

**The development of
a nitrogen dioxide
sonde**

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The development of a nitrogen dioxide sonde

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Abstract

A growing number of space-borne instruments measures nitrogen dioxide (NO₂) concentrations in the troposphere, but validation of these instruments is hampered by lack of ground-based and in-situ profile measurements.

5 The Royal Netherlands Meteorological Institute (KNMI) has developed a working NO₂ sonde. The sonde is attached to a small meteorological balloon and measures a tropospheric NO₂ profile. The NO₂ sonde has a vertical resolution of 5 m, and a measurement range between 1 and 100 ppbv. The instrument is light in weight (±700 g), cheap (disposable), energy efficient and not harmful to the environment or the person who finds the package after use. The sonde uses the chemiluminescent reaction of NO₂ in an aqueous luminol solution. The NO₂–luminol reaction produces faint blue/purple light (at about 425 nm), which is detected by an array of silicon photodiodes. The luminol solution is optimised to be specific to NO₂.

15 An on-ground comparison with measurements from a Photolytic Analyzer of RIVM shows that both instruments measure similar NO₂ variations in ambient air.

During the Cabauw Intercomparison campaign of Nitrogen Dioxide measuring Instruments (CINDI) in June/July 2009 six vertical profiles of NO₂ from the ground to 5 km altitude were measured, which clearly show that the largest amount of NO₂ is measured in the boundary layer. The measured boundary layer heights of the NO₂ sonde are in good agreement with boundary layer heights determined by a LD40 Ceilometer at Cabauw.

1 Introduction

25 Nitrogen dioxide (NO₂) is an important pollutant in the atmosphere, because it is toxic for living species, it forms photochemical ozone (O₃), and acid rain in the form of nitric acid (HNO₃). Nitrogen dioxide is a member of the nitrogen oxides (NO_x). In the troposphere they are typically formed as a by-product of the combustion of fossil fuels at

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high temperatures.

A growing number of space-borne instruments measures nitrogen dioxide concentrations in the atmosphere, but validation of these instruments is hampered by lack of ground-based and in-situ profile measurements of NO₂. This was one of the conclusions from the ACCENT-AT2 supported workshop on “Tropospheric NO₂ measured by satellites”, at KNMI, De Bilt, The Netherlands from 10 to 12 September 2007.¹

There is an extensive ground-based network of in-situ NO₂ sensors. Typically they use either a catalytic or photolytic converter to reduce NO₂ to NO, and this gas is then mixed with ozone. The reaction of NO with O₃ produces light, which is subsequently measured. Steinbacher et al. (2007) give a brief description of the catalytic and photolytic converter, and compare the two. Parrish et al. (1990) give a detailed discussion about the photolytic converter technique.

NO₂ has also been measured from aircraft, for example with the laser-induced fluorescence (LIF) technique, as reported by Boersma et al. (2008). The lower few hundred meters of the atmosphere, which contain a significant part of the tropospheric NO₂, are difficult to reach by aircraft. Aircraft measurements with the luminol NO₂ detector Luminol LMA-3 are described by Kelly et al. (1990).

An NO₂ sonde, described by Pisano et al. (1996), was used by Hasinoff (1997) in a field study at Kejimikujik National Park in Nova Scotia in 1996. The instrument weighs 1.195 kg, and uses the luminol-NO₂ reaction. The emitted light of the luminol-NO₂ reaction is detected by a photomultiplier tube. Hasinoff (1997) measured NO₂ profiles up to 1 km altitude while the instrument was suspended from a tethered balloon. She recommends for future studies to design and build a more reliable and more user-friendly NO₂ sonde, as this instrument was found to be extremely difficult to use.

Sitnikov et al. (2005) build a chemiluminescent balloon-borne instrument called NaDA to measure NO₂. The NaDA instrument uses the chemiluminescent reaction of luminol with NO₂. The instrument weighs approximately 1 kg, and uses a photomul-

¹This report can be found at http://www.knmi.nl/research/climate_observations/events/no2_workshop/presentations/NO2_report.pdf.

