Atmospheric Environment 44 (2010) 1490–1496

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Evaluation of a diode laser based photoacoustic instrument combined with preconcentration sampling for measuring surface–atmosphere exchange of ammonia with the aerodynamic gradient method

Andrea Pogány [a,*], Árpád Mohácsi [b], Stephanie K. Jones [c], Eiko Nemitz [c], Attila Varga [d], Zoltán Bozóki [b], Zoltán Galbács [e], Tamás Weidinger [f], László Horváth [g], Gábor Szabó [a]

[a] Department of Optics and Quantum Electronics, University of Szeged, Dóm tér 9, 6720 Szeged, Hungary
[b] Research Group on Laser Physics of the Hungarian Academy of Sciences, Dóm tér 9, 6720 Szeged, Hungary
[c] Centre for Ecology & Hydrology, Edinburgh, Bush Estate, Penicuik, Midlothian EH26 0QB, United Kingdom
[d] Hilase Developing, Producing, Servicing and Trading Ltd., Dóm tér 9, 6720 Szeged, Hungary
[e] Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, 6720 Szeged, Hungary
[f] Department of Meteorology, Eötvös Loránd University, Pázmány P. sétány 1/A, 1117 Budapest, Hungary
[g] Hungarian Meteorological Service, Gilice tér 39, 1181 Budapest, Hungary

ARTICLE INFO

Article history:
Received 12 November 2009
Received in revised form
26 January 2010
Accepted 27 January 2010

Keywords:
Photoacoustic spectroscopy
Ammonia
Flux
Aerodynamic gradient method

ABSTRACT

We present here a novel instrument for measuring surface–atmosphere exchange fluxes of ammonia. The instrument is the upgraded version of a recently developed near-infrared diode laser based photoacoustic ammonia concentration monitoring instrument, i.e. the original instrument is supplemented with two additional sampling lines, an appropriate gas handling system and an advanced software controlling gradient measurements. As a result of these developments, ammonia concentration can be measured simultaneously at three different heights above the ground and ammonia fluxes can be calculated from these data using the aerodynamic gradient method. The instrument operates fully automatically, requires minimal maintenance and has a temperature controlled, waterproof housing which makes it suitable for measurements even under harsh field conditions. Preliminary tests on stability and accuracy were carried out during two two-week field measurement campaigns, with the three sampling inlets being placed at the same height together with the inlet of a reference instrument. The readings of the three channels agreed well (with correlation coefficients above 0.96). Comparison to reference instruments showed good stability of the photoacoustic instrument, there was no measurable zero-drift or change in sensitivity during the tests. Flux measurements were carried out during a three-week field campaign in southern Scotland over fertilized grassland with reference to a wet-chemical AMANDA instrument in gradient configuration. Ammonia fluxes calculated from the data of the two instruments agreed well. Fluxes up to 2500 ng m^{-2} s^{-1} were observed after fertilization. The minimum detectable ammonia flux was calculated on the basis of "virtual ammonia fluxes", from measurements carried out with all inlets at the same height and was found to be ±60 ng m^{-2} s^{-1} which ensures reliable measurements above intensively managed grasslands or agricultural fields.

1. Introduction

The role of ammonia in atmospheric acid-base chemistry and fine aerosol formation, and its environmental impacts are well known (Seinfeld and Pandis, 1998; Aneja et al., 2001). Consequently, several instruments have been developed for atmospheric ammonia concentration monitoring, including continuous flow wet denuders (Wyers et al., 1993; Erisman et al., 2001), chemiluminescent ammonia monitors (Schwab et al., 2007), optical absorption spectrometers (Whitehead et al., 2007; Peeters et al., 2000), cavity ringdown spectrometers (Berden et al., 2000; Rella, 2008; Picarro Homepage) and photoacoustic spectrometers (Pushkarsky et al., 2003; Besson et al., 2006; Pogány et al., 2009). However, flux data are much more informative in environmental monitoring than simple concentration data, and therefore, an instrument capable of flux measurements is preferred in this area (Sutton et al., 1995; Fowler et al., 2009).

Trace gas fluxes can be calculated using different micrometeorological methods (Foken, 2008). The most direct and therefore

* Corresponding author. Tel.: +36 62 544 518; fax: +36 62 544 658.
E-mail address: andrea@titan.physx.u-szeged.hu (A. Pogány).

1352-2310/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2010.01.038

most preferred approach is the eddy covariance technique, which means the calculation of the flux directly as the covariance of fluctuations of vertical wind velocity and concentration. On the other hand, this technique sets particularly strict requirements for the measuring instrument: it requires fast response (i.e. 0.1 s time resolution) measurement of both vertical wind velocity and trace gas concentration. Such kind of fast response ammonia analyzers are hardly available, since ammonia is strongly adsorbed on the surfaces of the sampling tubes and the measuring cell, which results in a typical response time of some 10 s (Schmol et al., 2001). Although, eddy covariance ammonia flux measuring instruments are under development, those systems are fairly complicated and usually underestimate the fluxes due to adsorption–desorption processes on the walls of the sampling system (Famulari et al., 2004; Whitehead et al., 2008).

