Study of the sources of methane from Delta-Danube Black-Sea Region, using stable isotopes

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Methane is a natural greenhouse gas, which absorbs heat and radiates it back to the surface. In fact, the methane is more potent greenhouse gas than CO_2 on a molecular basis. If we wish to slow the accumulation of CH_4 in the atmosphere to avoid the changes in climate that could result, we must understand how CH_4 is transferred from the various components of the global carbon cycle and how humans have affected the processes that control it. Major sources of methane are natural wetlands, rice agriculture, ruminant animals, natural gas emissions due to geological venting, leakage in distribution systems and coal mining, landfills and biomass burning. The Danube Delta Black Sea region of Romania is an important wetland, and this preliminary study evaluates the significance of this region as a source of atmospheric methane.

Field sampling consisted of weekly samples collected from Black Sea Constanta (BSC) site by the National Oceanic and Atmospheric Administration/ Earth System Research Laboratory (NOAA/ESRL), Global Monitoring Division, network, as well as a field trip to Danube Delta region of Romania, ca. 100 km from BSC site. In the Danube Delta area, air and water samples were collected in eight different wetland habitats by boat. CH_4 concentration in flasks and headspace above water was analyzed using a gas chromatograph with flame ionization detector. $\delta^{13}C$ for methane was analyzed by continuous flow mass spectrometry.

The methane concentrations in air and water samples from Danube Delta are high, demonstrating that Danube Delta is an important source of atmospheric methane. Water samples have highest CH_4 concentration from 1.27 μmol L^{-1} to 9.83 μmol L^{-1}. Methane

concentration in air immediately above the wetland soil surfaces ranged from 2500 nmol mol^{-1} to 14000 nmol mol^{-1}. These concentrations are high compared to 1800 nmol mol^{-1} in background air (Dlugokencky et al., 1995). The $\delta^{13}C_{CH4}$ from air samples ranged from –47 ‰ (background air) to –58 ‰ (acetate fermentation pathway) in agreement with the values reported by Breas et al. (2001).

The methane concentration in air, $[CH_4]$, and its isotopic ratio, $\delta^{13}C_{CH4}$, may be derived from three main sources: microbially produced methane, $[CH_4]_{micr}$, fossil methane, $[CH_4]_{ff}$, and methane produced from biomass burning, $[CH_4]_{bmb}$.

$$[CH_4] = [CH_4]_{micr} + [CH_4]_{ff} + [CH_4]_{bmb} + [CH_4]_{bg} \quad (1)$$

In this equation, $[CH_4]_{bg}$ is the background for methane in air, which is defined as the smoothed marine boundary layer (MBL) at the latitude of interest (Dlugokencky et al. 1994).

We have combined the measurements of $\delta^{13}C$ with mixing ratios $[CH_4]$ in air samples to estimate the signature of the sources of methane in the Danube Delta wetland areas. We have determined these signatures with the two-end member-mixing model of Keeling. By plotting $\delta^{13}C$ vs. the inverse of the CH_4 concentration, the y-intercept is interpreted as isotopic signature of the source or sink. The isotopic signature of the methane source ranged from $\delta^{13}C$ = -61.1 ‰ to $\delta^{13}C$= -72.0 ‰ suggesting the source of methane in our sampling sites in springtime was most likely to be primarily from an acetate fermentation pathway. In Fig.1 is shown a Keeling plot from one of the sampling site in Danube Delta.

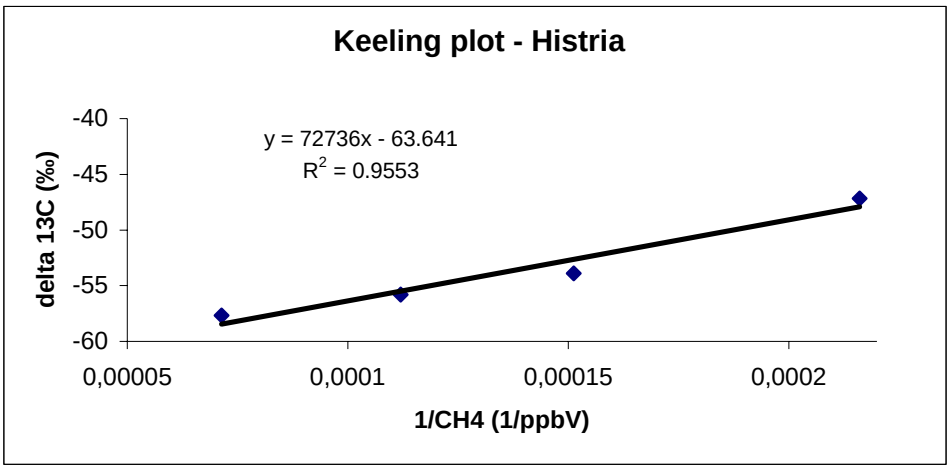

Figure 1 Keeling plot from Histria

The NOAA/ESRL CH_4 measurements from well mixed air samples were used to make the first cut of biogenic methane at the Black Sea sampling station at Constanta.