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tiplier tube, making it too heavy and too expensive for use in a disposable sonde.

The current study is aimed at the development of an instrument that can measure NO_2 in-situ, which is cheap (disposable), light in weight, energy efficient, can provide profiles up to 30 km altitude, and is not harmful for the environment or the finder of the package.

Our newly developed NO_2 sonde does not make use of a photomultiplier tube. Instead, an array of silicon photodiodes is used to detect the light from the chemiluminescent reaction. Photodiodes are light in weight, and do not require power or a high voltage. An amplifier is used to enhance the rather weak signal from photodiodes. This amplifier, together with the reaction vessel and photodiodes, is placed in a metal can to reduce electrostatic interference.

The luminol solution in the NO_2 sonde has been optimised for the reaction with NO_2 following Mikuška et al. (2000). They studied the application of surfactants and complexones for suppression of interferences from other pollutants in the determination of NO_2 with a Chemiluminescence Aerosol Detector (CLAD). Mikuška et al. (2000) use a luminol solution that is specific to NO_2 only and removes interference with O_3 and peroxy acetyl nitrate (PAN), by adding sodium EDTA and Triton X-100 to the luminol solution.

Section 2 gives a detailed description of the design of the instrument. The chemistry that is involved within the luminol solution is explained in Sect. 3. The calibration of the NO_2 sonde can be found in Sect. 4. Section 5 shows a comparison of the NO_2 sonde with an in situ monitor. The measured NO_2 profiles during the Cabauw Intercomparison campaign of Nitrogen Dioxide measuring Instruments (CINDI campaign) are presented in Sect. 6. Discussion and conclusions can be found in Sect. 7.

2 Design of the instrument

Figure 1 shows a picture of the NO_2 sonde. The instrument is housed in a polystyrene (PS) foam box. PS is light in weight and a good insulator. The size of the PS box is

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19×19×26 cm. The inside of the PS box is painted black, so ambient light is absorbed and can not disturb the measurement. To have an extra light barrier the instrument is placed in a black cardboard box (right side Fig. 1). A radio transmitter (Vaisala RS92 radiosonde) is attached to the outside of the PS box (left side Fig. 1). The weight of the NO₂ sonde is approx. 700 g, excluding the weight of the radio transmitter.

Figure 2 shows a schematic diagram of the design of the instrument. A luminol reservoir is shown on the right. The liquid pump moves the luminol solution to the reaction vessel. The liquid pump used is a small (30×15×3.8 mm) piezoelectric diaphragm pump (Bartels microComponents mp6). The Teflon air pump forces the ambient air into the reaction vessel with a flow of 4 ml/s. The tubes connected to the air pump are also made of Teflon. The gas is leaving the Teflon tube by two holes of 1 mm diameter. The NO₂ in the gas flow reacts with the luminol solution, which emits blue/violet light at a wavelength of 425 nm. The secondary function of the gas flow is to force the luminol solution out of the reaction vessel back to the luminol reservoir, so luminol is recycled continuously. The recycling of luminol is necessary to reduce acidification of the system by carbon dioxide (CO₂). The luminol solution contains Triton X-100 which causes foam and is able to escape in small proportions from the sealing of the luminol reservoir therefore absorption material is attached on the outside of the luminol reservoir. The volume of the luminol reservoir is 50 ml, but contains 35 ml of the luminol solution.

2.1 The detector

The heart of the detector is a glass reaction vessel with length of about 100 mm, and a diameter of 10 mm. A rubber cap is used to seal the reaction vessel, as the design of the instrument requires some pressure build up in the reaction vessel to force the excess liquid out.

