



## **Mixing ratio measurements and flux estimates of volatile organic compounds (VOC) from a cowshed with conventional manure treatment indicate significant emissions to the atmosphere**

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Agricultural activities are a known, large source of trace gas emissions to the atmosphere. Animal husbandry, as an example, has been documented as a significant global source of methane ( $\text{CH}_4$ ) and ammonia ( $\text{NH}_3$ ), and also nitrous oxide ( $\text{N}_2\text{O}$ ). Using chemical ionisation mass spectrometry (CIMS), we have investigated whether ruminant exhalations and manure decomposition in animal housings are also sources of volatile organic compounds (VOCs) to the atmosphere. A commercial Proton-Transfer-Reaction Mass Spectrometer (PTRMS) was set up inside a large cowshed of the Federal Agricultural Research Centre (FAL) in Mariensee, Germany, for a two-week long campaign to monitor some 43 masses at a 2-minute time resolution. The cowshed is housing 120 adult milk cows in a three double row tie-stalls setting with a typical solid manure treatment (straw litter) system. Mixing ratios of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  were simultaneously monitored by a commercial photo-acoustic spectrometer. Typical daytime mixing ratios inside the cowshed included 60 ppm methane, 4 ppm ammonia, and 0.5 ppm nitrous oxide. Typical VOCs (monitored mass and median mixing ratio in parentheses), for which much higher than ambient labels outside the cowshed were found, included ethanol/formic acid ( $m/z$  47, 1.4 ppm), methanol ( $m/z$  33, 140 ppb), isopropanol ( $m/z$  61+43+41, 170 ppb), acetaldehyde ( $m/z$  45, 27.5 ppb), acetone ( $m/z$  59, 22 ppb), trimethylamine (TMA;  $m/z$  60, 14 ppb), and DMS ( $m/z$  63, 7.5 ppb). During feeding hours and solid manure removal, large mixing ratio

spikes of several VOCs were observed and correlated with increased  $\text{CH}_4$  and  $\text{NH}_3$  levels. Timing of the emission spikes indicates that the alcohols are emitted primarily from the fodder while TMA and DMS stem from the cow manure. During “quiet” hours, almost all monitored mixing ratios decayed likely as a result of passive cowshed ventilation. Correlations of VOC mixing ratios with methane or ammonia during these “active” and “quiet” hours can be used to calculate cowshed emissions and to estimate potential national and global VOC emission rates.