The typical response time of ammonia monitoring instruments allows the application of two other types of flux calculation methods: accumulation and profile methods. These techniques require the fast measurement of micrometeorological parameters only; in case of trace gas concentration a time resolution of some 10 min is appropriate.

The eddy accumulation technique is almost as direct as eddy covariance, and it is based on conditional sampling i.e. collecting samples in two or more reservoirs. Trace gas flux is calculated from the difference in the concentration measured in upward and downward moving air (which are sampled into two separate reservoirs). One disadvantage of this method is that the difference in these two concentrations is rather small, usually less than ten percent of the ambient concentration of the trace gas, and therefore it requires extremely sensitive measuring instruments (Nemitz et al., 2001).

Profile methods are more empirical than eddy covariance and accumulation methods. They are based on the calculation of flux as the product of concentration profile or gradient and the eddy diffusivity coefficient (first described by Thornthwaite and Holzman, 1939 and a review given by Dyer, 1974). Concentration profile/gradient is calculated from concentrations measured at different heights above the ground, while the eddy diffusivity coefficient is calculated from wind velocity and temperature measured by meteorological sensors applying several restrictions and simplifying assumptions. Ammonia gradient measurements have been carried out using wet-chemical methods for fairly long time (Wyers et al., 1993; Milford et al., 2008). These instruments are usually used as a reference in the evaluation of newly developed flux measuring instruments since they are based on a well-established measurement principle and can be accurately calibrated with liquid samples, therefore ensure highly reliable concentration measurement (Famulari et al., 2004; Whitehead et al., 2008; Nemitz et al., 2001; Thomas et al., 2009). Spectroscopic techniques such as tunable diode laser based absorption spectroscopy (Warland et al., 2001) have also been used for ammonia gradient measurements.

Previously we have developed a compact photoacoustic instrument for ammonia concentration monitoring (Pogány et al., 2009), and in the present work our aim was to make it suitable for ammonia flux measurements. For flux calculation we have chosen the aerodynamic gradient method since this approach fits our instrument best and it allows direct comparison to wet-chemical instruments.

2. Experimental

2.1. System design and operation

A diode laser based photoacoustic instrument combined with a tungsten-oxide coated preconcentration unit (described in details by Pogány et al., 2009) was supplemented with two additional air sampling lines in order to make it suitable for gradient measurements (see Fig. 1).

Photoacoustic signal is generated in a photoacoustic cell (PAC in Fig. 1) made of polyvinylidene fluoride (PVDF), the geometry of which is identical to that of the cell used in our previous work (Szakáll et al., 2001). An electret microphone (Knowles, EK 3029) is attached to the cell for detecting the photoacoustic signal. The excitation light source is a wavelength modulated telecommunication type DFB diode laser (Furukawa Inc., DL in Fig. 1) radiating at 1532 nm with ~40 mW output light power.

The gas handling system consists of three sampling inlets, each starting with a 1 μm pore size Teflon pre-filter (Millipore, type FA, F in Fig. 1), which are changed regularly in order to eliminate interference from particles deposited on the them and ammonia originating from volatilization of ammonium particles. The filters are placed at the sampling points (usually at three different heights above canopy level) and are connected to the rest of the instrument by ~3 m long Teflon tubes with 8 mm inner diameter, heated to ~50 °C by means of self-regulating heating tapes. After the heated Teflon sampling tubes, each sampling line contains a magnetic valve (MV) and a preconcentration unit (a tungsten-oxide coated glass tube, described in detail by Pogány et al., 2009; Braman et al., 1982, PU in Fig. 1), and thereafter the sampling lines are connected. In the followings there are two streams, one for air sampling with high airflow rate (stream 1 in Fig. 1, containing a mass flow controller, MFC (Tylan 2900 Series)) and one for the subsequent concentration measurement (stream 2, containing the photoacoustic cell, PAC and a second mass flow controller). Airflow is maintained in either stream by the same membrane pump (MP).

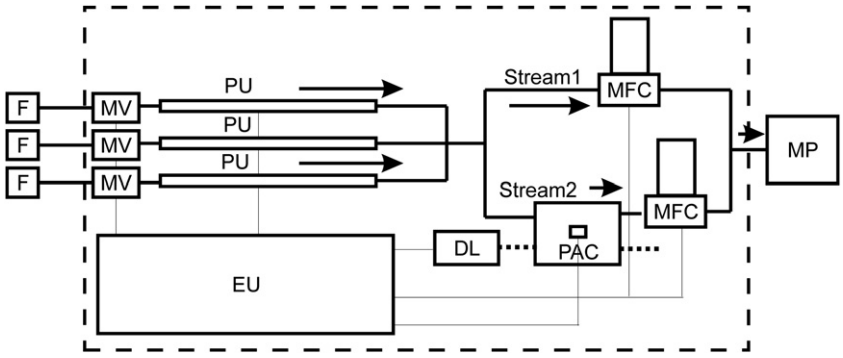

Fig. 1. Schematics of the photoacoustic ammonia flux monitoring instrument. F: particle filter, PU: preconcentration unit, MFC: mass flow controller, PAC: photoacoustic cell, DL: diode laser, MP: membrane pump, EU: electronic unit, MV: magnetic valve, dashed line indicates a waterproof, temperature controlled housing and arrows indicate the direction of airflow.