On opposite sides of the reaction vessel arrays of silicon photodiodes have been mounted (see Fig. 2). One array contains eight VTB8440 silicon photodiodes, with an active area of 5.16 mm² each. They are held into place with black shrink tubing. The photodiodes on the left of the reaction vessel (Fig. 2), the “seeing” array, are used

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to detect the emitted light from the chemiluminescent reaction. The right side of the reaction vessel is covered with aluminium foil (Fig. 2), to reflect the light towards the “seeing” photodiodes. The VTB8440 photodiodes produce a spurious signal when their temperature is changed, probably as a result of a heat flux through this device.

5 An identical array of photodiodes, the “blind” array, is mounted behind the aluminium foil to measure – and correct for – dark current and the effects of temperature changes.

Two essentially identical amplifiers are used to process the signals from the photodiodes. A typical current that is generated in the photodiodes is in the order of fA, which is converted and amplified to a readable signal in mV. The heart of the amplifier is a current to voltage converter built around an LMC6001 operational amplifier (OPAMP). Two resistors of 50 GΩ were used, one on each of the OPAMP’s inputs. To avoid leakage current, the resistors and the photodiodes were not mounted on the circuit boards. As the photodiodes are operated at zero bias, the noise of the amplifier is probably dominated by the Johnson noise of the resistors, which is in the order of 15 1 fA. The noise from each of the photodiodes is in the same order of magnitude. After amplification, the signal is sent to an RC filter with a time constant of 1 s, to remove the high frequency noise. An additional OPAMP is used to reduce the output impedance.

The reaction vessel and the amplifiers are mounted in a tin can of 100×70×20 mm, to shield against electrostatic and radio interference, and stray light. A single puncture is made in the otherwise airtight tin can, to prevent a pressure gradient. Some silica gel is added to prevent condensation of water on the electronic parts. A copper wire is inserted in the liquid to prevent build up of static electricity.

25 The amplifiers do not have a significant voltage offset. However, when the photodiodes are connected to the amplifiers, a temperature-dependent offset is present. This is probably caused by interplay between the non-ideal properties of the OPAMP (offset) and the photodiodes (finite resistance).

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2.2 The radiosonde

A Vaisala RS92SGP digital radiosonde is added as part of the package. This device measures ambient temperature, humidity, and air pressure. Furthermore it contains a GPS receiver, to measure its position, from which the wind speed and direction can be inferred. A radio transmitter sends the data to the ground station. The radiosonde is connected to a Vaisala RSA-11 ozone sonde interface. The device has four analogue inputs that are sampled once per second. Channels 3 and 4 are used to relay the signals from the NO₂ detector. Channel 2 is dedicated to the measurement of the temperature inside the air pump. Channel 1 remains unused in the current design, but could be used for an additional ozone sensor. Laboratory studies have shown that the response time of the chemical reaction is in the order of one second. The RC filter in the amplifiers prevents under sampling of the NO₂ profile. The resulting resolution of the NO₂ profile is thus in the order of 5 m.

3 The luminol solution

The aqueous luminol solution contains an additional number of chemical compounds to make the luminol solution specific to NO₂. The chemical compounds and their function are listed and described below.

- Potassium hydroxide (KOH) allows the luminol to dissolve in water by changing its polarity. White et al. (1963) studied the chemical reaction of luminol with O₂. They argued that the reaction of the hydroxide ion (OH⁻) with luminol is the first

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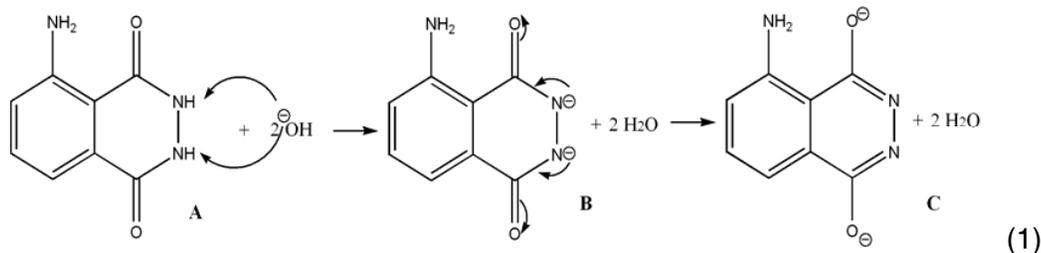
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step of the reaction, see Eq. (1).



