WHITE PAPER

Evaluating gas emission measurements using Minimum Detectable Flux (MDF)

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INTRODUCTION

Traditional vial-and-syringe-type measurements of closed chamber trace gas fluxes have provided researchers with massive amounts of insight into ecosystems ranging from old growth forests to heavily managed agricultural fields. However, anyone who has ever collected these types of gas samples knows that you can easily compromise your carefully collected samples in the blink of an eye, or with a trip down the stairs.

Even if you're careful, and get your vials back to the lab in one piece, data can still be lost during extraction and analysis. In a recent paper, Christiansen et al. (2015) compare trace gas (CO_2, CH_4, and N_2O) fluxes measured using a traditional vial-based chamber method to those measured in situ using a laser-based analyzer (Picarro G2508 Cavity Ring-Down Spectroscopy (CRDS)[1]). While the authors note that the qualitative results of the study (i.e. treatment effects) remained consistent between both methods, they report an incredible 4x higher methane flux sample recovery rate when using the laser-based system as compared to the Gas Chromatograph (GC) and vial method.

> *Overall there was a much smaller recovery of CH_4 fluxes measured with both techniques compared to CO_2 and N_2O. For GC eight out of 49 fluxes were significant compared to 32 out of 49 for CRDS, corresponding to a detection level of 16% and 65% of all CH_4 fluxes for GC and CRDS, respectively.*

The authors attribute this increased recovery rate of methane flux estimates to two causes. First, the sensitivity of the GC to sub-ambient methane concentrations (<2 ppm CH_4, indicating methane uptake in the soil chamber) was poor due to sample handling and processing errors in both the field and laboratory. In contrast, the in situ measurements made using the CRDS analyzer are not subject to these sample handling issues. Secondly, and perhaps more important, was the significantly increased temporal resolution of chamber concentration time series measurements using the laser-based analyzer. The data-density created by the rapid laser-based sampling allowed for detection of statistically significant but very small negative fluxes of methane that went undetected by the GC method.

These results led the authors to develop a metric called Minimum Detectable Flux (MDF) and to further discuss the significantly decreased MDF values that can be achieved using high-density data from laser-based analyzers. In the next couple of sections, we'll talk about how the MDF works, and how to extend it to your studies.

AN INTRODUCTION TO MDF

Christiansen et al. (2015) developed the Minimum Detectable Flux (MDF) metric and demonstrated its utility as a guideline for experimental design and data quality assurance for closed chamber measurements of trace gas flux. By combining the analytical accuracy of the instrument(s) being used to measure gas concentration, the chamber volume and surface area, and the total chamber closure time, the MDF produces a lower limit for flux rates that can be detected with a given methodology.

To calculate MDF (μmol/m^2/h) for a gas species, the equation below can be used:

$$MDF = \left(\frac{A_A}{t_c}\right)\left(\frac{V\,P}{SRT}\right) \qquad (1)$$

where A_A is the analytical accuracy of the instrument (ppm), t_C is the closure time of the chamber in hours, V is the chamber volume (m^3), P is the atmospheric pressure (Pa), S is the chamber surface area (m^2), R is the ideal gas constant (m^3 Pa K^{-1} mol^{-1}) and T is the ambient temperature (K).

Once calculated, the MDF for a given chamber design and analytical methodology is easily used to iterate experimental design, data quality assurance criteria and the experimental methods as necessary to ensure measured fluxes will be above the predetermined MDF limit thereby minimizing loss of field data. Alternatively, the MDF can be used as a post-hoc quality control metric on chamber measurements, and offers a quantitative assessment tool that researchers can use to identify and discard suspect flux values.

By applying the MDF to their chamber measurements, Christiansen et al. (2015) were able to show that closure times of 10 minutes or more allowed them to get good flux measurements (<5% relative error) that were well above the MDF limit for their custom 2.7 l (surface area of 0.3 m^2) chamber system using the CRDS analyzer in an agricultural monitoring experiment. Contrastingly, the GC-based measurements with this 10-minute chamber closure period worked well for carbon dioxide and nitrous oxide, but underperformed for measurements of methane fluxes. Only a small portion of the GC-based chamber data could be used for flux estimates due to a combination of sample contamination and in situ flux rates that were below the GC-based MDF limit.

Not only does this example demonstrate the use of MDF to perform a post-hoc quality control analysis of collected flux data, but it also demonstrates the utility of in situ measurements in minimizing potential contamination issues, as well as the application of high-resolution laser based devices to yield more accurate estimates of GHG flux. The MDF metric can be further extended to show the benefits of increased measurement frequency.

EXTENDING MDF TO HIGH-FREQUENCY MEASUREMENTS

As discussed previously, the MDF metric provides a useful experimental design and quality control criteria for flux measurements. However, it can be extended from the original formulation to show more clearly how increased measurement frequency, as provided by laser-based analyzers, like the Picarro G2508, can further lower the minimum detectable flux.

