SUMMARY OF PHD THESIS

DEVELOPMENT OF AN AMMONIA CONCENTRATION AND FLUX MONITORING INSTRUMENT FOR ENVIRONMENTAL RESEARCH APPLICATIONS

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1. Introduction

Measuring ambient concentration and surface-atmosphere exchange flux of ammonia is an important problem in environmental science. Ambient concentration of ammonia is rather low: background concentration in Hungary is as low as 2 ppbV (parts per billion by volume), and concentrations up to a few ten ppmV (parts per million by volume) occur near emission sources. Nevertheless, environmental impacts of ammonia are significant. Ammonia is an anthropogenic air pollutant, its most important emission source is agriculture, and environmental impacts include acidification, eutrophication and formation of secondary aerosol particles. During the past decades, ammonia as an air pollutant has been gaining increasing attention. Reasons for this increasing interest are increasing emission of ammonia as a result of increasing agricultural production, as well as success of previous environmental regulations on industrial air pollutants (e.g. sulfur-dioxide and nitrogen oxides). As environmental impacts of ammonia became clear, importance of regulations concerning emission of ammonia as well as monitoring and modeling tasks were recognized.

The NitroEurope project (2006-2011) aims to improve understanding of the nitrogen cycle – an important component of which is ammonia – at the European scale. Objectives of the project include establishment and operation of a network for measuring concentrations and fluxes of reactive nitrogen compounds, development and refinement of models at different scales, as well as evaluation and dissemination of data. The Photoacoustic Research Group at University of Szeged has started development of a novel ammonia monitoring instrument within the NitroEurope project in spring 2005. The task of our research group was to develop an instrument for measuring ambient concentrations and surface-atmosphere exchange fluxes of ammonia and operate the instrument at the Hungarian monitoring site of the project (Bugac-puszta).

I have joined this work as an undergraduate student in 2005 and continued the work during my PhD studies.

The greatest motivation of this research is the fact that none of the currently available ammonia concentration and flux monitoring instruments meet all requirements of environmental monitoring: either their accuracy and time resolution is not sufficient or they require frequent maintenance, which cannot be provided at most environmental monitoring sites. Diode laser based photoacoustic spectroscopy might be a solution to this problem. The method is highly sensitive and selective, while compactness of light sources and simplicity of the measurement set-up enables construction of automatic instruments with low maintenance requirement.

2. Objectives and methods

Previous results of our research group have proven that carefully designed diode laser based photoacoustic instruments are suitable for high-precision gas concentration monitoring even under field conditions [5]. The aim of my work was to improve performance of a diode laser based photoacoustic ammonia concentration monitoring system previously built by our group [6], to meet requirements of environmental monitoring. To achieve this aim, the minimum detectable concentration had to be decreased by at least two orders of magnitude.

My aim was to construct an automatic instrument with low maintenance requirement for monitoring ambient concentration and flux of ammonia and to prove the practical applicability of the instrument.

I have accomplished considerable reduction of detection limit by the application of preconcentration sampling. First I have investigated the applicability of sample preconcentration in photoacoustic spectroscopy and selected adsorbents to concentrate ammonia in the gaseous phase. After the selection and preparation of preconcentration units I have built an instrument based on diode laser based photoacoustic spectroscopy and preconcentration sampling that is capable of automatic measurement of ammonia concentration and flux under field conditions. Finally, I have carried out several field measurements to investigate practical applicability, detection limit and precision of the instrument.

3. New scientific results

1. I have prepared tungsten-oxide and vanadium-pentoxide preconcentration units for concentrating ammonia in the gaseous phase and built them into a diode laser based photoacoustic ammonia measuring system. I have proven experimentally that application of preconcentration sampling is suitable for decreasing minimum detectable concentration of the measuring system. I have shown that the lifetime of vanadium-pentoxide preconcentration units is several months, considerably longer than that of tungsten-oxide units, and they are therefore suitable for long-term monitoring [1].

2. I have built a prototype of the photoacoustic ammonia concentration measuring instrument combined with preconcentration sampling that is capable of automatic operation under field conditions; and calibrated it using a reference instrument. Results of calibration carried out under field conditions in different concentration ranges revealed that minimum detectable concentration of 0.5 ppbV can be achieved with time resolution between 8 and 30 minutes. This value is more than two orders of magnitude lower that that of a diode laser based photoacoustic ammonia monitoring instrument without preconcentration [1].

