Characterization of ^{13}C signature of CH_4 sources in Krakow and Silesia region, Southern Poland

Alina Jasek

TNA Request ID: 540

1. Introduction and motivation

Methane is the second most important anthropogenic greenhouse gas. Having high global warming potential, its slightest unnatural concentration variations in the atmosphere can trigger disproportionate changes in the system. Besides natural sources such as wetlands, methane emissions to the atmosphere are mostly anthropogenic: industrial, agricultural or waste management. In the Silesia and Krakow region all these sources can be found, as well as the city's natural gas transmission network, from which possible leakages could be detected.

The Upper Silesia is an industrial and mining region of Poland (Fig.1). Highly urbanized aboveground, underground there is a dense network of coal mines tunnels and shafts to be found. Several ventillation shafts are located thourought the area, in the undeveloped and industrial but also residential neighbour. The region is considered to be one of the methane hot spots in Europe. Previous studies of anthropogenic emissions of CH_4 in Southern Poland were focused mostly on the Krakow city itself (Kuc et al. 2003, Necki et al. 2009). Recently, in order to extend existing results to industrial CH_4 sources that can be found in the Silesia, several car transects throughout the region were performed using mobile CH_4 concentration analyzer. A number of methane sources of different strenght were found across the Silesia region. A need to identify the sources isotopically arose.

Figure 1. *Location of the Upper Silesia region (green highlight). Katowice is the largest city of the agglomeration, Krakow is a starting point for each transect [Google Earth].*

2. Scientific objectives

During CH_4 concentration transects performed in recent years, several methane sources were located in the Silesia region. However, only the spatial distribution and approximate strength of these were determined because of inability to measure stable isotopic composition of CH_4 in situ. Therefore, its anthropogenic origin could have been only a hypothesis to prove. It became necessary to determine the isotopic composition of the methane emitted from encountered sources in order to find whether it is of natural, mine or city gas network origin.

3. Reason for choosing station

The greenhouse gas laboratory at Royal Holloway University of London performs the measurements of CH_4 mixing ratio and its ^{13}C isotope composition to high precision. The visit at GGLES brought an opportunity to experience and learn several analytical methods for measurements of CH_4 concentration and its stable carbon isotopic composition in atmospheric samples: an automated continuous-flow IRMS and CRDS analyzer setup to measure CH_4 concentration of individual air samples.

4. Method and experimental setup

Two car transects throughout the Silesia region were performed in weekly interval: 10th and 17th June 2013, starting from early morning hours to have a stable atmospheric conditions. A mobile CH_4 concentration analyzer (Picarro G2101*i*) was installed onboard, as well as the system to collect air samples for further isotope analysis. During the transects, methane concentration was monitored online, as well as the GPS coordinates. When the concentration peak was noticed, the car stopped and an air sample (or samples) was taken. At several occasions, more throughout research was performed, driving around the neighborhood of possible CH_4 sources. For each transect, a sample of low CH_4 concentration, well-mixed atmospheric air was taken. Two samples were taken in Krakow 18th June to determine the ^{13}C signature of CH_4 in the city. In total, twenty three tedlar bags with sampled air were sent to GGLES to be measured during the visit. After arriving, the samples were measured for CH_4 concentration with Picarro G1101 analyzer, and then for $^{13}CH_4$ with Isoprime Trace Gas continuous-flow mass spectrometer.

Using the simple two-component mixing model for $^{13}CH_4$ (Keeling plot, Keeling 1961), the isotopic signature of each sampled CH_4 concentration peak was calculated.

5. Preliminary results and conclusions

The concentration transects revealed, as the previous study, presence of a number of CH_4 sources throughout the region. The highest CH_4 concentrations encountered during the campaigns were 20.03 ppm (10.06.13) and 14.46 ppm (17.06.13). Concentration changes measured during the transect are being presented in the Fig. 2. Although some of the CH_4 peaks were found in the similar locations in both transects (for example T1-1/T1-2, and T2-13), not all of them reoccurred, which can be assigned to the differences in wind direction or atmosphere stability.

The results of concentration and isotopic analysis of sampled air measurements at GGLES are being presented in Table 1.

