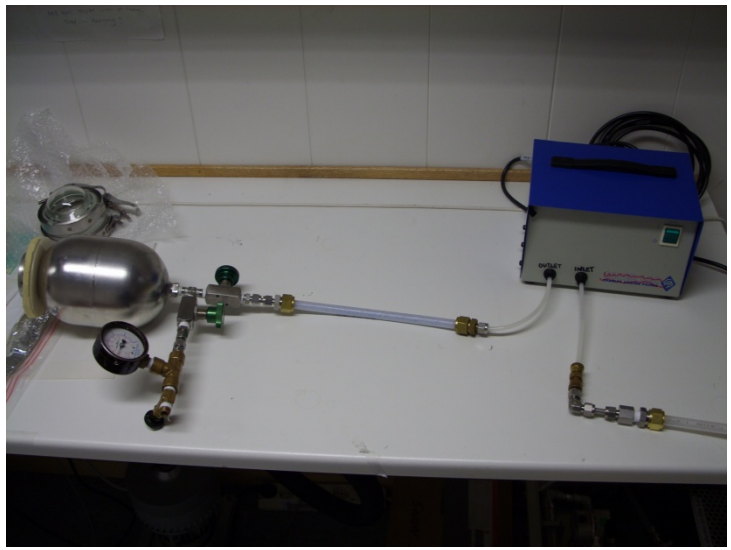
Air sampling for field methane isotopic measurements by Royal Holloway

- Air samples are collected in 5L Tedlar bags using small battery operated pumps, allowing low cost air sampling.

- CH_4 mixing ratios and $\delta^{13}C_{CH4}$ are stable in the bags even if stored for several months.

- This provides enough air for triplicate CH_4 mixing ratio measurements by GC-FID and triplicate $\delta^{13}C$ measurements by CF-GC-IRMS.

- Stainless steel or glass flasks are used for sites where CO_2, CO and H_2 measurements are also required.



Ambient air collection sites for regular methane isotopic measurements by Royal Holloway

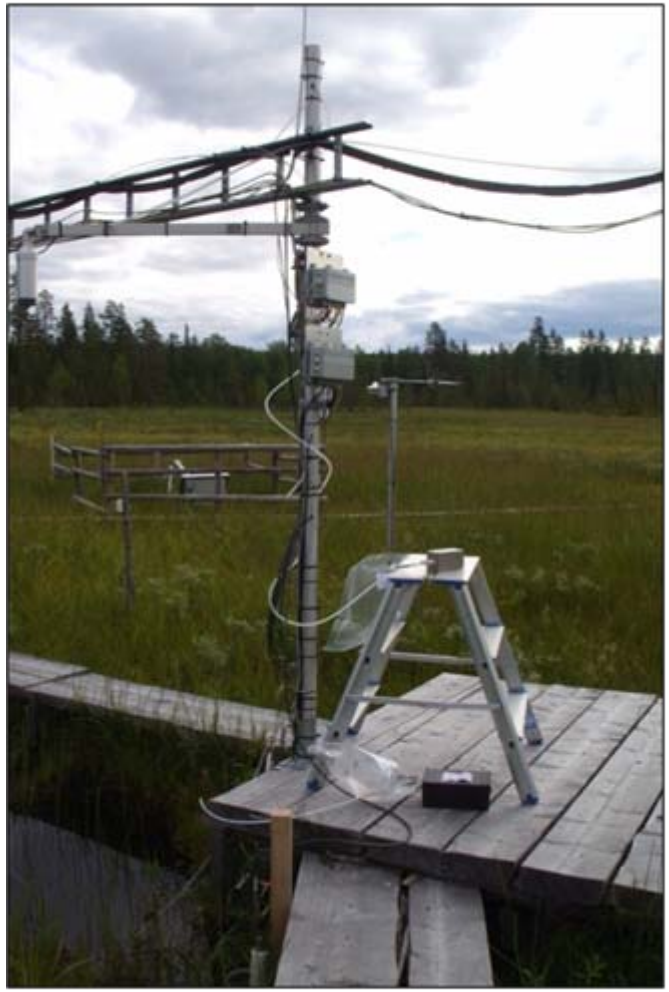
Site	Date sampling commenced	Sampling frequency
Zeppelin, Spitsbergen	July 2007	Fortnightly, with daily sampling Aug.-Sept. 2008, Mar.-May 2009, Sept. 2009
Pallas, Finland	August 2008	Weekly, with more regular sampling during field campaigns at Lompolojänkkä
Alert, Canada	2008	Selected UHEI samples
Mace Head	August 2008 (1996-2006 using large volume CF technique)	Weekly, with daily sampling Aug. –Sept. 2008
Egham, UK	2006 (1996-2006 using large volume CF technique)	Weekly with half hourly measurements during selected diurnal campaigns
Weybourne, UK	December 2008	Fortnightly
Troodos, Cyprus	March 2007	Fortnightly
Falkland Islands	October 2007	Fortnightly
Ascension Island	August 2009	Fortnightly
Cathcart, S. Africa	December 2003	Monthly

Pallas Sammaltunturi, Northern Finland

FINNISH METEOROLOGICAL INSTITUTE

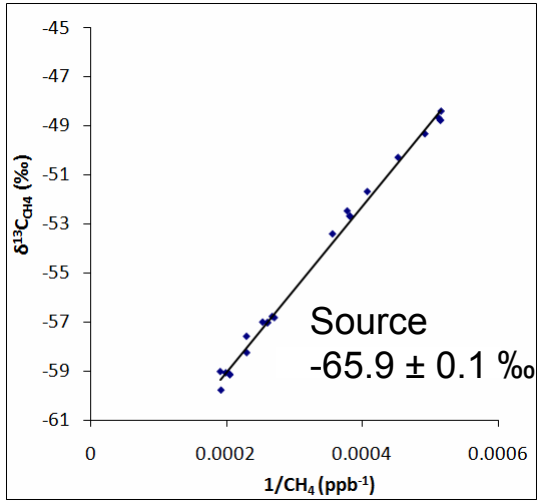
Wetland source studies: Lompolojänkkä, Pallas (FMI site)

- Diurnal campaigns to identify source signature of wetland emissions
- Technique compared with chamber measurements at the same site
- Seasonality of the source signature investigated