3. I have proven the practical applicability of the instrument described in point 2 during an international field inter-comparison campaign. Performance of eleven different ammonia concentration monitoring instruments has been evaluated during the three-week campaign. Results of the campaign prove that detection limit and time resolution of the photoacoustic instrument fulfill requirements of environmental monitoring. Moreover, the photoacoustic instrument requires less maintenance and is easier to operate than most other instruments [2].

4. I have investigated the applicability of the instrument described in point 2 for long-term monitoring at the Hungarian monitoring site of the NitroEurope project in Bugac. I have conducted ammonia concentration measurements for two and a half years. I have found that measured concentration data are suitable for analyzing seasonal and diurnal variation of ammonia concentration, and show good agreement with concentrations measured at the nearby K-puszta monitoring station [3].

5. I have supplemented the instrument described in point 2 with two further sampling lines, thereby made it suitable for measuring vertical profile of ammonia concentration, which is the basis of flux calculation with the gradient method. Based on the agreement between concentrations measured by the three channels of the photoacoustic instrument I have determined the minimum detectable ammonia flux to be ±60 $ng \cdot m^{-2} \cdot s^{-1}$ and precision of flux measurements between 20-150 $ng \cdot m^{-2} \cdot s^{-1}$, depending on sampling time. I have proven with two field measurement campaigns that detection limit and time resolution of the instrument is suitable for measuring ammonia flux over agricultural fields and measured flux data show good agreement with flux data measured by a reference instrument [4].

4. Publications

My results are based on the following publications:

[1] Pogány, A., Mohácsi, Á., Varga, A., Bozóki, Z., Galbács, Z., Horváth, L., Szabó, G. (2009) A compact ammonia detector with sub-ppb accuracy using near-infrared photoacoustic spectroscopy and preconcentration sampling. Environmental Science and Technology 43: 826-830

[2] von Bobrutzki, K., Braban, C. F., Famulari, D., Jones, S. K., Blackall, T., Smith, T. E. L., Blom, M., Coe, H., Gallagher, M., Ghalaieny, M., McGillen, M. R., Percival, C. J., Whitehead, J. D., Ellis, R., Murphy, J., Mohacsi, A., Pogany, A., Junninen, H., Rantanen, S., Sutton, M. A., Nemitz, E. (2010) Field inter-comparison of eleven atmospheric ammonia measurement techniques. Atmospheric Measurement Techniques 3: 91-112

[3] Weidinger, T., Pogány, A., Horváth, L., Machon, A., Bozóki, Z., Mohácsi, Á., Pintér, K., Nagy, Z., Gyöngyösi, A. Z., Istenes, Z., Bordás, Á. (2010) Concentration gradient measurements and flux calculation of atmospheric ammonia over grassland (Bugac-puszta, Hungary), Chapter 15, Advances in environmental modeling and measurements, Ed: D. T. Mihailovic, B. Lalic, Nova Science Publishers Inc.

[4] Pogány, A., Mohácsi, Á., Jones, S. K., Nemitz, E., Varga, A., Bozóki, Z., Galbács, Z., Weidinger, T., Horváth, L., Szabó, G. (2010) Evaluation of a diode laser based photoacoustic instrument combined with preconcentration sampling for measuring surface-atmosphere exchange of ammonia with the aerodynamic gradient method. Atmospheric Environment 44: 1490-1496

Further publications:

[5] Bozóki, Z., Pogány, A., Szabó, G. (2010) Photoacoustic instruments for practical applications: present, potentials and future challenges. Applied Spectroscopy Reviews 46(1): 1-37

[6] Huszár, H., Pogány, A., Bozóki, Z., Mohácsi, Á., Horváth, L., Szabó, G. (2008) Ammonia monitoring at ppb level using photoacoustic spectroscopy for environmental application. Sensors and Actuators B 134: 1027-1033

[7] Hanyecz, V., Mohácsi, Á., Pogány, A., Bozóki, Z., Kovács, I., Szabó, G. (2010) Multi-component photoacoustic gas analyzer for industrial applications. Vibrational spectroscopy 52: 63-68

[8] Szakáll, M., Varga, A., Pogány, A., Bozóki, Z., Szabó G. (2009) Novel resonance profiling and tracking method for photoacoustic measurements. Applied Physics B 94: 691-698