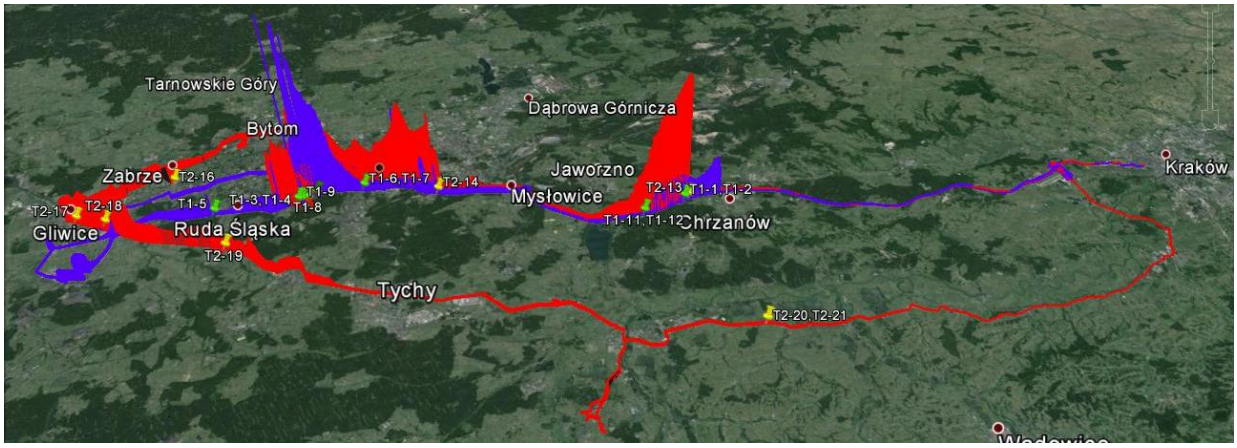

Figure 2. *CH_4 concentration transects throughout the Upper Silesia region along with the sampling points. The measurements were performed 10.06.2013 (blue line, green marks) and 17.06.2013 (red line, yellow marks) [Google Earth].*

Table 1. *Results of CH_4 concentration and ^{13}C isotopic composition measured at GGLES.*

Sample name	Date and time (UTC)	Location	CH_4 (ppm)	$\delta^{13}CH_4$ (‰)
T1-1	2013-06-10 03:57	Balin	5.295	-53.57
T1-2	2013-06-10 03:57	Balin	4.830	-53.16
T1-3	2013-06-10 04:39	Świętochłowice	3.579	-48.57
T1-4	2013-06-10 04:39	Świętochłowice	3.527	-48.44
T1-5	2013-06-10 04:44	Ruda Śląska	3.131	-47.86
T1-6	2013-06-10 06:05	Katowice	5.088	-48.45
T1-7	2013-06-10 06:05	Katowice	4.655	-48.58
T1-8	2013-06-10 07:25	Ruda Śląska KWK Wujek	5.933	-48.97
T1-9	2013-06-10 07:34	Ruda Śląska Oświęcimska (in the forest)	13.478	-50.02
T1-10	2013-06-10 07:42	Ruda Śląska KWK Śląsk	13.259	-50.58
T1-11	2013-06-10 08:04	Background	2.185	-47.98
T1-12	2013-06-10 08:04	Background	2.185	-48.07
T2-13	2013-06-17 03:00	Balin	11.584	-54.85
T2-14	2013-06-17 03:18	KWK Wieczorek	8.589	-49.62
T2-15	2013-06-17 03:56	KWK Śląsk shaft IV	5.147	-48.82
T2-16	2013-06-17 06:26	Zabrze ul. Miarki	4.013	-49.72
T2-17	2013-06-17 06:54	Gliwice ul. Pszczyńska	4.106	-49.66
T2-18	2013-06-17 07:10	KWK Sośnica shaft IV	4.135	-47.54
T2-19	2013-06-17 07:47	Ruda Śląska ul. Gliwicka/Przelotowa/Oświęcimska	3.463	-49.00
T2-20	2013-06-17 10:20	Background	2.129	*
T2-21	2013-06-17 10:23	Background	2.107	-47.67
KR-22	2013-06-18 03:07	Kraków	2.110	-47.77
KR-23	2013-06-18 08:00	Kraków (background)	2.014	-47.23

**not enough air for $^{13}CH_4$ analysis*
KWK = coal mine

For all the samples, source $\delta^{13}CH_4$ signature was calculated. The results are being presented in Fig. 3 and Tab. 2.

