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1352-2310(95)00066-6

NON-INTRUSIVE, FAST AND SENSITIVE AMMONIA DETECTION BY LASER PHOTOTHERMAL DEFLECTION

H. S. M. DE VRIES,* F. J. M. HARREN,* G. P. WYERS,† R. P. OTJES,†
J. SLANINA,† and J. REUSS*

*Department of Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands and

†Netherlands Energy Research Foundation ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands

(First received 1 August 1994 and in final form 23 January 1995)

Abstract—A recently developed non-intrusive photothermal deflection (PTD) instrument allows sensitive, rapid and quantitative detection of local ammonia concentrations in the air. Ammonia is vibrationally excited by an infrared CO₂ laser in an intracavity configuration. A HeNe beam passing over the CO₂ laser beam (multipass arrangement) is deflected by the induced refractive index gradient. The detection limit for ammonia in ambient air is 0.5 ppbv with a spatial resolution of a few mm³. The time resolution is 0.1 s (single line) or 15 s (multi line). The system is fully automated and suited for non-stop measuring periods of at least one week. Results were compared to those obtained with a continuous-flow denuder (CFD).

Key word index: Ammonia, trace gases, photothermal deflection

INTRODUCTION

Ammonia and ammonium contribute to soil acidification and disturb the nutrient cycle. In The Netherlands dry deposition of ammonia, mainly originating from domestic emission sources (livestock wastes), is responsible for approximately 33% of the total acidifying deposition (Heij and Schneider, 1991).

Fast and sensitive detection methods for ammonia are needed to quantify air-to-surface exchange fluxes (Erisman *et al.*, 1988). Attempts towards quantitative detection of ammonia employing (isotopic) CO₂ laser based photoacoustic spectroscopy and (less sensitive) direct absorption detection systems lately received attention (Olafsson *et al.*, 1989; Meienburg *et al.*, 1990; Rooth *et al.*, 1990; Sauren *et al.*, 1991). Ammonia possesses high absorption coefficients and a clear fingerprint spectrum in the ¹²CO₂ and ¹³CO₂ laser wavelength regions (Trushin, 1992). The photoacoustic method allows detection of ammonia at sub-ppbv levels. Spectral interference can be minimized either by tuning the laser or by making use of the Stark shift induced in polar gases by an external electric field. A serious drawback of the photoacoustic technique is the necessity to use a flow-through system to lead gases from the sampling zone into the photoacoustic cell. Due to sticking of polar gases to wall material of tubing and photoacoustic cell, unavoidable memory effects of ammonia (large permanent dipole moment) impede fast concentration measurements (Henningsen, 1994).

Another laser based detection system, VUV/photofragmentation laser-induced fluorescence, is more sensitive (10 pptv for 1 min integration periods) and free of interferences (Schendel *et al.*, 1990), but also requires a closed cell. The cost of this equipment will probably limit its widespread use. At this moment a Cavity Ring Down technique, which allows to determine 10 ppbv ammonia over a path length of typically 500 mm with a temporal resolution of 50 μs, is being developed (Jongma *et al.*, 1995). Its sensitivity can probably be increased by at least one order of magnitude; not, however, its spatial resolution.

A relatively inexpensive, thoroughly tested and reliable detection system for ammonia (sufficiently selective and sensitive: 8 pptv) is the continuous-flow denuder (CFD; Wyers *et al.*, 1993). This instrument is used for routine deployment in the field and micrometeorological measurements of exchange fluxes. However, its response time (1 min) is inadequate for eddy correlation measurements that rely on the covariation of fluctuations in vertical wind speed and concentration to derive ammonia fluxes.

Here, the photothermal deflection (PTD) technique was applied to perform fast and *in situ* measurements of ammonia concentrations in ambient air. The method is closely related to the photoacoustic technique in which a change in pressure is detected by a microphone (Harren *et al.*, 1990). In PTD, a change in temperature induces a change in refractive index which is being probed by a second laser beam

(Jackson *et al.*, 1981). Non-intrusive measurements can be performed under normal atmospheric conditions in open air (de Vries *et al.*, 1993).

In this paper the suitability of PTD for ammonia measurements is demonstrated. The characteristics of PTD are compared to results obtained with the continuous flow denuder. Attention was paid to the absolute and relative precision in determining ammonia concentrations, to response time under different conditions and to the effect of interfering gases.

