



Application of isotope analysis for atmospheric methane and CO sources identification in the TROICA campaigns

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TROICA (www.troica-environmental.com) campaigns have taken place since 1995. In the campaigns a complex of equipment for atmospheric measurements was installed in the train-carriage travelling along the Trans-Siberian rail road from Moscow to Khabarovsk. In the report the summer campaigns of 1999 (T-5) and 2001 (T-7) and spring campaign 2004 (T-8) are discussed specifically concerning the use of stable isotope analysis. The 1999 campaign included an exploratory study along the river Ob using a ship as a platform for atmospheric measurements.

In the campaigns both in situ measurements and air sample collection were done. The samples were later subjected to the laboratory analysis to define the isotopic composition of methane and CO.

The concentration and stable isotope (^{13}C , D) signatures of CH_4 were measured in all reported expeditions (T-5 including river part, T-7, T-8), while concentration, radio-carbon (^{14}C) and stable isotope (^{13}C and ^{18}O) content of CO were only measured in the campaign of 1999 both along Trans-Siberian rail road and Ob river.

For the boat and train parts of the T-5 campaign CH_4 concentrations over wetlands in Western Siberia, especially in the Middle Ob area were significantly enhanced relative to the background mixing ratios. The source isotopic signature detected in this region points to biogenic sources with $\delta^{13}\text{C}_{\text{source}} = -62.9 \pm 0.7$ per mil (n=5) and $\delta\text{D}_{\text{source}} = -$

369±11 per mil (n=5). CO mixing ratios, its stable isotopes and the abundances of ^{14}CO over West Siberia were similar to those found at remote northern hemispheric baseline monitoring stations. Identified sources of CO along the Ob (in T-5 boat part) point to methane oxidation based on an inferred $\delta^{13}\text{C}_{\text{source}}=-36.8\pm 0.6$ per mil, while the value for $\delta^{18}\text{O}_{\text{source}}=9.0\pm 1.6$ per mil identifies it as burning. At the same time, for several samples a clear anthropogenic impact can be seen. Along the Trans-Siberian Railroad background CO was to various degrees contaminated with CO from methane combustion ($\delta^{13}\text{C}_{\text{source}} = -35.7\pm 6.2$ per mil and $\delta^{18}\text{O}_{\text{source}}=10.3\pm 1.8$ per mil). The impact of industrial burning was discernable in the vicinity of Perm-Kungur, where methane isotopic signature shows a substantial contribution of the natural gas ($\delta^{13}\text{C}_{\text{source}}=-52.6\pm 1.3$ per mil and $\delta\text{D}_{\text{source}}=-283\pm 3$ per mil) to elevated methane levels.

In summer 2001 the campaign (T-7) took place only along the Trans-Siberian railroad where methane concentration and $\delta^{13}\text{C}$ were measured. Methane source estimates ($\delta^{13}\text{C}_{\text{source}}$) were inferred to be in the range between -54.1 ± 2.8 per mil and -67.4 ± 1.6 per mil for different regions along the route, showing its primary biogenic origin. As for the previous expedition T-5 clear anthropogenic contribution into elevated methane levels was obvious in Perm-Kungur region ($\delta^{13}\text{C}_{\text{source}}$ (#8) $=-52.42$ per mil).

In the spring expedition T-8, which took place along the Trans-Siberian railroad, methane and both stable isotopes were measured. The individual source signatures defined for the collected air samples were more uncertain as deviations of methane concentration from a background were rather small. The evident contribution of the natural gas was only seen in the air sample collected in Novosibirsk ($^{13}\text{C}_{\text{source}}$ (#79) $=-53.2\pm 0.8$ per mil and $\delta\text{D}_{\text{source}}$ (#79) $=-289\pm 7$ per mil).

The use of isotope data in combination with the mobile TROICA platform appears to be useful for methane source identification yet was a bit less informative for CO sources identification due to more complex isotopic measurements and limited set of data.

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