INGOS TNA5 report - Methane $\delta^{13}C$ air analysis at GGLES: CATARINA cruise

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Introduction

25 ambient air samples were collected in Tedlar bags onboard the CATARINA cruise across the North Atlantic, between 25 June 2012 and 22 July 2012.

The air samples were posted to the UK and analysed in the Greenhouse Gas Laboratory, Dept. of Earth Sciences (GGLES), Royal Holloway University of London. Methane mixing ratios were measured using a Picarro G1301 cavity ringdown spectrometer (precision ± $3x10^{-4}$ ppm). Isotopic composition of the methane ($\delta^{13}C$) was measured using a modified Isoprime 'Trace Gas' and Isoprime continuous flow mass spectrometer (Fisher et al., 2006). The isotopic composition of each sample was measured at least 3 times.

Results

A map of the sample collection locations and measured methane mixing ratio and $\delta^{13}C$ is shown below.

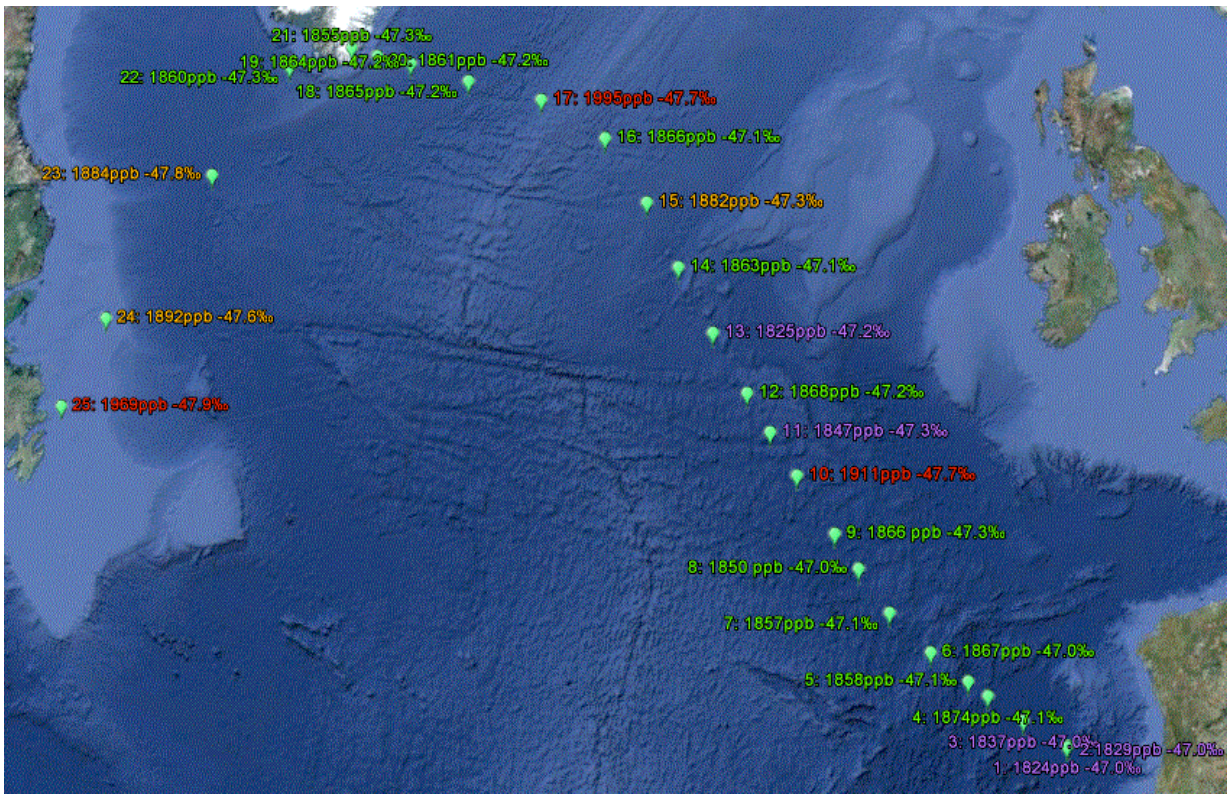


Figure 1 Air sample collection locations, measured methane mixing ratio and $\delta^{13}C$. Font colour represents methane concentrations: violet 1820-1849 ppb; green 1850-1879 ppb; orange 1880-1909 ppb; red >1910 ppb

The sample collection times and ship location, methane mixing ratio and $\delta^{13}C$ are listed in Table 1. The mean standard deviation in the $\delta^{13}C$ measurements was ±0.05 ‰.