THE PHOTOTHERMAL DEFLECTION SETUP

The PTD setup consists of a high power waveguide CO₂ pump laser and a deflection unit positioned inside the cavity of the CO₂ laser (Fig. 1). The CO₂ laser emits radiation in the infrared between 9 and 11 μm at about 90 different laser lines. Due to a high reflecting output coupling mirror (98.5% reflectivity) the maximum intracavity laser power is 100 W. The curved output mirror and an intracavity ZnSe lens ($f = 75$ mm) form a sharp intracavity focus with a (calculated) waist of 0.282 mm (Harren *et al.*, 1990). The infrared CO₂ laser radiation promotes ammonia into a ro-vibrational level of the ν_2 mode. The strong difference in absorption strength of ammonia at the neighbouring 10R8 and the 10R10 CO₂ laser lines ($20.5 \text{ atm}^{-1} \text{ cm}^{-1}$ at $\lambda = 10.334 \mu\text{m}$ and $0.542 \text{ atm}^{-1} \text{ cm}^{-1}$ at $\lambda = 10.318 \mu\text{m}$, respectively; Brewer and Bruce, 1978) allow one to determine the ammonia concentration corrected for any background absorption.

Due to non-radiative collisional decay the laser interaction zone and the immediate surrounding region are heated, causing a change of refractive index. A probe HeNe laser beam (632.8 nm) passes (perpendicularly to the pump beam) close to this heated zone; its deflection, due to the refractive index gradient induced by the CO₂ laser, is proportional to the concentration of the absorbing gas and the available CO₂ laser power. The sensitivity of the system is enhanced by using a parallel-mirror multipass arrangement for the probe beam; it traverses the heated region 31 times (de Vries *et al.*, 1992). The spatial resolution of the PTD instrument is defined by the waist of the CO₂ laser and the spatial overlap of CO₂- and HeNe-laser beam and has the shape of a cylinder with a diameter of 0.56 mm and a length of 25 mm. The interaction length can be reduced (from 25 to 2 mm) using cylindrical lenses and mirrors instead of flat mirrors for the multipass probe laser setup, however, in this setup the overall sensitivity of the system is reduced (de Vries *et al.*, 1995).

The pump laser is periodically interrupted by a mechanical chopper (20 Hz or 60 Hz; home built), giving rise to a modulated deflection of the probe beam. The deflection is phase sensitively measured by

a position sensing quadrant detector (Centronic, QD 50-2), the output of which is fed into a lock-in amplifier (PAR 5204). The whole setup is computer controlled and capable of unattended long term operation.

