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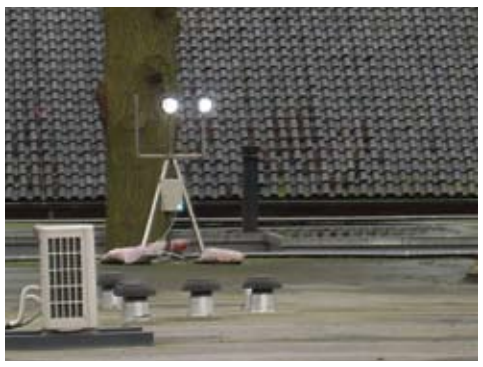
Measuring Atmospheric Ammonia Concentrations Using Differential Optical Absorption Spectroscopy

Introduction

Most traditional techniques to measure atmospheric ammonia concentrations are sampling techniques. They therefore involve direct contact with the highly adhesive ammonia. This often results in memory effects which may lead to erroneous measurements. This problem can be avoided using optical remote sensing techniques. Differential optical absorption spectroscopy (DOAS) is such a technique. The National Institute for Public Health and the Environment (RIVM) has developed a DOAS system to measure atmospheric ammonia concentrations: the RIVM Ammonia Measurement System by UV-Spectroscopy (RAMSUS). Other advantages of the system are the low maintenance demands and the high up-time.

Two of the three RIVM Ammonia Measurement System(s) by UV-Spectroscopy: RAMSUS 1 and RAMSUS 2 in the laboratory in Bilthoven, The Netherlands.

Two-path measurement at the weather station at the Haarweg in Wageningen, The Netherlands.



Two of the three retroreflectors placed on a roof, approximately 50 meters from the DOAS laboratory in Bilthoven, The Netherlands.

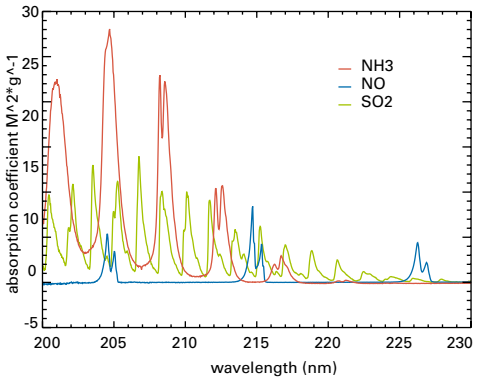
Measurement Principle

The DOAS technique is based on the wavelength dependent absorption of light over a specified light path. The absorption depends on the concentrations of the different trace gases present in this light path. This is expressed by Lambert-Beer's law:

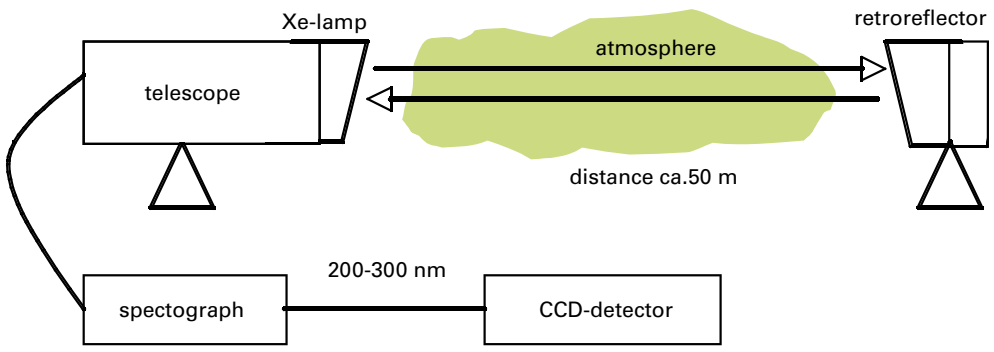
$$I_\lambda = I_{0,\lambda} * e^{-\alpha(i,\lambda)*C(i)*L} \qquad (1)$$

with I_λ the received light intensity at wavelength λ, $I_{0,\lambda}$ the emitted light intensity at wavelength λ, α(i,λ) the absorption coefficient for trace gas *i* at wavelength λ, C(i) the concentration of trace gas i and L the length of the light path.