Deprotonation (**A**, Eq. 1) occurs when the strong base (OH^-) reacts with the weak acid secondary amino groups ($-\text{NH}$) forming a negative charge on the carbonyl oxygen ($-\text{C}=\text{O}$) to form what is known as an enolate (**C**, Eq. 1). The enolate anion is stabilized by resonance. The next step of the NO_2 -luminol reaction is not well understood. Maeda et al. (1980) reported that in the absence of KOH in luminol solution, no chemiluminescence was observed. When the concentration of KOH exceeded 10^{-5} mol/l chemiluminescence was detected and the intensity was increased with the increase of KOH concentration.

- Sodium sulphite (Na_2SO_3) is an anti-oxidant and is capable to capture sulphur dioxide (SO_2) and ozone (O_3). Wendel et al. (1983) discovered that Na_2SO_3 increases the duration of the stable period of the luminol solution. Na_2SO_3 also increases the emitted light signal, as shown in Fig. 4, which is consistent with the results of Maeda et al. (1980).
- Ethanol makes the luminol solution more specific to NO_2 . Wendel et al. (1983) discovered that the addition of a primary alcohol – in their case methanol – increased the sensitivity and specificity for NO_2 . The signal doubled at a concentration of 0.05% v/v and then decreased at higher concentrations. An advantage of using ethanol, which is also a primary alcohol, is that it is less harmful than methanol.

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- Nguyen et al. (2006) also saw an increase in the light signal when using a luminol solution with a primary alcohol. Why the primary alcohol makes the luminol solution more specific to NO_2 is not well understood.
- Sodium EDTA (ethylenediaminetetraacetate) is a complex former. Mikuška et al. (2000) claim that sodium EDTA is amplifying the functioning of Na_2SO_3 . It makes the removal of O_3 and PAN more efficient. The preferred solution of Mikuška et al. (2000) lowers the interference of O_3 (mixing ratio 50 ppbv NO_2 with 170 ppbv O_3) to 0.2% of the total signal and lowers PAN interference (mixing ratio 50 ppbv NO_2 with 81 ppbv PAN) to 1.2% of the signal (in combination with Triton X-100).
 - Triton X-100 (4-octylphenol polyethoxylate) makes the luminol reaction more specific to NO_2 . Triton X-100 decreases the surface tension, thereby enhancing the contact surface between air and liquid. Mikuška et al. (2000) argued that the enhancement of NO_2 response arises from an increase in the concentration of luminol molecules at the surface of triton micelles (A micelle is an aggregate of surfactant molecules dispersed in a liquid collide. A micelle in aqueous solution forms an aggregate with the hydrophilic “head” regions in contact with surrounding solvent, isolating the hydrophobic single tail regions in the middle centre.) with subsequent diminution of vibrational quenching of excited species, which improves the fluorescent quantum yield of excited luminol. A radical molecule like NO_2 , with an unpaired electron, probably provides different electrostatic interactions with triton micelles in comparison with those by O_3 and PAN that have no unpaired electron in the molecule.
 - Oxygen is needed to activate the NO_2 luminol reaction. Without oxygen, luminol does not emit light when exposed to NO_2 . Adding oxygen is only relevant for laboratory studies, as the ambient air contains sufficient oxygen for the reaction.

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3.1 Optimizing the luminol solution

The chemicals that are listed above can be categorised into two groups; the reaction group (luminol, KOH, Na₂SO₃, O₂) and the protecting group (Triton X-100, Na EDTA, ethanol). The chemicals listed in the reaction group fulfil an important role in the luminol-NO₂ reaction and the chemicals in the protecting group lower the interference of other strong oxidizers like PAN and O₃.