In their paper, Christiansen et al. (2015) use the raw noise (no time averaging) of the Picarro G2058 instrument as the estimate of the analytical uncertainty. However, this uncertainty metric is not fully-descriptive for instruments that provide high-frequency measurements of gas concentration. In this case, it is arguable that the raw noise should be replaced with a measure similar to the statistical standard error (assuming the noise is approximately normally distributed):

$$A_{SE} = \frac{A_A}{\sqrt{n}} \tag{2}$$

where A_{SE} is a modification to A_A in the original MDF calculation (Equation 1) and n is the number of measurements of the gas concentration during the chamber closure period. Note that this standard error approach is a first order approximation for the MDF from high-frequency measurements and that the "true" MDF is a function of the chamber timeseries fit type as well (i.e. Linear, exponential, quadratic).

$$MDF_{SE} = \left(\frac{A_A}{t_C \sqrt{\frac{t_C}{p_s}}} \right) \left(\frac{VP}{SRT} \right) \tag{3}$$

where p_S is the sampling periodicity (i.e. every 10 s) in hours. This MDF_{SE} metric is equally applicable to instruments such as the GC, as long as multiple samples are drawn during the chamber closure period; however when using these manual sampling approaches the reduction of the MDF is typically significantly less than when using instruments that make measurements with periods on the order of seconds.

Using this new MDF_{SE} approximation, the increased temporal resolution of measurements in laser-based analyzers means that the analytical uncertainty of a GC or similar lab-based measurement devices would need to be better by a factor of about √n in order to yield the same MDF_{SE}, given the same chamber system and deployment period.

Since it is not desirable to deploy chambers for a long period of time due to the disturbance they cause on the soil gas diffusion profile (as mentioned by Christiansen et al.), it is also useful to turn this new MDF_{SE} metric around to show that chambers that are coupled to high-frequency concentration analyzers can be deployed for a factor of √n less time and yield the same data quality as a chamber that is being measured using the traditional techniques (i.e. Gas Chromatography). The other benefit this offers is that users can measure √n more frequently – whether this is more measurements of fluxes across space, or measurements of the temporal dynamics at a single location.

As a more concrete example of the benefits, take the case of deploying a chamber of 0.5 m effective height (effective height is equal to volume divided by surface area) to measure methane fluxes. Assume that is is necessary to measure fluxes of 0.1 μmol/m^2/s and above for the purposes of the example. From Figure 1, the CRDS system (which measures concentrations about once every 10 seconds) requires a closure of about 15-17 minutes to stay above the prescribed MDF limit for our hypothetical study. The same chamber sampled every 5 minutes (300 s) for GC based analysis (assuming the GC has the same analytical accuracy as the CRDS) needs to be deployed for more than an hour and sampled 12 times during that period to achieve an above MDF_{SE} limit flux measurement.

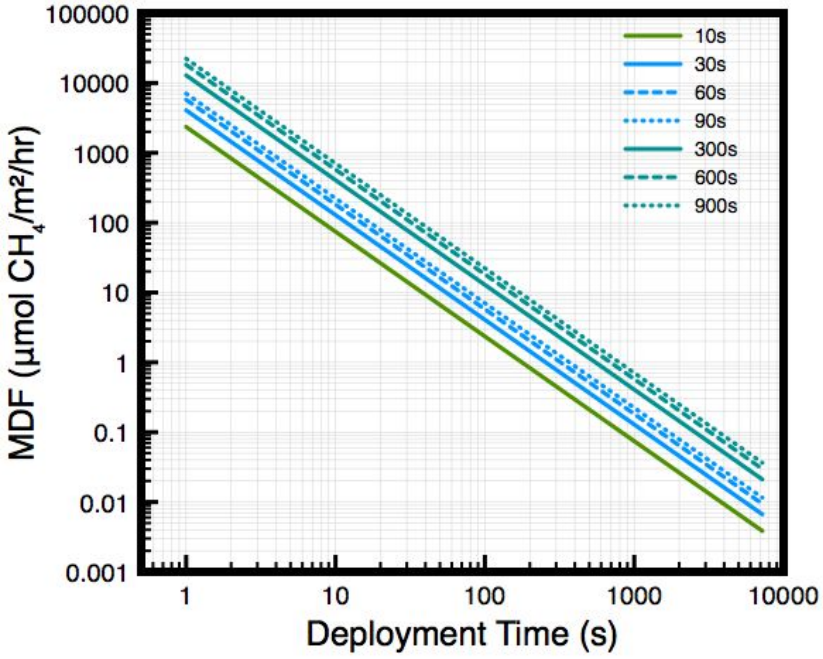

Figure 1. Calculated MDF for a laser-based instrument (i.e. Picarro G2508 CRDS) and MDF curves for GC based analysis with the same precision as the CRDS, but varying frequency of gas concentration sampling (see legend).

From this example it is easy to see that users with high-frequency measurement instruments could either measure more sites in the approximate 45 minutes of time saved by using the CRDS, or alternatively measure the flux at the same position 3 more times to get a better idea of the variability or trend over time.

Conclusions

The MDF metric, as proposed by Christiansen et al. (2015) and the modifications that have been made in this article offer chamber users a new method to ensure experimental design and quality control criteria are met during greenhouse gas flux measurement campaigns. The MDF and work of Christiansen et al. (2015) also clearly demonstrates the utility of the relatively new high-resolution, in situ greenhouse gas analysis systems in accurately monitoring greenhouse gas emissions from a variety of environments and across a large range in efflux rates.

References

Christiansen, J.R., Outhwaite, J., Smukler, S.M., 2015. Comparison of CO2, CH4, and N2O soil-atmosphere exchange measured in static chambers with cavity ring-down spectroscopy and gas chromatography. *Agricult Forest Meterol* 211(2015): 48-57

1. http:/www./picarro.com/technology/cavity_ring_down_spectroscopy

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