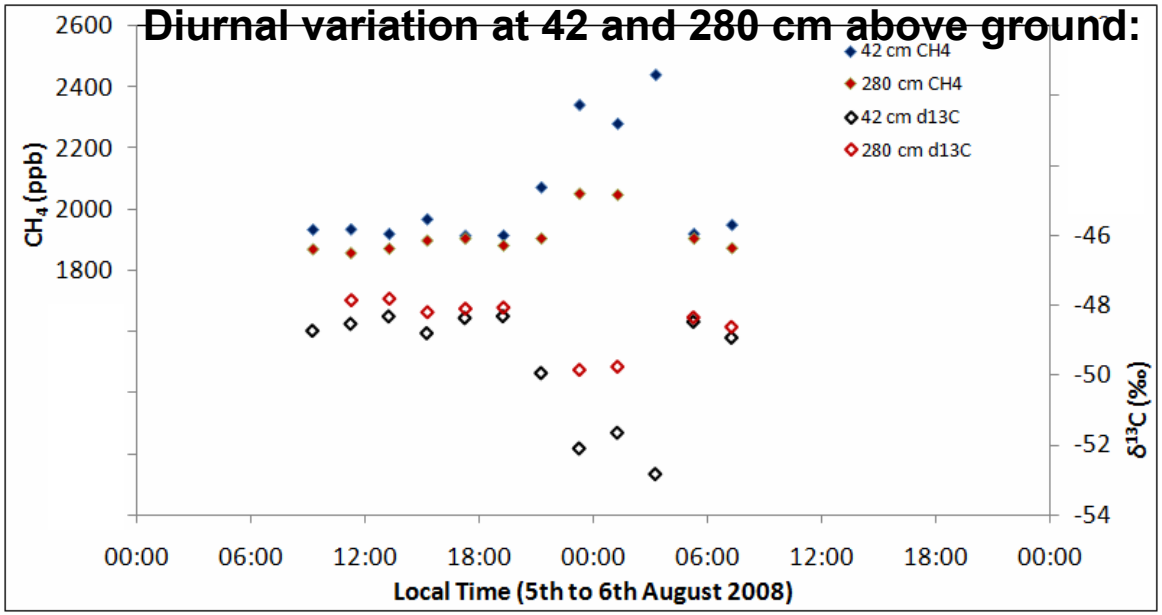


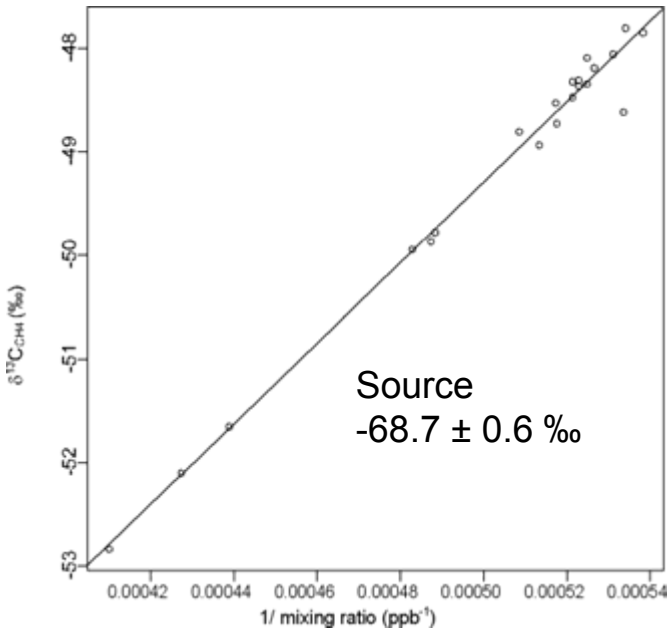
Chamber and diurnal studies at Lompolojänkkä, Pallas, August 2008

Chamber measurements:



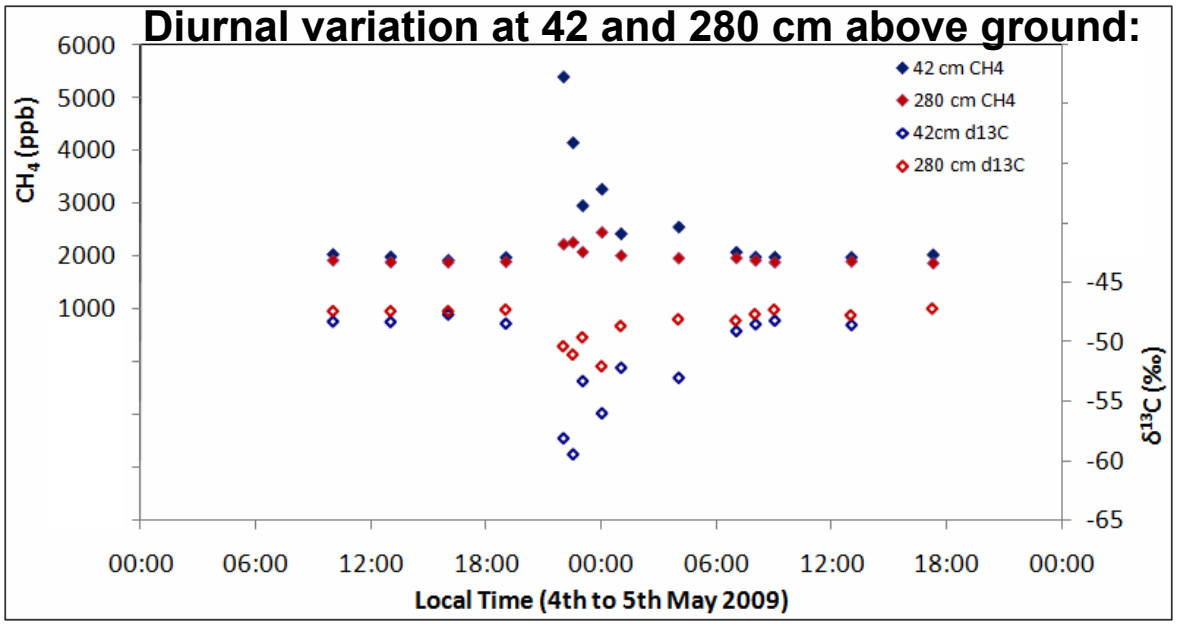
Diurnal variation at 42 and 280 cm above ground:

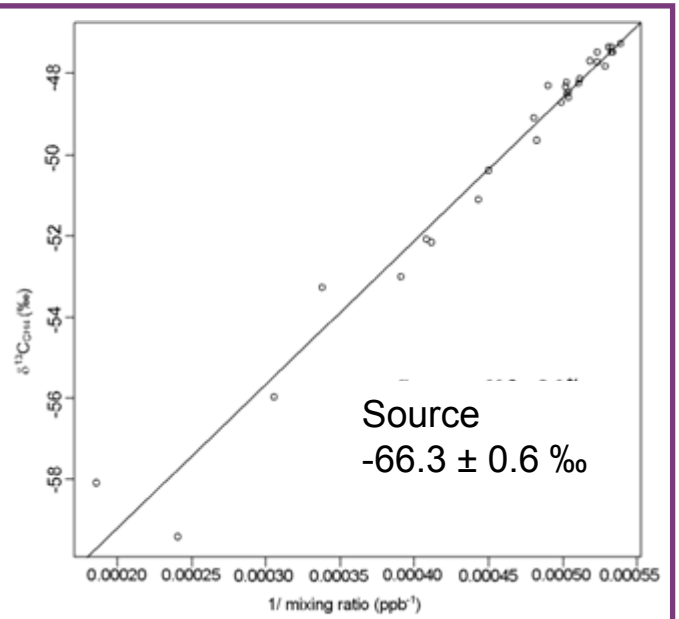


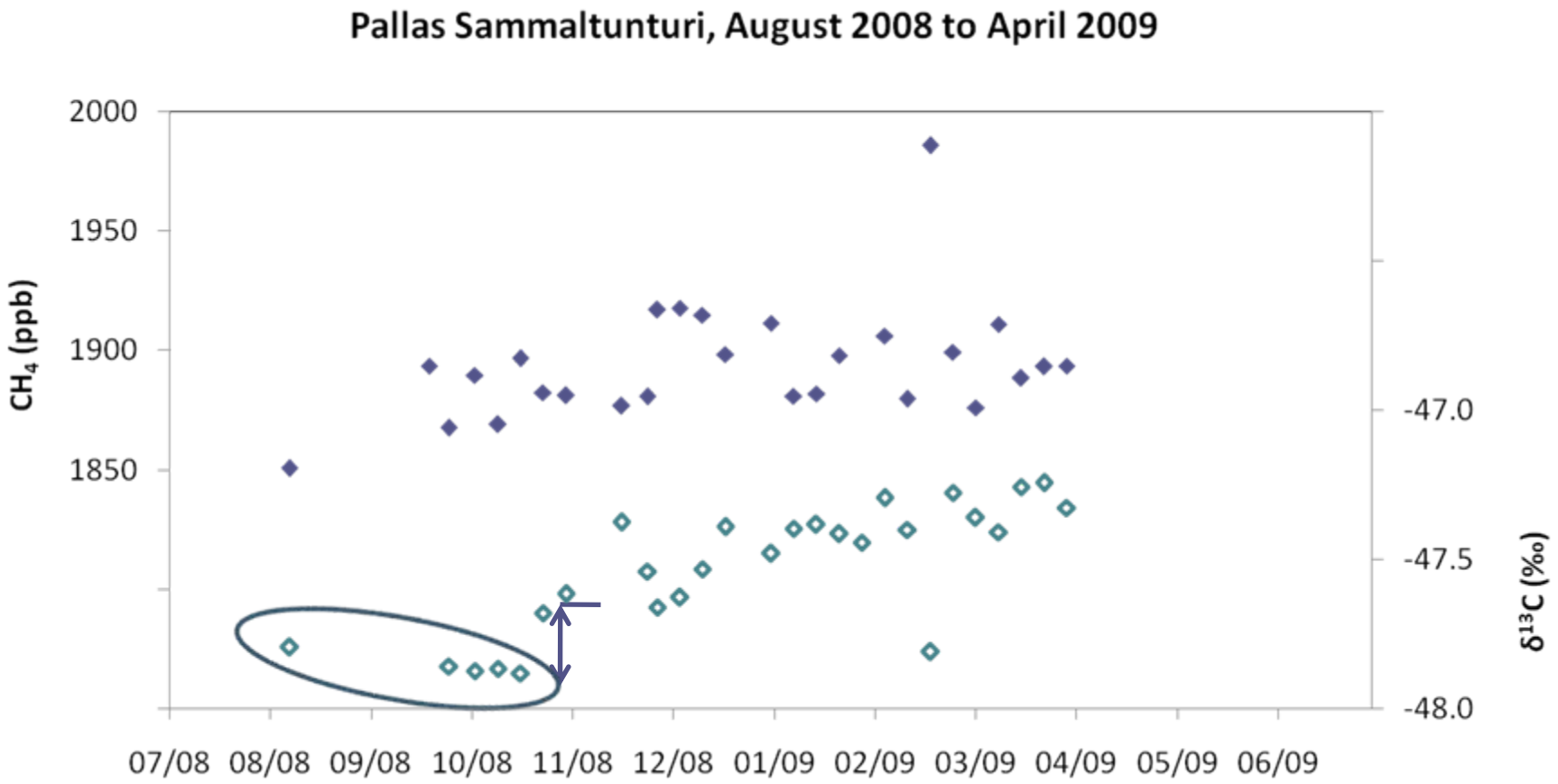


Diurnal studies at Lompolojänkkä, Pallas, May 2009

- Sampling campaign time coincided with the snowmelt.
- Large pulses of methane observed as surface of wetland melted and refroze
- Spring melt diurnal source signature (-66.3 ± 0.6 ‰) slightly more enriched than the summer signature (-68.7 ± 0.6 ‰)







CH_4 depleted in ^{13}C at Pallas in summer and autumn – wetland sources

0.2‰ enrichment in $\delta^{13}C$ at end of wetland emission period, coinciding with first snowfall

Dynamics of gas hydrates along the West Spitsbergen continental slope

- RRS James Clark Ross
- 23rd August to 23rd September 2008

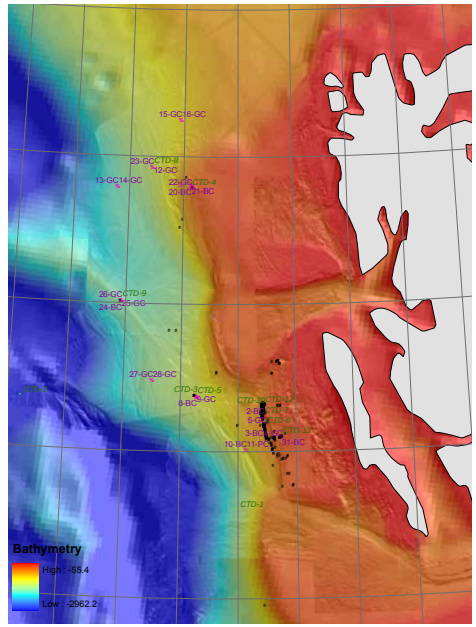
Field of gas plumes (Westbrook et al., GRL, 2009)

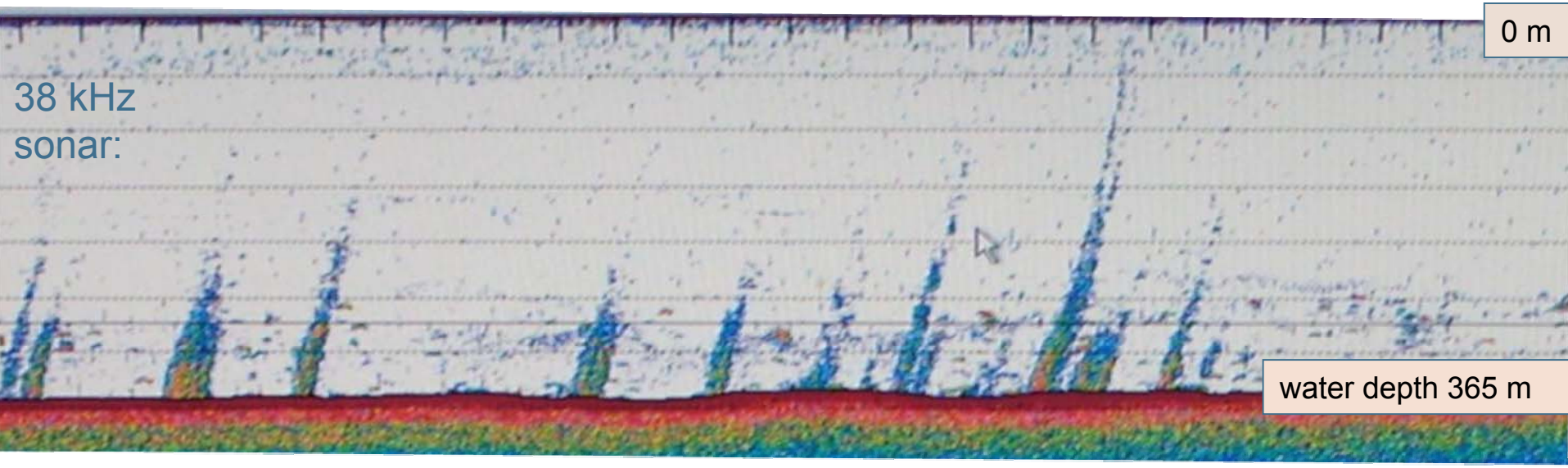
Identified using 38kHz sonar (Simrad EK60 ‘fishfinder’)

