Gas chromatography vs. quantum cascade laser-based N2O flux measurements using a novel chamber design

Recent advances in laser spectrometry offer new opportunities to investigate the soil-atmosphere exchange of nitrous oxide. During two field campaigns conducted at a grassland site and a willow field, we tested the performance of a quantum cascade laser (QCL) connected to a newly developed automated chamber system against a conventional gas chromatography (GC) approach using the same chambers plus an automated gas sampling unit with septum capped vials and subsequent laboratory GC analysis. Through its high precision and time resolution, data of the QCL system were used for quantifying the commonly observed nonlinearity in concentration changes during chamber deployment, making the calculation of exchange fluxes more accurate by the application of exponential models. As expected, the curvature values in the concentration increase was higher during long (60 min) chamber closure times and under high-flux conditions (F-N2O > 150 μg N m⁻² h⁻¹) than those values that were found when chambers were closed for only 10 min and/or when fluxes were in a typical range of 2 to 50 μg N m⁻² h⁻¹. Extremely low standard errors of fluxes, i.e., from similar to 0.2 to 1.7% of the flux value, were observed regardless of linear or exponential flux calculation when using QCL data. Thus, we recommend reducing chamber closure times to a maximum of 10 min when a fast-response analyzer is available and this type of chamber system is used to keep soil disturbance low and conditions around the chamber plot as natural as possible. Further, applying linear regression to a 3 min data window with rejecting the first 2 min after closure and a sampling time of every 5 s proved to be sufficient for robust flux determination while ensuring that standard errors of N2O fluxes were still on a relatively low level. Despite low signal-to-noise ratios, GC was still found to be a useful method to determine the mean the soil-atmosphere exchange of N2O on longer timescales during specific campaigns. Intriguingly, the consistency between GC and QCL-based campaign averages was better under low than under high N2O efflux conditions, although single flux values were highly scattered during the low efflux campaign. Furthermore, the QCL technology provides a useful tool to accurately investigate the highly debated topic of diurnal courses of N2O fluxes and its controlling factors. Our new chamber design protects the measurement spot from unintended shading and minimizes disturbance of throughfall, thereby complying with high quality requirements of long-term observation studies and research infrastructures.

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