The chemicals in the reaction group are optimized with respect to the light signal. This is done by varying the concentration of one component over a range while holding all of the other compounds constant, as detailed in the right column of Table 1. The setup of this experiment is shown schematically in Fig. 3. NO₂ was supplied from a gas cylinder (10 ppmv NO₂ in N₂), and diluted with CO₂-free air to an NO₂ concentration of 1.4 ppmv. The concentrations of the chemicals that are used are expressed in molar (M=mol/l).

Figure 4 shows the measured light signal as a function of concentration of the chemicals in the reaction group, luminol, Na₂SO₃ and KOH (top to bottom). The largest light signal is reached for a luminol concentration between 1×10^{-4} M and 2×10^{-4} M. For larger luminol concentrations the light signal decreases again, probably as a result of self-absorption. The optimum Na₂SO₃ concentration is between 0.01 and 0.02 M and the optimum pH value is between 12 and 12.2, corresponding to KOH concentrations between 0.01 M and 0.016 M.

Table 1 gives an overview of optimal concentration ranges of the luminol solution, and the standard concentrations actually used in this paper. The optimal luminol solution is the one which gives the highest light signal. The standard concentration of KOH used in the flying sondes is slightly higher in an attempt to reduce the effect of acidification (discussed below) and hence lengthen the time the sensor can be used.

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3.2 Acidification of the luminol solution

When the NO₂ sonde is measuring ambient air, carbon dioxide (CO₂) will acidify the luminol solution (already suggested by Maeda et al., 1980). The relevant reactions are:



Figure 5 shows the degradation of the pH as a function the time. In Sect. 3.1 it was shown that a pH between 12 and 12.2 gives the optimal light signal. In sonde flights the pH is initially brought to 12.5, to have an extended measuring time without a large degradation of the light signal. Also a fluid reservoir has been added to the sonde, so it can operate for about 2.5–3 h in a pH range of 12.5–11.6. Figure 4c shows that for this pH range the signal variation is less than 10%. The sonde data is corrected for the acidification using parameterizations of pH as a function of time and of signal as a function of pH, based on the measurements from Figs. 5 and 4c, respectively (see Sect. 4).

4 Calibration

The calibration of the measured signal is preformed using the relation:

$$n = f \cdot (S_1 - S_2 - O(T_d)), \quad (4)$$

where n is the number density of NO₂, S_1 is the measured signal in the seeing array of photodiodes and S_2 is the measured signal of the blind array of photodiodes, O is an offset which depends on the detector temperature T_d (see Fig. 6), and f is a scaling factor. The number density n is converted to volume mixing ratio ν using the relation:

$$\nu[\text{ppbv}] = 1.38 \times 10^{-12} \times n[\text{cm}^{-3}] \times \frac{T_p[\text{K}]}{\rho[\text{hPa}]}, \quad (5)$$

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where p is the pressure of the ambient air and T_p is the temperature inside the air pump.

The scaling factor f is almost constant during the first few hours of the measurement, meaning that the signal is almost linear with the amount of NO_2 . Its value depends on the chemical solution (see Sect. 3.1) and on the amplifiers used (see Sect. 2). Figure 7 shows the signal as a function of the amount of NO_2 for two different versions of the detector. These measurements were performed in the RIVM calibration facility, where the NO_2 concentration can be controlled.

The change in pH value during the measurement results in a small change in the scaling factor of about 10% in 2.5 h (see Sect. 3.2). The scaling factor also depends on the temperature of the solution, as can be seen in Fig. 8. The change in the scaling factor is 2.0% per degree Celsius for temperatures between 20 °C and 40 °C, a typical temperature range inside the sonde box (air temperature outside the sonde box can of course be much lower).

Six sondes were launched during the CINDI campaign, June–July 2009 in Cabauw, the Netherlands (see Sect. 6). The temperature dependence of the offset was not characterized before launch, and so the offset is estimated to be a third order polynomial in time. This is an iterative fit through a selection of measurement points. At each iteration step those points are selected for which the difference to the polynomial is less than 1.5σ , starting with all measurement points and ending when the selection does not change anymore. Here σ is the root mean square difference of the selected measurement points of the previous iteration to the fitted polynomial. This procedure could lead to an underestimation of NO_2 in the free troposphere.