More than 250 plumes of gas bubbles from the seabed, some rising to 50 m below the surface

Landward side of gas hydrate stability zone (GHSZ), depth range 150-400 m

Occurrence and activity controlled by the GHSZ, which is sensitive to the effect of changes in water temperature. Increasing temperature will cause the release of methane from the dissociation of hydrate that is present





Methane hydrate in sediment cores

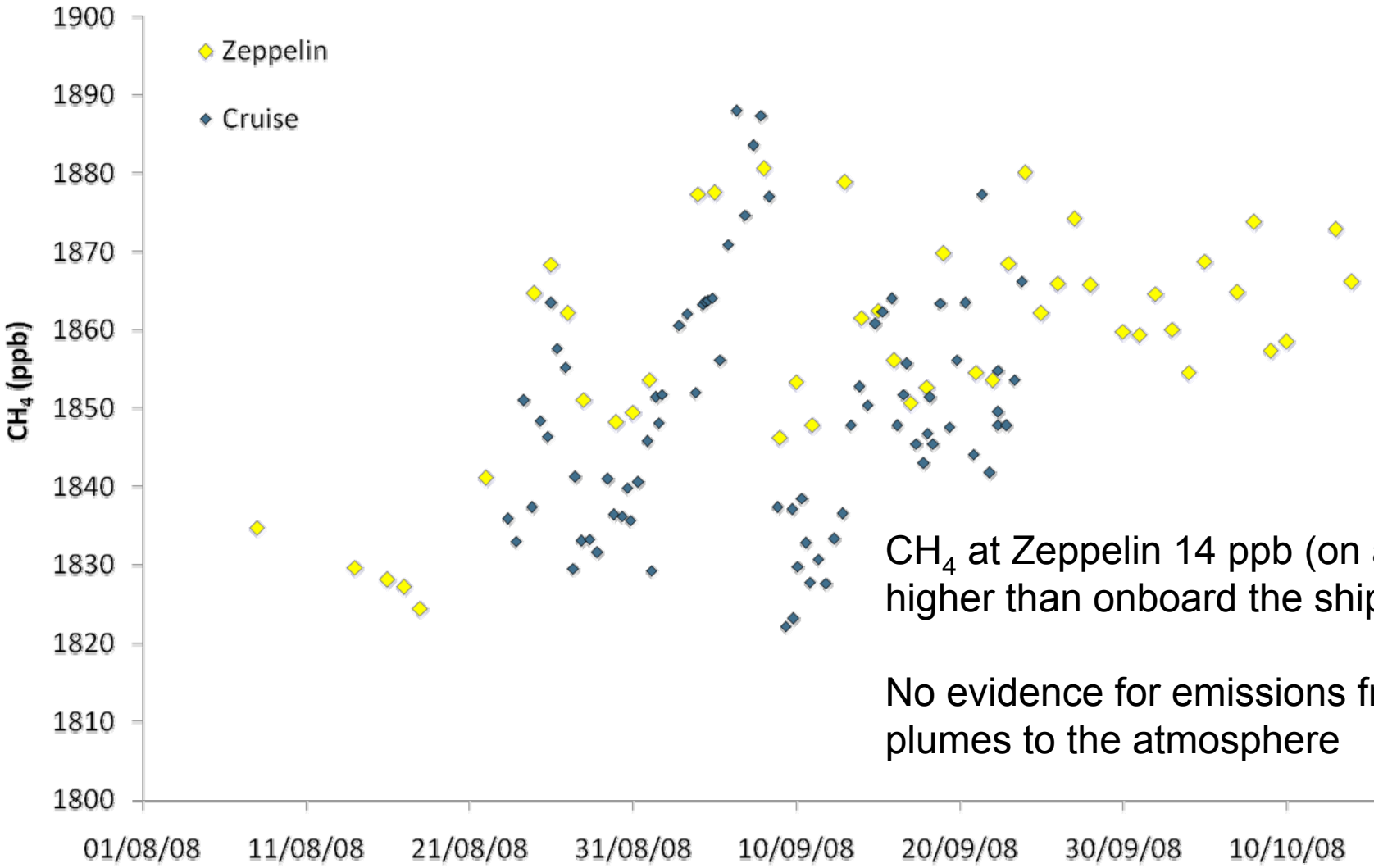
Methane hydrate recovered from two sediment cores collected down slope of the observed gas plumes

Core JR211-04GC sec 4: $\delta^{13}C$ -51.3 ‰

Core JR211-26 sec 8: $\delta^{13}C$ -50.3 ‰

Any methane released at the surface, following oxidation of CH_4 in the water column will be more enriched than -51 ‰.

Methane mixing ratio in air samples collected on JCR slightly lower than in daily samples from Zeppelin Station