The most noticeable aspect of the BSC data is that the methane concentrations average 100-150 μmol mol^{-1} higher than the MBL. We analyzed these data to extract the contribution of biogenic sources from global methane emissions. We assume the main influences on the mixing ratios of methane samples from BSC are biogenic, $[CH_4]_{bio}$, and anthropogenic (pollution), $[CH_4]_{ff}$. Thus, the CH_4 mole fraction is the sum of contributions from some regional background and regional fluctuations due to biogenic source and sinks and fossil fuel emissions. We can estimate $[CH_4]_{bio}$ by taking advantage of CO measurements made on the same air used to determine $[CH_4]$ (Miller et al., 2003). We assume that the main source of CO is pollution, mainly fossil fuel, and that there is a constant molar emission ratio of CH_4 to CO of R=0.6 for fossil fuel pollution. We estimated the methane concentrations that resulted only from biogenic and background (MBL) sources by subtracting the fossil fuel source:

$$[CH_4]_{bio,t} = [CH_4]_{BSC,t} - \Delta CO_{BSC,t} R \qquad (2)$$

Figure 2 shows the estimated $[CH_4]_{bio,t}$ from BSC corrected according to Eq. 2, with the MBL curve for comparison. We note that the corrected $[CH_4]$ data averages roughly 100 ppb higher than the MBL curve, showing a consistent and significant biological source. We concluded that the most of the methane at the BSC station is not from pollution.

Preliminary Keeling plots from the BSC air flask samples show a lower $\delta^{13}C$ source value in summer (-55‰), similar to the microbial methanogenesis value, and a higher value in winter (-51‰). These isotope data are consistent with the possibility of greater biological contributions to elevated CH_4 concentrations in summertime, and greater anthropogenic contributions to elevated concentrations in winter at the Black Sea – Constanta sampling station.

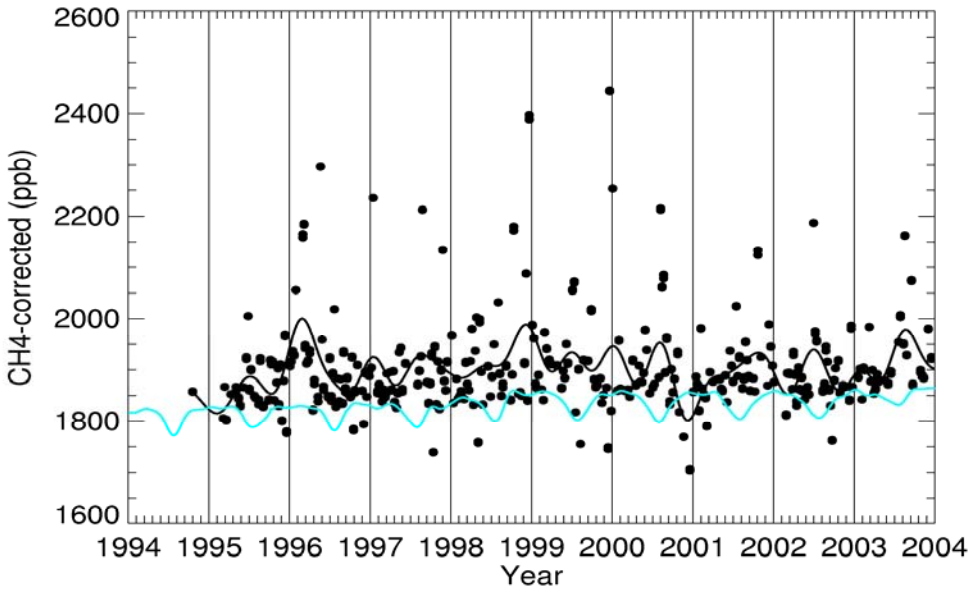

Figure 2. Time series of [CH_4] from BSC corrected to remove the fossil fuel source. Black line, smoothed curve fit to the corrected CH_4 data; grey line, MBL reference.

The Delta Danube is a biological source of methane, but the samples collected at BSC have biogenic, fossil fuel and geological methane contributions.

References

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