Ammonia has strong absorption lines with narrow features in the wavelength range 200-230 nm. Other trace gases with narrow absorption features in this wavelength range are nitrous oxide and sulfur dioxide. The absorption features of those three trace gases are least squares fitted to the ratio of emitted and received light in the wavelength range 200-230 nm using the standard DOAS technique. This results in the determination of the concentration of those trace gases.



Absorption coëfficiënts for ammonia (NH_3), nitrous oxide (NO) and sulfer dioxide (SO_2) in the wavelength range 200-230 nm.



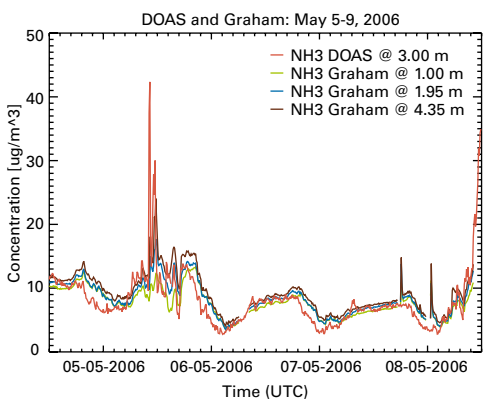
System set-up of the RIVM Ammonia Measurement System by UV-Spectroscopy (RAMSUS).

System Set-up

The system uses a combined sender/receiver unit, consisting of a 150W Xenon lamp and a telescope. A corner cube retroreflector directs the lamplight directly back to the telescope. An interference filter is used to suppress stray light. The retroreflector is placed at approximately 50 meters from the sender/receiver unit. This results in an effective light path of approximately 100 meters. A spectrograph separates the light from the telescope by wavelength. A charge coupled device (CCD) detector measures the light intensities at the different wavelengths. Drifting of these wavelengths over the CCD is prevented by using a zinc-lamp for wavelength-tracking. Data is averaged for five minutes to increase the signal-to-noise ratio. All system control and data storage is managed by one computer.

Field Experiments

During a one-year period, RAMSUS measured at the weather station at the Haarweg in Wageningen. Comparisons were made with the measurements of a GRadient Ammonia - High Accuracy - Monitor (GRAHAM), located at the same site. The GRAHAM measured at three altitudes: 4.35, 1.95 and 1.00 meter. RAMSUS measured at an altitude of 3.00 meter.



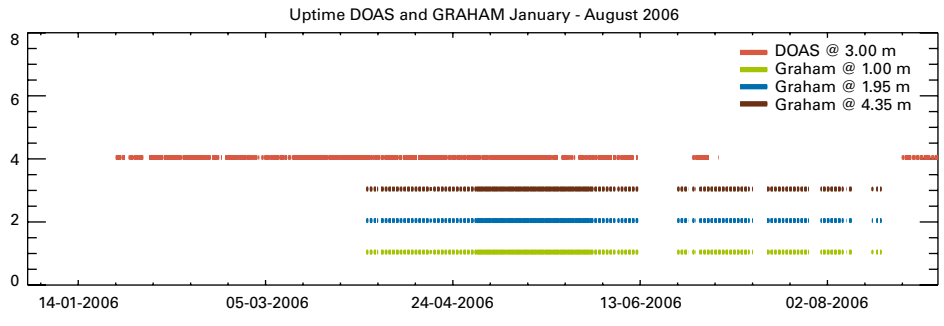
Typical period of ammonia concentrations measured by the RIVM Ammonia Measurement System by UV-Spectroscopy (RAMSUS) and by the GRAHAM, a more traditional denuder system.

Conclusions and Outlook

It has been shown that RAMSUS has

1. a fast response (seconds to minutes) and no memory effects;
2. a precision for ammonia better than 0.3 µg/m^3 for a 5-minute average;
3. low maintenance demands and a high up-time (better than 85%).

In 2007 we will develop an operational ammonia deposition system. To this end, three of these systems will be placed above each other, each system measuring at a different altitude.



Uptime for the RIVM Ammonia Measurement System by UV-Spectroscopy (RAMSUS) and for the GRAHAM, a more traditional denuder system, for the period January – August 2006. During the hot summer of 2006, RAMSUS encountered some problems. Shortness of personnel in this period prevented service.

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