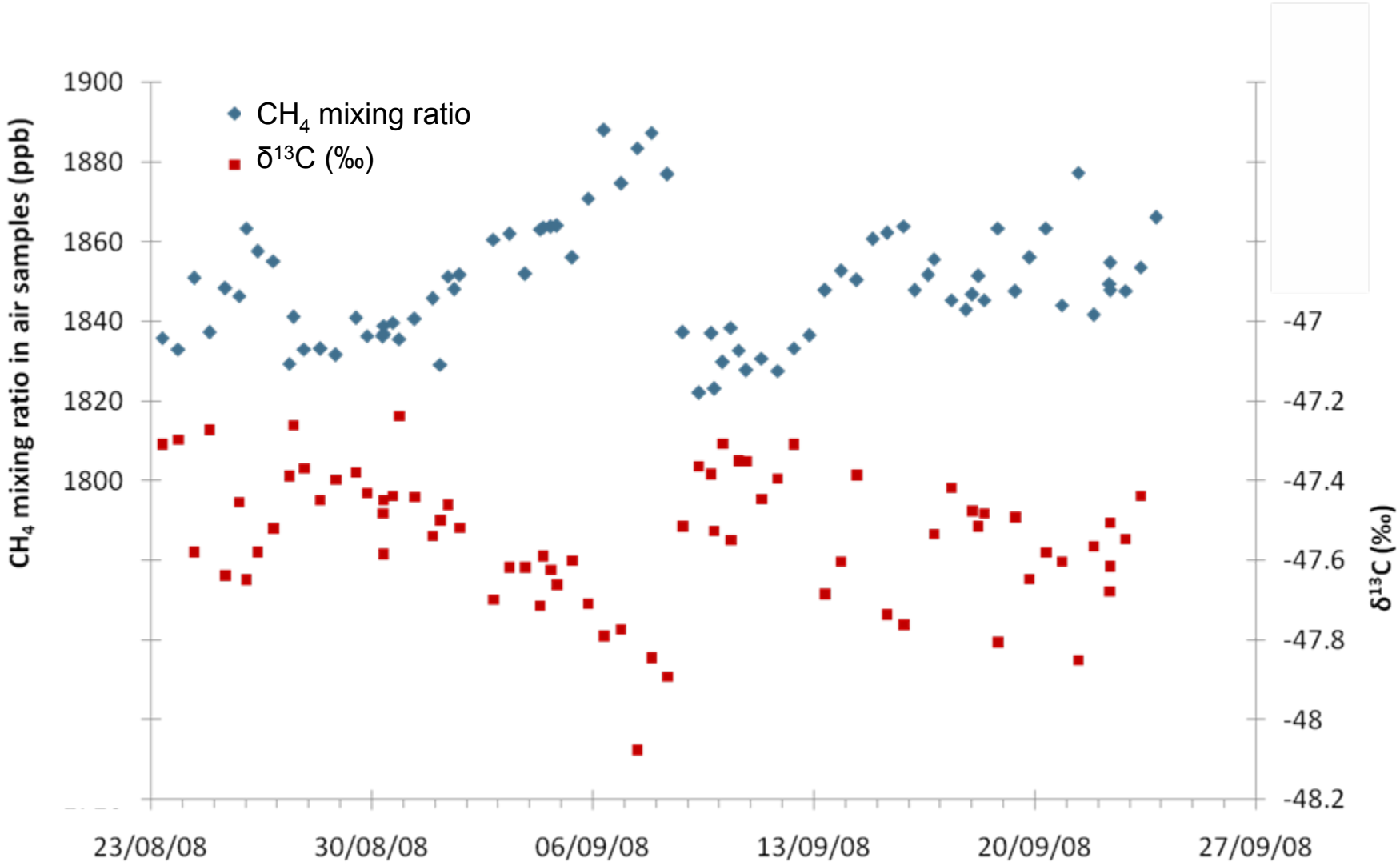


CH_4 at Zeppelin 14 ppb (on average) higher than onboard the ship

No evidence for emissions from gas plumes to the atmosphere

Ambient air methane mixing ratio and $\delta^{13}C$, Cruise JR211

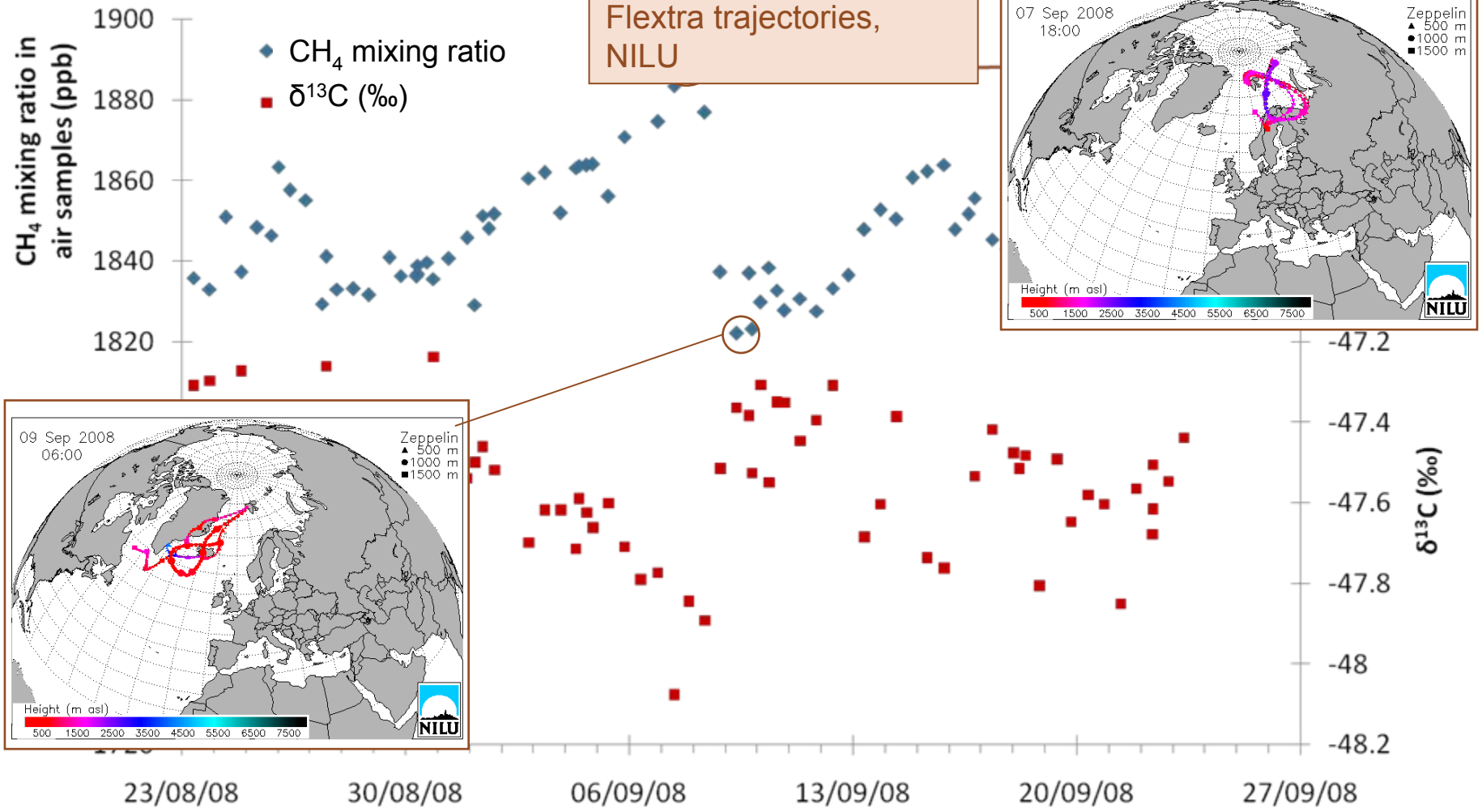
Samples collected on JCR west of Spitsbergen 23rd August to 23rd September 2008



Back trajectory analysis

4th – 8th September highest methane mixing ratio: Air passed over Ob river area, NW Siberia. Keeling plot for these days gives $\delta^{13}C$ source signature = -61 ± 3 ‰ (40% gas leak, 60% wetland?)