The scaling factor is determined using simultaneous in-situ measurements by a Thermo Environmental Instruments (TEI 42 TL) chemiluminescence analyzer with a Blue Light Converter, operated by EMPA during the CINDI campaign. The scaling factor at launch is the average offset-corrected measurement signal of the sonde before launch divided by the interpolated 10 min values of the in-situ monitor. The correction factor for the change in pH-value during the flight is estimated to be $1 - 0.07 \cdot (t[\text{h}] - 1.4)^2$,

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following from the data in Figs. 4 and 5.

5 Comparison of the NO₂ sonde with an in situ monitor

The NO₂ sonde is compared with an M200E Photolytic Analyzer of Teledyne-API Inc. operated by RIVM. The M200E Photolytic Analyzer measures NO and NO_x (NO+NO₂), and derives NO₂ from it. The main goal of this comparison was to look if both instruments measure the same dynamical range in NO₂ concentration variations during a certain period of time. Both instruments measured the NO₂ concentration in ambient air at the same location on the roof of a building at approximately 20 m altitude, during rush hour. For this comparison a standard luminol solution is used (see Table 1).

The M200E Photolytic Analyzer reports one-minute averaged NO₂ values. The NO₂ sonde data is also averaged over one minute in this comparison. As the sonde has not been calibrated with a known concentration of NO₂, an assumption for the scaling factor had to be made. The measurement of the NO₂ sonde shown in Fig. 9 is corrected for temperature (see Sect. 4) and pH (see Sect. 3.2).

Four comparisons were made, but only one was without technical problems. The results are shown in Fig. 9. The technical difficulties that occurred for the other three comparisons were a broken liquid pump, and leakage at the sealing of the reaction vessel. In the case of the broken liquid pump, the luminol solution was not recycled and this caused rapid acidification of the luminol solution, resulting in a loss of signal.

Figure 9 shows that both instruments measure the same dynamical range of changing NO₂ values and that variations of 1 ppbv in NO₂ are well captured. Noticeable are small differences between the two data sets, slowly changing with time, which suggest that the NO₂ sonde has either a degrading sensitivity as a function of time or some non-linearity in the scaling factor. This effect is still under investigation.

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6 CINDI campaign

During the Cabauw Intercomparison campaign of Nitrogen Dioxide measuring Instruments (CINDI) in June/July 2009, six NO₂ sondes were launched and measured six vertical profiles of NO₂. The launch site was located at Lopik, the Netherlands (51.97° N, 4.93° E). Figure 10 shows the six profiles that were measured. All NO₂ sondes were launched at approximately 10:30 UTC, or 12:30 local time. The NO₂ sondes were treated with clean air just before launch, to determine the dark current of the detector. The NO₂ sondes were scaled to in-situ measurements performed by EMPA (TEI 42 TL chemiluminescence analyzer, with BLC) just before launch. The vertical velocity of the sonde flights was 5 m/s. The response of the NO₂ sonde to changing NO₂ concentrations is 1 s, giving a resolution of 5 m. In Fig. 10 the boundary layer heights are clearly visible in the profiles. They are in good agreement with boundary layer heights determined from meteorological measurements at Cabauw (LD40 Ceilometer, backscatter profiles).

The first NO₂ sonde was launched on 18 June 2009, Fig.10a. This profile shows a maximum NO₂ concentration around 930 m altitude, and a clear top of the boundary layer at 2 km. Its vertical resolution is higher than that of the other sondes, because it had a smaller vertical velocity.

The profile of 23 June 2009 (Fig. 10b) shows at an altitude of 4.8 km a peak in NO₂ concentration. This peak could have been caused by a layer of airplane exhaust.