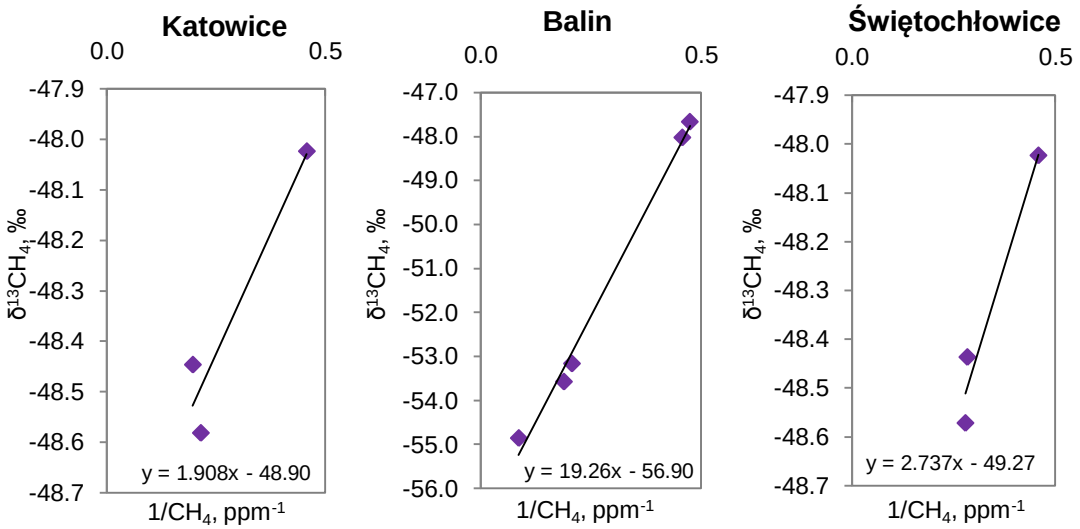

***Figure 3**. Keeling plots for the locations where more than one sample was taken.*

***Table 2.** CH_4 source isotopic ^{13}C signature for sampled peaks.*

Sample names	Peak location	CH_4 source signature (‰)
T1-1,T1-2,T1-11,T1-12,T2-13	Balin	-56.90
T1-3,T1-4,T1-11,T1-12	Świętochłowice	-49.27
T1-5,T1-11,1-12	Ruda Śląska	-47.50
T1-6,T1-7,T1-11,T1-12	Katowice	-48.90
T1-8,T1-11,T1-12	Ruda Śląska KWK Wujek	-49.53
T1-9,T1-11,T1-12	Ruda Śląska Oświęcimska (in the forest)	-50.40
T1-10,T1-11,T1-12	Ruda Śląska KWK Śląsk	-51.08
T2-14,T2-21	KWK Wieczorek	-50.25
T2-15,T2-21	KWK Śląsk shaft IV	-49.62
T2-16,T2-21	Zabrze ul. Miarki	-51.99
T2-17,T2-21	Gliwice Pszczyńska	-51.76
T2-18,T2-21	KWK Sośnica shaft IV	-47.41
T2-19,T2-21	Ruda Śląska Gliwicka/Przelotowa/Oświęcimska	-51.08
KR-22,KR-23	Kraków local CH_4 dome	-59.04

KWK = coal mine

The signature of Balin peak (T1-1,T1-2 and T2-13 samples) confirms the hypothesis of the biogenic origin of CH_4 – nearby the sampling points there is a local landfill located.
City network gas in Southern Poland originates in most cases from Syberia and its $\delta^{13}C$ signature is –51‰. Therefore, the peaks T1-9, T1-10 and possibly T2-16 and T2-17 originate from the city network gas leak.
Remaining CH_4 peaks possibly originate from the mines, however as the Silesian coal mine $^{13}CH_4$ isotopic signature is still being determined, this is an hypothesis to be confirmed.
The Kraków dome $^{13}CH_4$ signature indicates that it is biogenic. However, KR-22 cannot be treated as a representative for all the city as it is only one sample.

6. Outcome and future studies

The results indicate several different sources of methane around the region of Silesia, both biogenic and anthropogenic, with $^{13}CH_4$ isotopic signature ranging from -47.41 to -59.04‰. This research is a part of an extended study of methane sources in the Silesia, consisting of CH_4 concentration transects throughout the region, $^{13}CH_4$ analyses of encountered peaks and

isotopic analyses of coal mine methane. The combined results are going to be presented in the form of a research article. A systematic research, including eddy covariance CH_4 flux measurements and quasi-continuous CH_4 concentration measurements in the Silesia region is being planned.

References

Keeling C.D., 1961. The concentrations and isotopic abundances of atmospheric carbon dioxide in rural and marine air. Geochim. Cosmochim. Acta, 24, 277-298.

Kuc T., Rozanski K., Zimnoch M., Necki J., Korus A., 2003. Anthropogenic emissions of CO_2 and CH_4 in an urban area environment. Applied Energy, 75(3-4), 193-203.

Necki J., Zimnoch M., Miroslaw J., Lasa J., 1999. Construction of local atmospheric CH_4 and CO_2 balance in heavily polluted urban areas on the example of Krakow city. Chemia analityczna, 44(5), 841-847.