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DIODE LASER BASED PHOTOACOUSTIC INSTRUMENT FOR AMMONIA CONCENTRATION AND FLUX MONITORING

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ABSTRACT

A diode laser based near infrared (1532 nm) photoacoustic ammonia monitoring instrument was combined with a preconcentration unit in order to reach sub-ppb detection limit with a compact, automatic measuring instrument. The system has no measurable cross-sensitivity to common atmospheric gases, most importantly to water vapor and carbon dioxide. The minimum detectable amount of ammonia is 2.9 ng, which means a minimum detectable concentration of 0.5 ppb with a 30-minute measurement time. The instrument was calibrated with the widely accepted, wet-chemical AMANDA instrument, and was tested in several inter-comparison campaigns with various instruments. Results of the inter-comparison campaigns show that the instrument is highly reliable even under harsh field conditions and accurate enough for environmental ammonia concentration monitoring.

The instrument can be operated with three sampling inlets and thus can be used for ammonia flux measurements with the gradient method. The instrument was successfully tested in a measurement campaign on an agricultural field near a cattle farm, the purpose of which was to quantify ammonia load to the field originating from the cattle farm, taking use of the wide dynamic range of the instrument. In a second campaign, long term flux measurements were carried out for several months above semi-natural grassland, where the stability of the instrument was tested. In this campaign, ammonia emission was observed during the day (with a typical maximum of about 220 $\mu gN/m^2 \cdot h$) and deposition during the night (-10 $\mu gN/m^2 \cdot h$ on average), and the measured flux values were within the theoretically estimated range.

Keywords

ammonia, concentration, flux, photoacoustic spectroscopy, preconcentration

1. INTRODUCTION

Ammonia is the most important alkaline gas in the troposphere, therefore plays a crucial role in atmospheric acid-base chemistry. Increased ammonia load might alter the pH of soil and water and thereby damage sensitive ecosystems. Besides this, ammonia is the third-most abundant nitrogen-containing compound in the atmosphere, which means that higher amounts of ammonia mean an increased nitrogen load and might cause eurtophication. Furthermore, ammonia contributes to atmospheric fine aerosol formation, through its reactions with sulfur and nitrogen oxides, and effect global radiation budgets and has adverse effects on human health.

Due to the above mentioned facts, ammonia is considered as an air pollutant; however its importance has been discovered only recently. The Gothenburg Protocol of the UN Convention on Long-Range Transbounday Air Pollution in Europe was the first international convention regulating ammonia emissions.

Besides its concentration, fluxes of ammonia are also important from the environmental point of view, since this provides information about the direction and magnitude of ammonia exchange between the atmosphere and biosphere.

Several ammonia monitoring instruments have been developed in the past few decades, however, none of them is ideal for long-term ammonia flux monitoring in the field, therefore developing ammonia monitoring instrument remains an unsolved problem.

We have developed a compact, automatic instrument based on diode laser based photoacoustic spectroscopy, combined with chemical preconcentration of the sampled air, which ensures the high sensitivity and selectivity. The instrument can be supplemented with more sampling inlets which make it suitable for flux measurements based on gradient methods.

2. EXPERIMENTAL

We have combined a near-infrared diode laser based photoacoustic ammonia monitoring system described in Ref. 1 with preconcentration sampling (Ref. 2). The instrument can be supplemented with more sampling inlets and therefore used in flux measurements. The main characteristics of the instrument are the following: detection limit of 0.5 ppb, time resolution between 5 and 30 minutes, no measurable cross sensitivity to water vapor, carbon dioxide and aerosol particles, compact design and capability of unattended, automatic operation.

3. RESULTS

Long term ammonia flux measurements were carried out with the instrument in Bugac, above semi-natural grassland in the Hungarian Great Plain. A cattle farm is located near the monitoring station that causes relatively high ammonia concentration during the day.

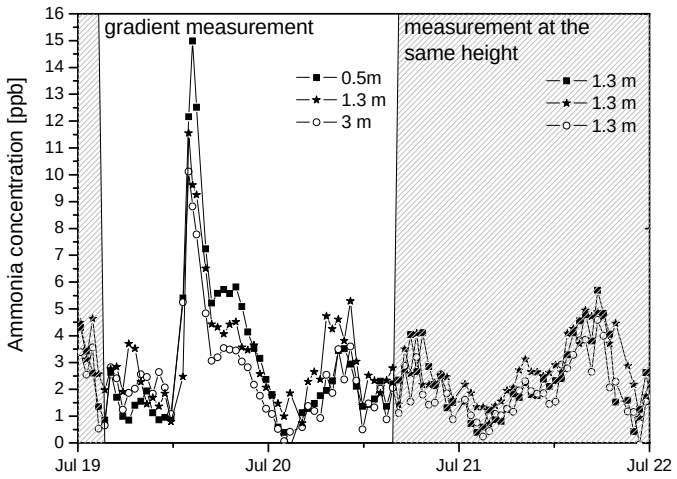

Figure 2: Ammonia concentration measured by the three inlets of the photoacoustic instrument in Bugac. Shading indicates when all three inlets were placed at the same height

Figure 2 shows a 3-day part of the measurements. White area indicates when the three sampling inlets of the instrument were placed at 0.5, 1.3 and 3 m, respectively for gradient measurements. Shading indicated when the inlets were brought to a common height (1.3 m) for self-checking and determination of correction factors if necessary. The Figure shows that in case of gradient measurements higher concentrations were observed closer to the ground, which indicates emission of ammonia.

Ammonia fluxes were calculated from the concentration data measured at three different heights using the aerodynamic gradient method. Fluxes were averaged to determine the average daily variation of the ammonia flux. Figure 3 shows this daily variation for the period 2nd July – 5th October, 2008.

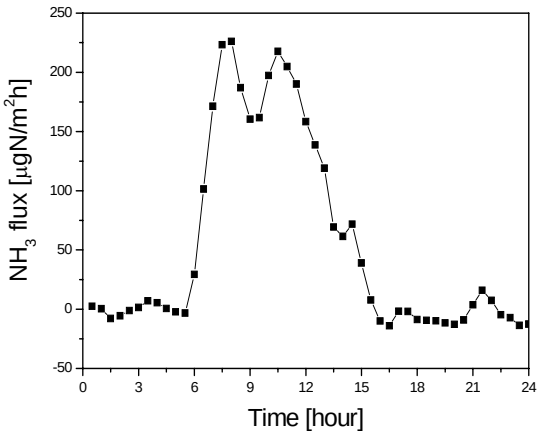

Figure 3: Average daily variation of ammonia flux, calculated from the measurement data from three different heights for the period between 2nd July and 5th October, 2008

The Figure shows that ammonia is emitted during the day and weakly deposited during night. The net balance of ammonia is positive, the site is an emission source of ammonia, which is a result of the nearby cattle farm.

4. CONCLUSION

We have developed a novel ammonia monitoring instrument that is suitable for measuring ammonia concentration at three different heights simultaneously. The obtained data can be used for ammonia flux calculation based on the gradient method. Several months of test measurements show that the instrument is well suited for long-term environmental monitoring.

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