



A new method for semi-continuous atmospheric methanol measurements and its application to measure soil-atmosphere methanol exchange

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Current methods for measuring atmospheric methanol mixing ratios suffer from a variety of problems. For instance, poor precision (adsorbent trapping followed by chromatography) or high cost and limited field portability (chemical ionisation mass spectrometry). We developed a new, semi-continuous methanol measurement method employing selective catalytic methanol-to-formaldehyde conversion followed by formaldehyde detection using a commercial wet-chemical formaldehyde analyser. The efficiency of conversion using a molybdenum-rich, iron molybdate catalyst was optimised and then tested for possible interferences from abundant atmospheric species, such as methane and selected VOCs. Optimum conversion efficiency (>95 %) occurred at catalyst temperatures of 345 °C for a 1:4 (w/w) mixture of catalyst in quartz sand and an estimated air/catalyst contact time of < 0.2 s. No significant formaldehyde formation was recorded upon passage of either methane or a variety of VOCs through the catalytic converter under optimal conditions. Measurements of methanol in real air show typical diurnal methanol variations. Direct comparison of this technique with other methanol measurement techniques, such as CIMS, has also been undertaken during the ACCENT OVOC intercomparison campaign conducted at the large photochemical simulation chamber (SAPHIR) located at the Research Centre Juelich. Currently, we are using this technique to measure soil-atmosphere methanol exchanges in a laboratory glass chamber. First results indicate that a dry agricultural soil produces methanol with an activation energy of $\sim 50 \text{ kJ mol}^{-1}$, a value nearly identical to in-situ micrometeorological measurements above the same soil in 2003.

Wetting of the soil leads to heightened, short-term methanol emissions. Simultaneous CO₂ flux measurements indicate that the process is likely not linked to soil microbiological activity, but constitutes a physico-chemical process similar to that observed for CO production in the soil.