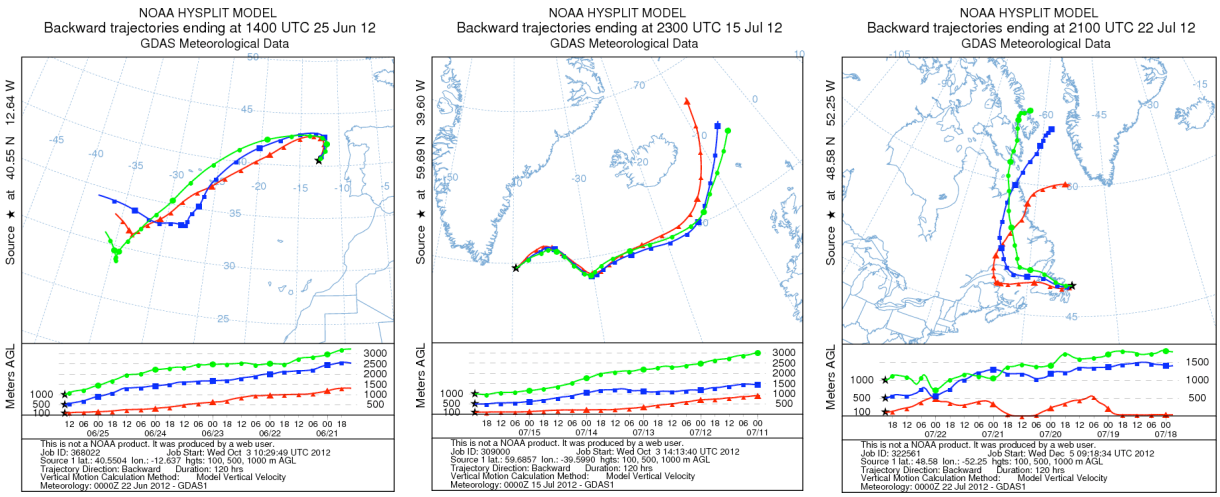
Sample number	Date/Time (UT)	Latitude	Longitude	CH_4 (ppm)	$\delta^{13}C$ (‰)	Standard deviation (‰)
1	25/06/12 14:27	40.5504	-12.6372	1.8241	-47.02	0.04
2	26/06/12 15:00	40.5727	-12.6701	1.8286	-47.04	0.03
3	27/06/12 13:31	41.5548	-14.1109	1.8371	-46.95	0.03
4	28/06/12 11:07	42.4592	-15.3034	1.8741	-47.12	0.03
5	29/06/12 11:57	42.9628	-15.9598	1.8578	-47.11	0.11
6	30/06/12 10:45	43.9219	-17.2188	1.8665	-47.03	0.03
7	01/07/12 15:05	45.1416	-18.5764	1.8568	-47.06	0.03
8	02/07/12 15:05	46.4040	-19.5627	1.8502	-46.98	0.03
9	03/07/12 11:20	47.3832	-20.3336	1.8663	-47.28	0.05
10	05/07/12 12:21	48.9859	-21.5891	1.9109	-47.65	0.07
11	06/07/12 12:29	50.1548	-22.5082	1.8468	-47.27	0.13
12	07/07/12 11:05	51.2009	-23.3221	1.8675	-47.16	0.08
13	08/07/12 12:30	52.7995	-24.5808	1.8247	-47.25	0.05
14	09/07/12 13:05	54.5361	-25.9425	1.8628	-47.15	0.03
15	10/07/12 13:30	56.2519	-27.2924	1.8822	-47.28	0.06
16	12/07/12 12:45	57.9720	-29.2793	1.8655	-47.12	0.03
17	13/07/12 15:50	58.9736	-32.5555	1.9948	-47.72	0.06
18	14/07/12 21:24	59.3627	-36.3966	1.8645	-47.18	0.07
19	15/07/12 22:50	59.6857	-39.5990	1.8636	-47.17	0.04
20	16/07/12 13:30	59.7822	-41.4946	1.8609	-47.18	0.02
21	17/07/12 12:38	59.9024	-42.9901	1.8552	-47.30	0.03
22	18/07/12 16:15	59.0768	-46.0792	1.8599	-47.27	0.02
23	19/07/12 21:30	55.7385	-48.3538	1.8840	-47.80	0.03
24	21/07/12 17:00	51.2458	-51.3659	1.8916	-47.63	0.04
25	22/07/12 21:24	48.5795	-52.2465	1.9685	-47.90	0.03

Table 1. Sampling times and locations, measured methane mixing ratio and $\delta^{13}C$ for all the samples collected during the CATARINA cruise.

Discussion

5 day air mass back trajectories for each of the air samples have been plotted using the NOAA Hysplit 4 model. Examples are shown in Figure 2.

Lowest methane mixing ratios, and highest $\delta^{13}C$ were measured in samples 1 to 3, the southernmost samples. The air masses sampled were from lower latitudes in the Atlantic. This is expected as uptake of methane by tropospheric OH is greatest at low latitudes. Samples from closer to the coast of Canada, i.e. samples 23 to 25, contained elevated methane concentrations and were depleted in ^{13}C. The source signature of the elevated methane in sample 25 was -60‰ indicating that this excess was predominantly from biogenic methane sources, such as wetland emissions. The reason for the elevated methane concentrations in samples 10 and 17 were not clear from the back trajectory analyses. The elevated methane in both of these cases was depleted in ^{13}C (source signatures -63‰ and -56‰ respectively in samples 10 and 17), i.e. from a biogenic source.



1: 1824 ppb, -47.02 ‰

Atlantic background

19: 1864 ppb, -47.17 ‰

Arctic background

25: 1969 ppb, -47.90 ‰

Canadian wetland emissions added

Figure 2: 5 day back trajectories for air samples 1, 19 and 25 modelled using the NOAA ARL Hysplit 4 model

Conclusions

Daily shipboard sampling has allowed the summer Atlantic and Arctic background methane isotopic composition to be identified, as well as the isotopic signature of source regions. The largest methane source observed during the campaign was a biogenic source, -60‰, measured when air had crossed over Canadian wetland. The source signature agrees with the regional wetland signature (-60.0 ± 3.2 ‰) measured in diurnal studies at Fraserdale in Ontario, Canada (Kuhlmann et al., 1998). The results support previous studies showing that wetland sources are the dominant source of methane to Arctic regions in the summer, e.g. Fisher et al., 2011.

References

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.

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Kuhlmann, A.J., Worthy, D.E.J., Trivett, N.B.A. and Levin, I. 1998. Methane emissions from Canadian wetlands: An atmospheric approach. *J. Geophys. Res., 103,* 16,009-16,016.