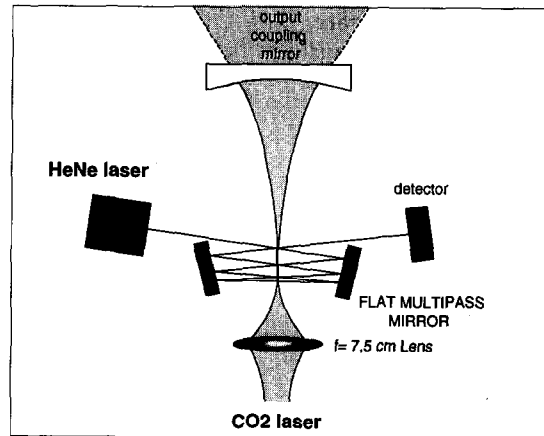
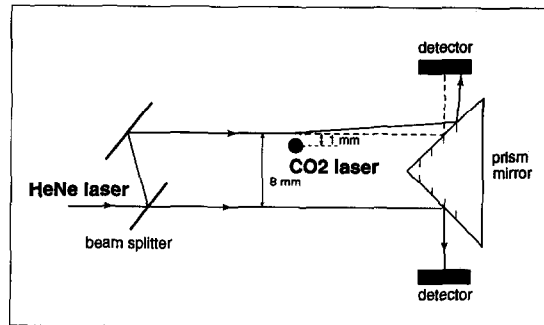
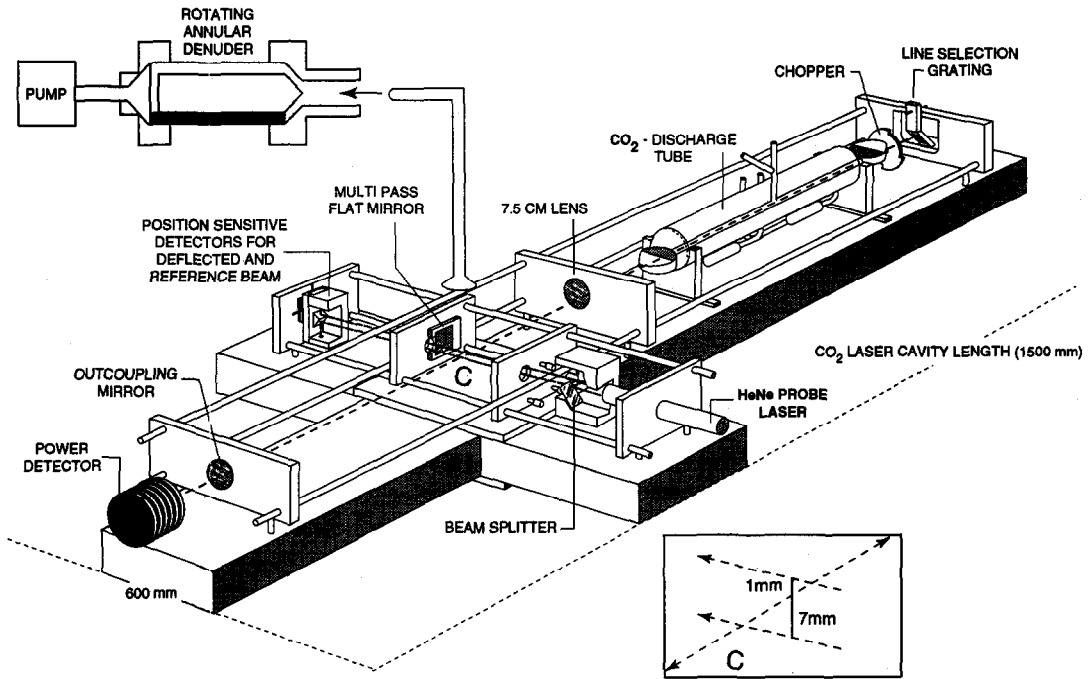
The probe HeNe laser beam with the multipass system and the position sensitive detector are all stably mounted in a frame constituting the deflection unit. The frame of the pump CO₂ laser and the deflection unit are rigidly coupled to avoid mechanical vibrations between the two laser beams.

The effect of air turbulences is minimized by shielding the entire frame (except for the detection region) and by utilizing a double probe beam arrangement. In this double probe beam setup one HeNe laser beam is affected by the induced refractive index gradient (crossing about 1 mm from the CO₂ laser waist) and the other not (crossing 7 mm below). Upon subtracting both signals the influence of air turbulence is reduced by a factor of two (de Vries *et al.*, 1993). All measurements presented in this paper were performed with the double probe beam arrangement.

For operation at one single CO₂ laser line the temporal resolution is determined by the RC-time of the lock-in amplifier (0.1 s). To detect very low concentrations of ammonia one must take into account changes in concentrations of other (interfering) gases noted as background signals. Therefore, switching between two neighbouring CO₂ laser lines, one strongly and one weakly absorbing line will spectroscopically purify the ammonia signal. In our current setup the switching time between the two laser lines, including piezo optimization, was 15 s.

Interfering gases

In the wavelength region of the CO₂ laser the most important gases spectroscopically interfering with ammonia are CO₂ and H₂O with ambient concentrations in the order of 360 ppmv and 0.5–1.5%, respectively. The interfering absorption spectrum of atmospheric CO₂ is the inverse vibrational hot band transition from which CO₂ laser radiation is generated, resulting in a background signal equivalent to 34 ppbv NH₃ at the 10R8 (Devir and Oppenheim, 1969). At 294 K the background signal due to atmospheric water vapour concentration is two orders of magnitude lower (< 0.6 ppbv NH₃, Loper *et al.*, 1983). Fortunately, absorption coefficients for CO₂ and H₂O at 10R8 and 10R10 are comparable so that variations in concentration of these gases will contribute equally to the deflection signals on both lines. Only the difference in absorption strength will affect the real ammonia concentration (maximum 4.6 and 0.1 ppbv for 360 ppmv CO₂ and 1.5% water vapor, respectively). Since water, like ammonia, has a dipole moment strong memory effects can appear in flow through systems; due to the intrinsic contact-free PTD method this problem is avoided and precise



