

## Stable isotope ratios of atmospheric CO<sub>2</sub> and CH<sub>4</sub> over Siberia measured at ZOTTO

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The boreal and arctic zones of Siberia housing the large amounts of carbon stored in the living biomass of forests and wetlands, as well as in soils and specifically permafrost, play a crucial role in earth's global carbon cycle. The long-term studies of greenhouse gases (GHG) concentrations are important instruments to analyze the response of these systems to climate warming. In parallel to GHG observations, the measurements of their stable isotopic composition can provide useful information for distinguishing contribution of individual GHG source to their atmospheric variations, since each source has its own isotopic signature. In this study we report first results of laboratory analyses of the CO<sub>2</sub> and CH<sub>4</sub> concentrations, the stable isotope ratio of  $\delta^{13}\text{C-CO}_2$ ,  $\delta^{18}\text{O-CO}_2$ ,  $\delta^{13}\text{C-CH}_4$ ,  $\delta\text{D-CH}_4$  measured in one-liter glass flasks which were obtained from 301 height of ZOTTO (Zotino Tall Tower Observatory, near 60°N, 90°E, about 20 km west of the Yenisei River) during 2008 – 2013 and 2010 – 2013 for stable isotope composition of CO<sub>2</sub> and CH<sub>4</sub>.

The magnitudes of  $\delta^{13}\text{C-CO}_2$  and  $\delta^{18}\text{O-CO}_2$  in a seasonal cycle are  $-1.4\pm 0.1\text{‰}$  ( $-7.6 - -9.0\text{‰}$ ) and  $-2.2\pm 0.2\text{‰}$  ( $-0.1 - -2.3\text{‰}$ ), respectively. The  $\delta^{13}\text{C-CO}_2$  seasonal pattern opposes the CO<sub>2</sub> concentrations, with a gradual enrichment in heavy isotope occurring during May – July, reflecting its discrimination in photosynthesis, and further depletion in August – September as photosynthetic activity decreases comparatively to ecosystem respiration. Relationship between the CO<sub>2</sub> concentrations and respective  $\delta^{13}\text{C-CO}_2$  (Keeling plot) reveals isotopic source signature for growing season (May – September)  $-27.3\pm 1.4\text{‰}$  and  $-30.4\pm 2.5\text{‰}$  for winter (January – March). The behavior of  $\delta^{18}\text{O-CO}_2$  associated with both high photosynthetic rate in the June (enrichment of atmospheric CO<sub>2</sub> by <sup>18</sup>O as consequence of CO<sub>2</sub> equilibrium with “heavy” leaf water) and respiratory activity of forest floor in June – October (depletion of respired CO<sub>2</sub> by <sup>18</sup>O because of the use of “light” soil water by microorganisms).

There is large temporal variation of  $\delta^{13}\text{C-CH}_4$  ( $-50.0 - -46.1\text{‰}$ ) with clear minimum in the late summer (August) that corresponds to CH<sub>4</sub> concentration maximum and reflects biogenic sources of methane in the surrounding peatbogs. The  $\delta\text{D-CH}_4$  varies from  $-77.4$  to  $-110.2\text{‰}$  and showed no seasonal cycle with many irregular spikes throughout a year. Keeling plot analysis between the CH<sub>4</sub> concentration and isotopic composition revealed that isotopic signature of source in the winter (December – February) is  $-61.3\pm 2.2\text{‰}$  and  $-247.5\pm 17.7\text{‰}$  for  $\delta^{13}\text{C-CH}_4$  and  $\delta\text{D-CH}_4$ , respectively. For growing season (June – September) the corresponding values for  $\delta^{13}\text{C-CH}_4$  and  $\delta\text{D-CH}_4$  are  $-76.4\pm 2.6\text{‰}$  and  $-342.2\pm 14.8\text{‰}$ . The strong depletion of methane in heavy isotopes throughout a year is the indication of continuous CH<sub>4</sub> emissions from biogenic sources.

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