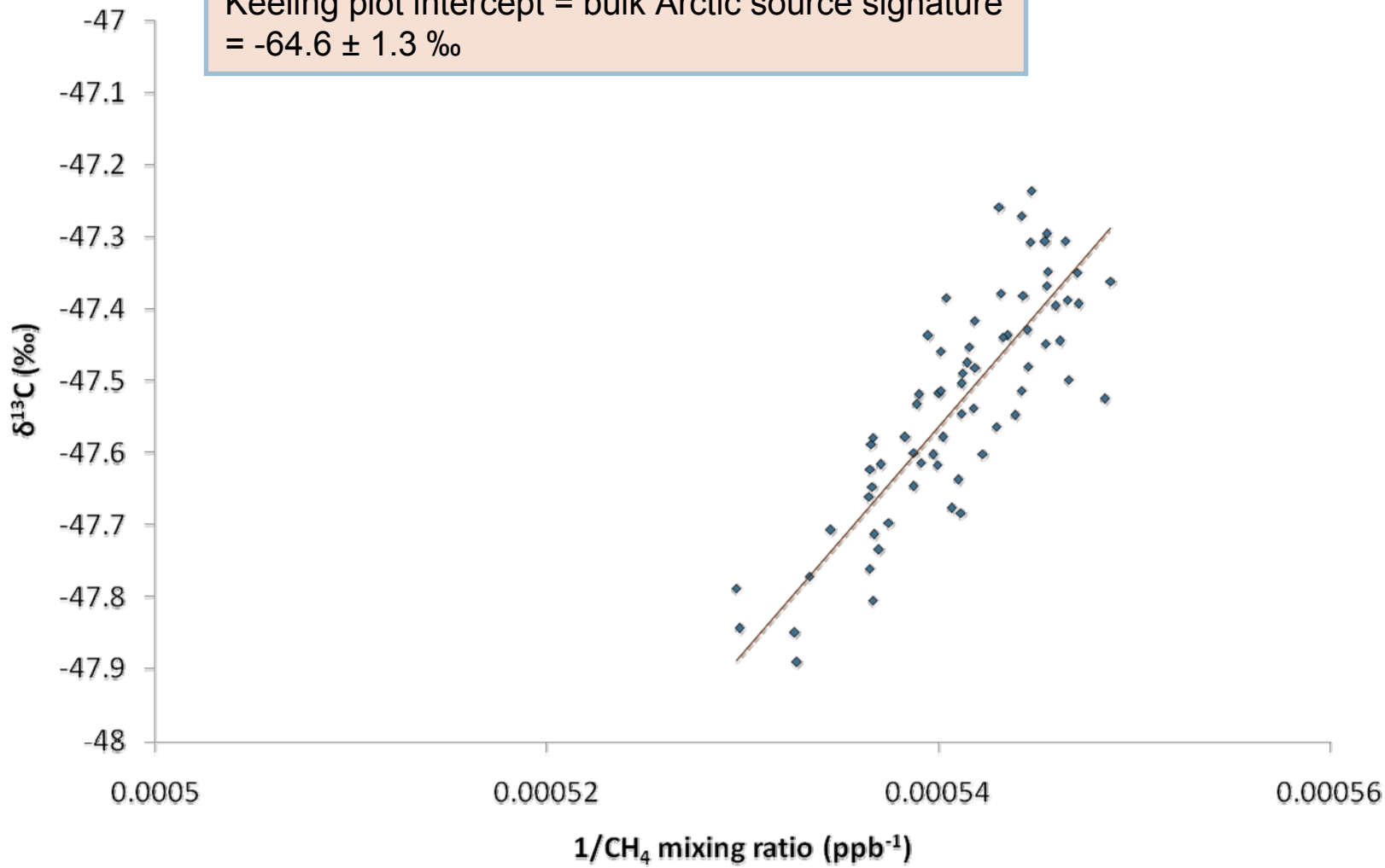
Flextra trajectories, NILU



Ambient air methane mixing ratio and $\delta^{13}C$, Cruise JR211

Samples collected on JCR west of Spitsbergen 23rd August to 23rd September 2008

Keeling plot intercept = bulk Arctic source signature
= -64.6 ± 1.3 ‰

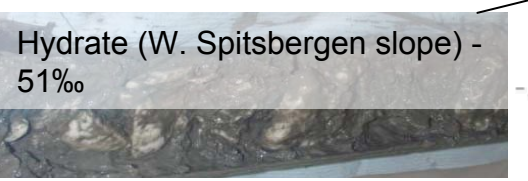


Ambient air methane mixing ratio and $\delta^{13}C$, Cruise JR211

Other Arctic methane sources:
Forest Fires -28 ‰
Thermokarst lakes (Walter et al., Nature , 2006) -83 to -58 ‰