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Fig. 1. The rigid body frame for PTD consists of an intracavity CO₂ laser setup (including line selecting grating, chopper, convergent lens ($f = 75$ mm) and output coupling mirror) and dual HeNe probe laser beams. The dual beams are obtained by a beam splitter unit (dimensions are indicated). The air is sampled above the multipass area by the rotating annular denuder unit. The interaction region of probe beam and CO₂ laser beam is presented in detail. The probe beam influenced by the mirage effect traverses the CO₂ laser beam at a distance of 1 mm; the reference beam at a distance of 7 mm under the CO₂ laser beam (upper part). In the interaction region a multipass configuration is implemented (lower part).

measurements of water concentrations are possible. A good coincidence exists between a single rotational transition of water ($J(K_{-1}, K_1) = 13(4, 9) \leftarrow 12(1, 12)$; Hinderling *et al.*, 1985) and the 10R20 CO₂ laser line; at the 10R20 the absorption is approximately 20 times higher than that at the 10R18 laser line. As mentioned above ¹²CO₂ has a broad absorption spectrum on ¹²CO₂ laser lines; on ¹³CO₂ laser lines (Trushin, 1992) it has a clear fingerprint spectrum.

Calibration

The system was calibrated using a certified mixture of 1.2 ppmv ethylene in purified nitrogen. Ethylene is a well known calibration gas without any wall adsorption problems. Additional calibration was made for 1.2 ppmv (certified) and ambient (about 4 ppbv) ethylene levels with a flow-through system employing photoacoustic spectroscopy (Harren *et al.*, 1990) and by comparing PTD detection on gaseous ammonia levels in open air with the values obtained by a continuous-flow denuder system.

CONTINUOUS-FLOW DENUDER

In order to compare (estimated) ammonia concentrations in the PTD detection zone with values obtained with a continuous-flow denuder (CFD), a polyethylene tube, to sample air, was positioned above this zone.

The CFD is a wet-chemical detector specific to ammonia. Air is pumped through the CFD at a rate of 30 l min⁻¹. The ammonia present in the air is absorbed in a NaHSO₄ solution, covering the denuder inner wall. Further downstream this solution is mixed with NaOH, resulting again in gaseous ammonia, that diffuses through a semi-permeable membrane. On the other side of the membrane, ammonia is dissolved in bi-demineralized water and the concentration determined conductometrically. This system was calibrated using a blank, a 50 ppbv and a 500 ppbv aqueous solution of NH₄⁺ (Wyers *et al.*, 1993).

APPLICATION TO VARYING AMMONIA CONCENTRATIONS

Comparison of absolute values

Ambient ammonia concentration levels were determined independently with PTD and CFD systems in a laboratory during periods of one week (non-stop). During the night ammonia concentrations were on average 3 ppbv lower than daytime levels (that fluctuated slowly between 10 and 20 ppbv). The denuder tubing was positioned 0.1 m above the PTD sampling zone. Solutions of 0.25–2.5% of ammonia in demineralized water were prepared and localized at a distance of 0.5 m from denuder tube and PTD detection zone, resulting in concentrations of about 10, 30, 60 and 120 ppbv in the sampling zone. The

correlation of CFD and PTD signals yielded a straight line (Fig. 2; slope of 1.02(5)). For CFD the calibration is based on reference solutions, while PTD calibration relies on C₂H₄ measurements. Absorption strengths (20.5 atm⁻¹ cm⁻¹ for NH₃ on the 10R8 and 13.4 atm⁻¹ cm⁻¹ for C₂H₄ on the 10P14) and the laser power were taken into account. The absorption coefficient for C₂H₄ on the 10P14 is lower than mentioned in literature (30.4 atm⁻¹ cm⁻¹, Brewer *et al.*, 1978) due to saturation effects.

