Tracing local natural gas oxidation by means of oxygen to carbon dioxide ratio measurements

Markus Leuenberger, Chiara Uglietti and Peter Nyfeler

Climate and Environmental Physics, Physics Institute, University of Bern, Switzerland

15th WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration, other Greenhouse Gases and Related Tracer Measurement Techniques, Jena, Germany

September 9, 2009
• Measuring system for combined CO₂ and O₂ measurements
• Selected time intervals with high carbon oxidation factors (COFs)
• Carbon isotope signature of corresponding CO₂
• Methane budget for Berne city
• Conclusions and Outlook
Measuring system

Combined CO₂ and O₂ system at Berne city (46°57’05”N, 7°26’19”E, 575 m.a.s.l.)

CO₂: Licor 7000 instrument

CO₂: Fuel cells (Oxzilla) and paramagnetic cell

Control: CO₂ and O₂ measurements on IRMS (DELTA⁺XP)
Fig. 1: Three hour interval of CO$_2$ and O$_2$ recordings (one minute averages) on the 1$^{st}$ of September 2008 at Berne
Fig. 2: Top, sectional display of the record given in Fig. 1. Bottom, correlation between $O_2$ and $CO_2$ with an apparent slope for normal fossil fuel mix oxidation.
Combined CO$_2$ and O$_2$ records

Fig. 3: Top, sectional display of the record given in Fig. 1. Bottom, correlation between O$_2$ and CO$_2$ with an apparent slope for methane oxidation.

Steigung: \(-2.02\) O$_2$/CO$_2$ [ppm/ppm]

corrcoef(y,x): 0.72
Fig. 4: A day interval of CO₂ and O₂ recordings (one minute averages) on the 1st of January 2009 at Berne.
Combined CO$_2$ and O$_2$ records

**Fig. 5:** COFs for the record shown in Fig. 4. Slopes indicate CH$_4$ oxidation

\[ y = -1.98x + 718.38 \]
\[ R^2 = 0.57 \]

\[ y = -2.01x + 724.12 \]
\[ R^2 = 0.91 \]
Fig. 6: Carbon isotope composition of measured CO₂.
Combined CO₂ and δ¹³C records

\[ y = -31.08x + 30.16 \]
\[ R^2 = 1.00 \]

\[ y = -29.60x + 23.59 \]
\[ R^2 = 0.94 \]

\[ \delta^{13}C \text{ Signature of methane} \]

Fig. 6: Carbon isotope signature of CH₄ measured on CO₂.
More than 20% of the annual energy consumption of Berne city is based on natural gas.

This corresponds to 1’200’000 MWh/yr, i.e. 120 Mm³/yr CH₄ or 5.36 Gmol/yr CH₄.

This corresponds to twice as much mol consumption of oxygen (O₂), i.e. 10.7 Gmol/yr O₂.

Assuming a square area of Berne city of 10x10 km² with a vertical well mixed air height of 500 m corresponds to a volume of 5 x 10¹⁰ m³, i.e. 2.2 x 10¹² mol of air.

Since methane is to more than 80 percent used for heating purposes there is a strong seasonality present. Therefore, during winter months about 8.56 Gmol O₂/120 days, i.e. 70 Mmol O₂/day is consumed.

This corresponds to (70 Mmol O₂/day) / (0.2095 x 2.2 x 10¹² mol of oxygen), 150 permeg change in O₂ and about 15-16 ppm change in CO₂.

Hence, realistic signal strengths are obtained, which are in the range of observed signals.
Conclusions:

• Short term slopes of O₂/CO₂ ratios (COFs) of -2 mol O₂/mol CO₂ are observed, especially in autumn and spring. In winter such slopes are observed for much longer periods.

• Methane oxidation seems to be reasonable due to high natural gas consumption in Berne city for heating purposes.

• Estimates of signal strengths are compatible with daily consumption rates.

Outlook:

• δ¹³C signature of natural gas mixtures in Berne is not known, should be determined.

Thank you