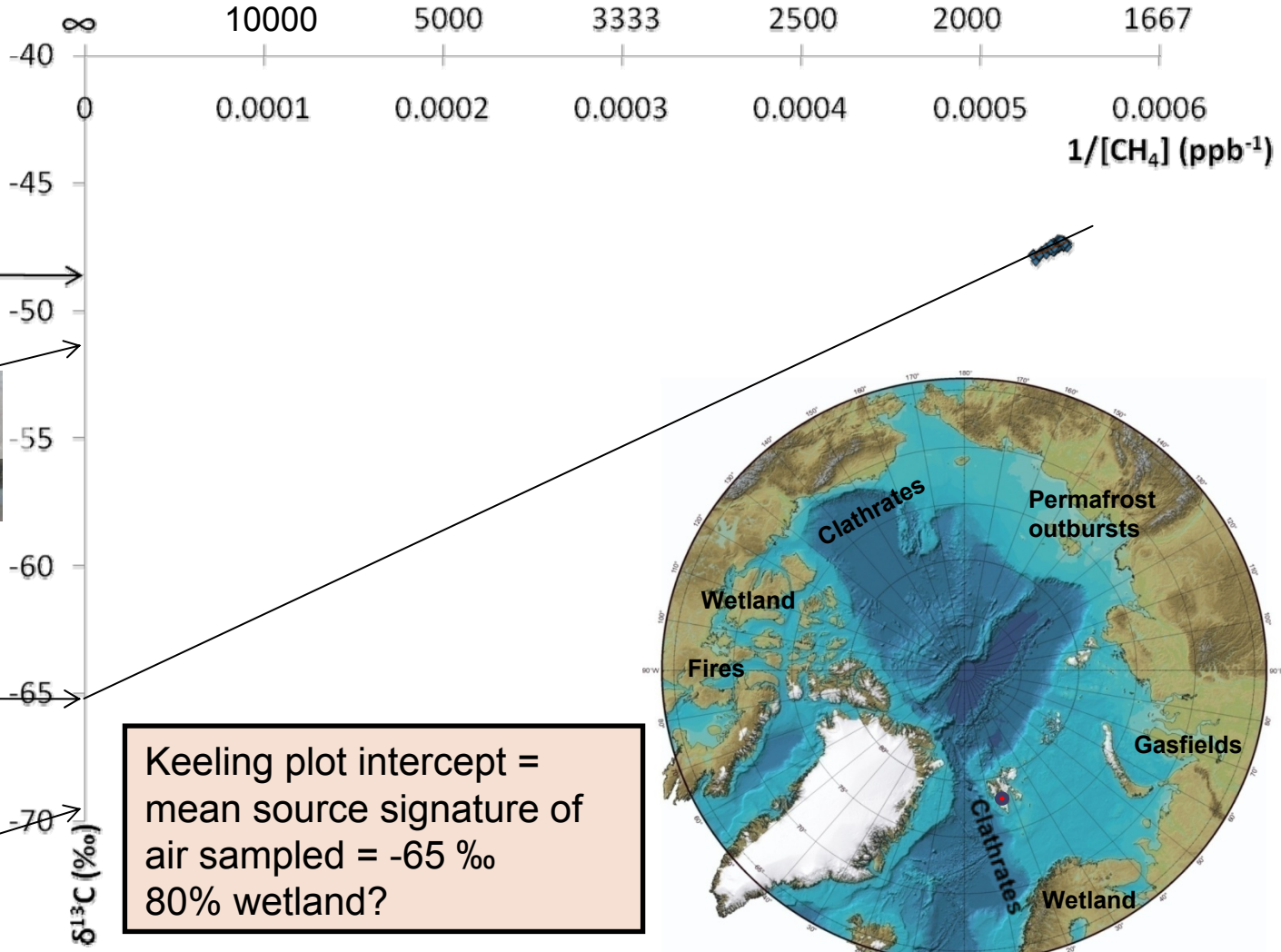
Gas field (Ob River, Siberia) -49‰

Hydrate (W. Spitsbergen slope) -51‰



Measured on JR211 -65‰

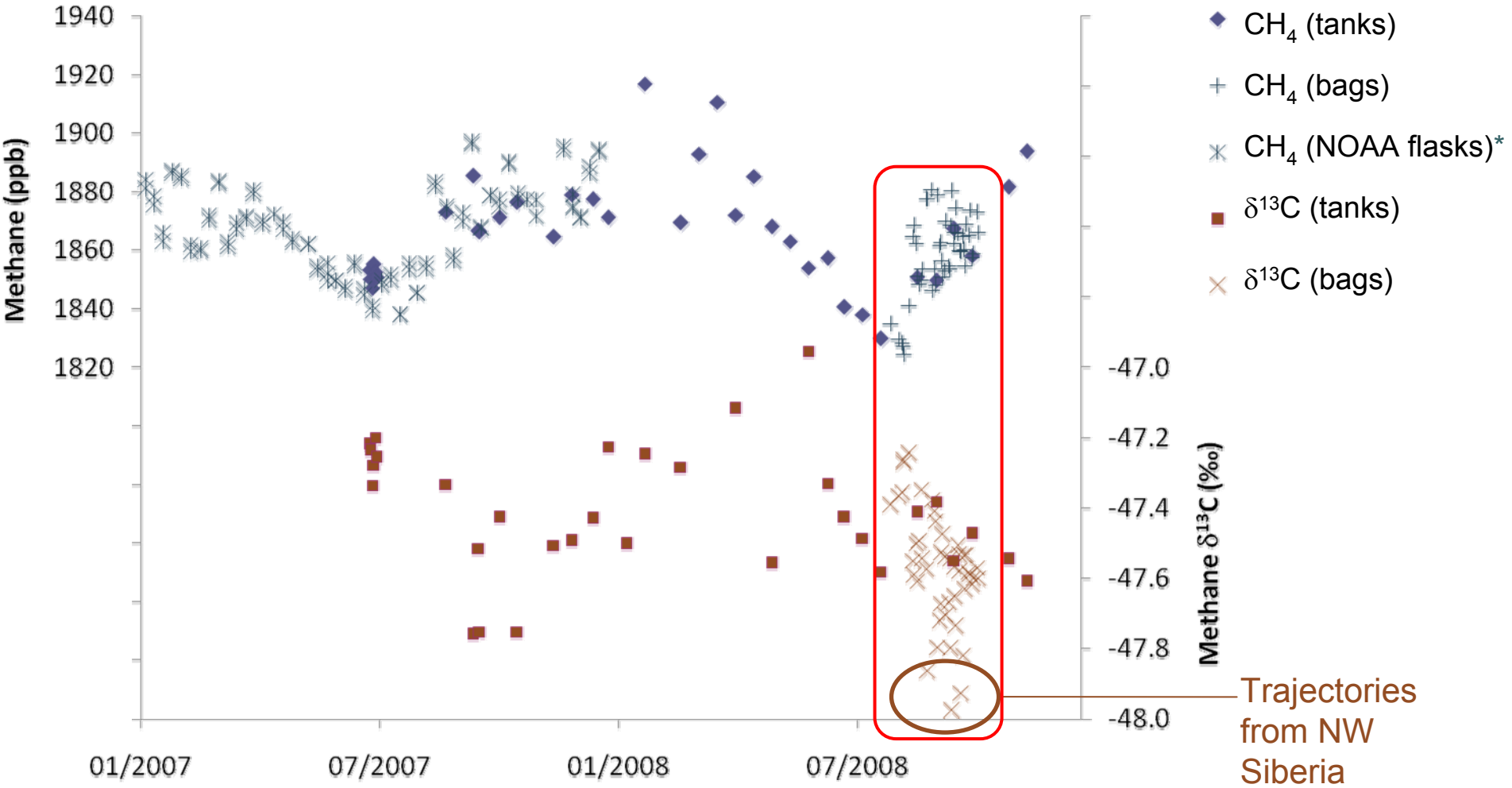
Wetland, Finland -69‰



Keeling plot intercept = mean source signature of air sampled = -65 ‰
80% wetland?

Methane in air collected at the Zeppelin Station, Ny-Ålesund

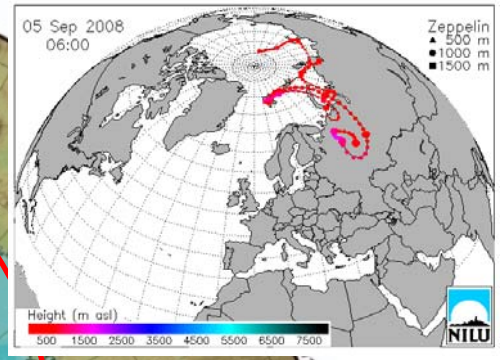
Flasks collected fortnightly since July 2007, bags daily during summer 2008



*2007 NOAA flask CH_4 data compiled by E. Dlugokencky, NOAA ESRL www.esrl.noaa.gov/gmd/ccgg/

Subdividing Zeppelin Summer 2008 methane measurements according to back trajectory direction