Different ammonia concentrations, measured by PTD and CFD, observed as a function of time are shown in Fig. 3. Ambient ammonia levels at $t = 0$ are displayed. Following $t = 0.2$ h the ammonia level is seen to rise, due to a source (2.5% aqueous ammonia) placed 0.5 m from the detection area. At $t = 0.52$ h the ammonia source was removed which resulted in ambient levels again. Short term variations in ammonia

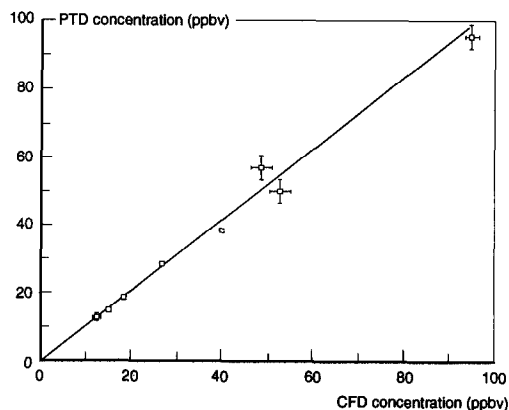


Fig. 2. Correlation of ammonia concentrations obtained with CFD and PTD.

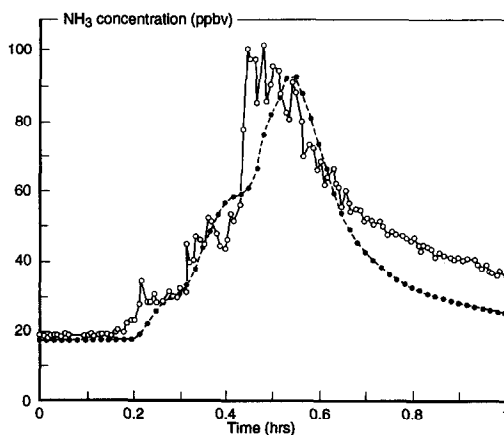


Fig. 3. Ammonia concentrations in detection zone measured by PTD (-o-) and just above detection zone by CFD (-●-). Initial, ambient levels were observed. Then, after 0.2 h, an ammonia solution was positioned about 50 cm from the detection zone and an increase in ammonia amounting to 100 ppbv observed. At $t = 0.52$ h the solution was removed leading to ambient levels again.

concentration of 10 ppbv (on an average concentration of 100 ppbv) were observed only by PTD. Because of its integrating character such rapid changes of ammonia concentrations cannot be observed by CFD. The noise on the PTD signal (equivalent to 0.5 ppbv NH_3 at $t = 0$, Fig. 3) is much less than the fluctuations observed on the peak signal (10 ppbv at $t = 0.5$ h). These increased fluctuations are due to occurrence of air turbulences in the source/sample region, to relatively small dimensions of the ammonia source (when compared to the sampling volume) and to high CFD suction rates. The relatively small ammonia source did not yield a steady ammonia concentration in the sampling zone. High suction rates perturb local concentrations even more, causing rapid concentration changes in the surroundings of the denuder tubing, whereas ammonia concentrations in the PTD zone change merely through diffusion. This also explains the steeper tail of the CFD curve. Consequently, comparison of absolute ammonia concentrations by PTD and CFD systems in an open air environment is allowed only for large sampling volumes under steady ammonia conditions.

Fast ammonia fluctuations

A double flow system, utilizing either normal air (containing ambient ammonia concentrations) or air containing above-ambient ammonia levels, was used for rapid switching (seconds) between different ammonia concentrations. The flowing gas was led directly into the detection zone (flow rate 15 l h^{-1}), through a tubing positioned 20 mm below the intersection region of pump and probe laser beams. The denuder tubing was installed 20 mm above the multipass system. Such short distances allowed investigation of rapidly changing ammonia concentrations reaching quasi-simultaneously both detection systems; results

are presented in Fig. 4. The arrows indicate time instants at which higher ammonia levels were purged into the detection region, during 1, 2 or 3 s. The CFD technique displays a smeared-out effect (dashed curve), whereas the PTD setup (single line operation on the ammonia absorbing laser line (10R8)) detects ammonia passing in pulses through the detection zone.

The signal on the less strongly absorbing 10R10 laser line (lower trace in Fig. 4) remains constant. An important conclusion is that the signal is affected neither by air turbulences nor by varying water concentrations. However, with the actual PTD system it was not possible to carry out simultaneous measurements on the 10R8 and 10R10 CO_2 laser lines faster than 15 s. Therefore, the measurements of Fig. 4 were performed directly after each other. Note that the ammonia concentration can be calculated by subtracting signals on the 10R8 and 10R10, taking into account absorption coefficients and intracavity laser power on these lines, as it is done for the results in Figs 2 and 3. The figures suggest no influence of water vapour.

The shape of the ammonia concentration profile, determined by PTD (10R8), depends on the relative position of the tube openings of the double flow system with respect to the detection zone. Results acquired at another position of the tube opening are shown in the insert of Fig. 4.

CONCLUSIONS

Table 1 summarizes sensitivity, data on temporal resolution and important experimental features in measuring ammonia for both PTD and CFD. One major conclusion is that the PTD setup enables

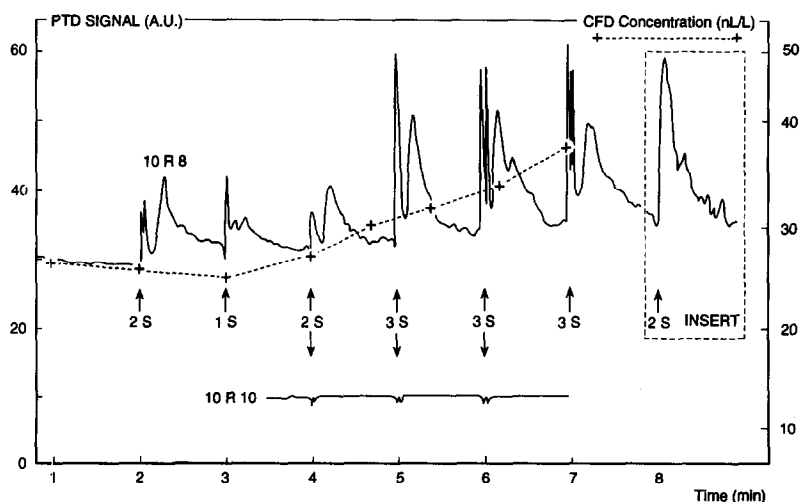


Fig. 4. Fast ammonia changes produced by flushing ammonia enriched air through detection area for 1, 2 or 3 s. The CFD displays a slowly increasing curve (dashed), while PTD registers rapid changes on the 10R8 ammonia absorbing laser line and no change on 10R10 non-absorbing laser line. A PTD curve is inserted on the right showing that the profile is dependent on a position of the tube above the detection zone.

Table 1. Comparison between the PTD setup and the CFD for ammonia measurements; the sensitivity for the two laser line measurements is given in Fig. 3

	PTD	CFD
Sensitivity	0.5 ppbv (RC-time 1 s, 20 Hz)	8 pptv (RC-time 60 s)
Time response	15 s (two laser lines) 0.1 s (one laser line, RC-time 0.1 s, 60 Hz)	1 min
Condition	Non-intrusive local detection Detection zone 25 mm × $\pi(0.282 \text{ mm})^2$	Suction gas sampling

measurements of absolute ammonia concentrations with a detection limit of 0.5 ppbv (signal-to-noise ratio = 1). The range of 10–120 ppbv is covered experimentally. Within this range the photothermal response is linear with the applied concentrations (verified by CFD) under steady ambient conditions. At low concentrations the PTD signal is reproducible within the detection limit; at high concentrations (S/N larger than 1000) the error is determined by detector noise.

Another major conclusion is that the time responses of PTD (15 s on double line operation, 0.1 s on single line operation) are significantly faster than that of CFD, allowing observations of rapid changes in ammonia concentrations. Neither changes in water vapour nor CO₂ concentrations perturb ammonia measurements. By using other CO₂ laser lines the setup is also suitable for calibrated water vapour measurements.

The advantage of PTD over currently existing techniques is the possibility to determine local ammonia concentrations in an open air environment, without perturbation of the environment and without wall adsorption problems, which makes it suitable for eddy correlation measurements. Further objectives will be detection of reactive (ozone) or adsorbing gases (e.g. water and ammonia); from which ammonia measurements will be performed in relation to nitrogen fixation problems (reduction of N₂ to ammonia in cyanobacteria).

Acknowledgements—We would like to thank N. Dam for comments and suggestions on this paper, and M. van Lieshout for experimental support and an unknown referee for thoroughly reviewing this manuscript.

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