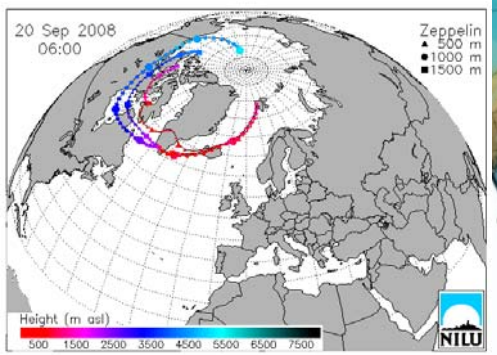
$$\delta^{13}C_{source} = \frac{\left(\delta^{13}C_{air} \times c_{air} - \delta^{13}C_{background} \times c_{background}\right)}{\Delta c}$$



Arctic Ocean
Mean 1854 ppb
Source $\delta^{13}C$ -66.4 ‰
± 3.2 ‰

Greenland/Canada/Alaska
Mean 1852 ppb
Source $\delta^{13}C$ -67.0 ‰
± 1.6 ‰

Siberia
Mean 1871 ppb
Source $\delta^{13}C$ -62.5 ‰
± 1.7 ‰



Atlantic
Mean 1849 ppb
Source $\delta^{13}C$ -63.8 ‰
± 2.8 ‰

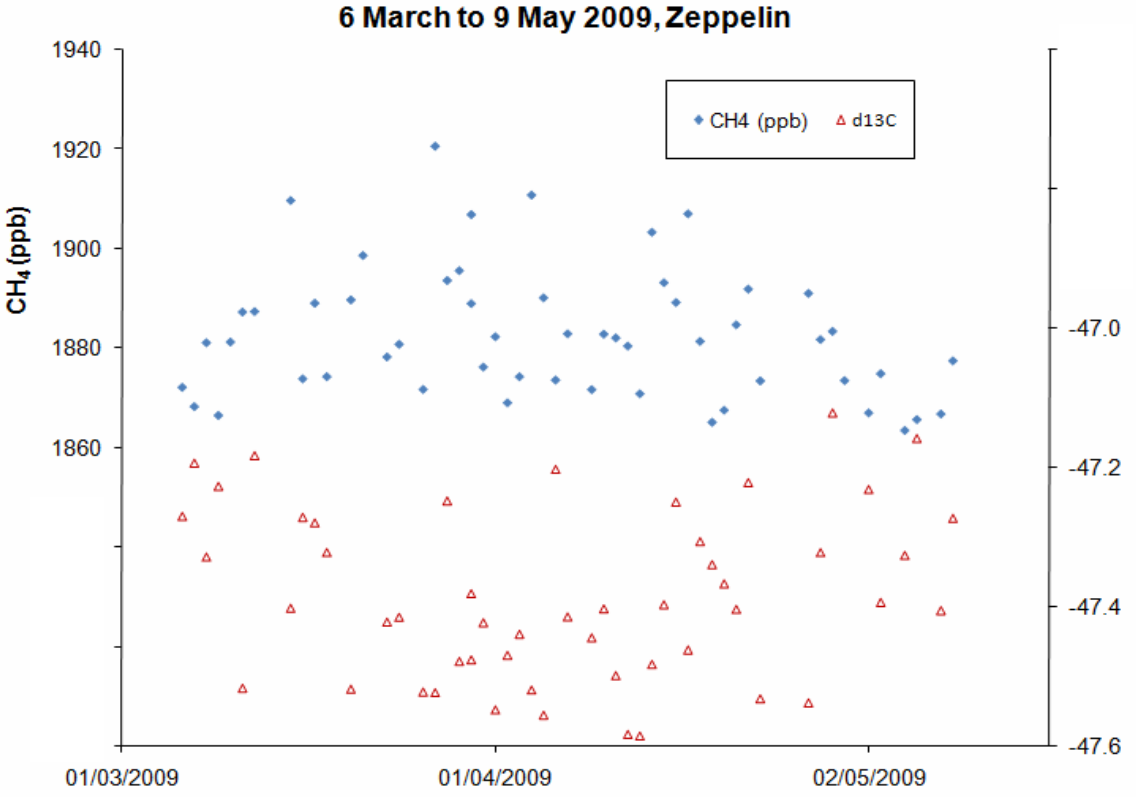
Europe
Mean 1866 ppb
Source $\delta^{13}C$ -64.4 ‰
± 1.5 ‰

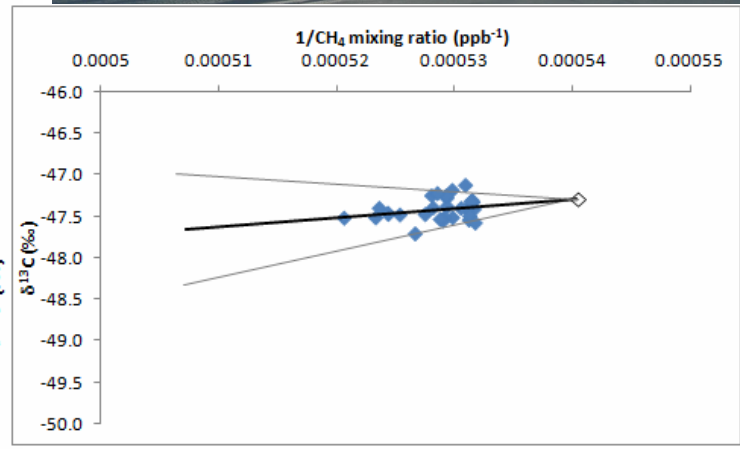
Mean source $\delta^{13}C_{CH4}$ for all directions -65.4 ‰

Seasonal variation in the bulk Arctic methane source signature as measured from the Zeppelin station

Daily sampling of air from Zeppelin March 6th to May 9th 2009 to obtain Spring isotopic source signature before wetlands start emitting.

Air collected daily during spring 2009 at the Zeppelin Station, Ny-Ålesund





Mace Head background 1850 ppb, -47.3 ‰ used as a fixed point in the Keeling plot

Spring bulk Arctic source signature -52.6 ± 6.4 ‰: significantly more enriched than summer signature. Spring sources are predominantly gas leakage (and perhaps clathrate)

Summary (1)

- Methane $\delta^{13}C$ measurements in air arriving at Arctic sites provide important information on key methane sources.

- Tedlar bag sampling allows low cost sampling of air for methane $\delta^{13}C$ analysis

- Keeling plots of diurnals in local source areas valuable technique for looking at local source signatures

- Back trajectory analysis of daily air samples from remote sites used to identify regional source signatures.

Summary (2)

- CF-IRMS can be run automatically. Semi-continuous (e.g. half hourly) measurement of $\delta^{13}C_{CH4}$ would be extremely valuable at some sites.

- More continuous CH_4 isotope measurements likely in the coming years, either by CF-IRMS or improvements in laser based systems

- Need more intercomparison work between the laboratories measuring CH_4 isotope in ambient air

Thanks to:

NERC

Juha Hatakka and Tuula Aalto, FMI

Staff at Norsk Polarinstitutt (Ny-Ålesund) and NILU for air sampling at Zeppelin