The profile of 30 June 2009 (Fig. 10e) shows a second NO₂ layer (1–3 km) above the boundary layer (0–1 km). The origin of this “second layer” could not be determined from meteorological measurements at Cabauw.

7 Discussion/conclusion

The NO₂ sonde is light in weight, cheap (disposable), energy efficient and not dangerous for the environment. The sonde has a fast response to changing NO₂ con-

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centrations which results in an unsurpassed vertical resolution of 5 m. It measures in the range 1–100 ppbv. The NO₂ sonde can measure under all weather conditions irrespective of the amount of clouds.

The NO₂ sonde developed at KNMI has demonstrated its capability to measure in-situ NO₂ profiles in the lower atmosphere. Six profiles have been collected during the CINDI campaign in June/July 2009. The top of the boundary layer is clearly visible in the profiles, and are in good agreement with boundary layer heights determined from meteorological measurements at Cabauw (backscatter profiles, LD40 Ceilometer).

Comparison with the M200E Photolytic Analyzer shows that variations of 1 ppbv in NO₂ are well captured. Both instruments measure the same dynamical range in NO₂ variations in ambient air during a 2.5 h period.

Further validation of the NO₂ sonde is desirable and can be done by a comparison with the NO₂ LIDAR.

The NO₂ sonde can measure for approximately 2.5–3 h. After that time the solution becomes increasingly acid due to CO₂. Longer continuous measurements can be established by using a good buffer solution or a CO₂ scrubber to keep the pH constant.

In theory the sonde can make NO₂ profiles up to the stratosphere, but because the temperature within the sonde rises up to 40 °C, the luminol solution begins to boil at low pressure. To prevent this in the near future, a redesign of the pump drivers is required.

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References

- 5 Boersma, K. F., Jacob, D. J., Bucsela, E. J., Perring, A. E., Dirksen, R., van der A, R. J., Yantosca, R. M., Park, R. J., Wenig, M. O., Bertram, T. H., and Cohen, R. C.: Validation of OMI tropospheric NO₂ observations during INTEX-B and application to constrain NO_x emissions over the Eastern United States and Mexico, *Atmos. Environ.*, 42, 4480–4497, 2008.
- 10 Hasinoff, L. C.: Vertical profiles of NO₂ and O₃ at Kejimikujik National Park, Nova Scotia, Thesis, Graduate programme in Chemistry, York University, North York, Ontario, 1997.
- Kelly, T. J., Spicer, C. W., and Ward, G. F.: An assessment of the luminol chemiluminescence technique for measurement of NO₂ in ambient air, *Atmos. Environ.*, 24A(9), 2397–2403, 1990.
- 15 Maeda, Y., Aoki, K., and Munemori, M.: Chemiluminescence method for the determination of nitrogen dioxide, *J. Anal. Chem. Soc.*, 52, 307–311, 1980.
- Mikuška, P. and Večeřa, Z.: Effect of complexones and tensides on selectivity of nitrogen dioxide determination in air with a chemiluminescence aerosol detector, *Anal. Chim. Acta*, 410, 159–165, 2000.
- 20 Nguyen, D. H., Berry, S., Geblewicz, J. P., Couture, G., and Huynh, P.: Chemiluminescent detection of explosives, narcotics, and other chemical substances, U.S. patent no.: US6,984,524 B2, 2006.
- Parrish, D. D., Hahn, C. H., Fahey, D. W., Williams, E. J., Bollinger, M. J., Hübler, G., Buhr, M. P., Murphy, P. C., Trainer, M., Hsie, E. Y., Liu, S. C., and Fehsenfeld, F. C.: Systematic variations in the concentration of NO_x (NO plus NO₂) at Niwot Ridge, Colorado, *J. Geophys. Res.*, 95(D2), 1817–1836, 1990.
- 25 Pisano, J. T. and Drummond, J. W.: A lightweight NO₂ instrument for vertical height profiles, *J. Atmos. Ocean. Tech.*, 13, 400, 1996.
- Sitnikov, N. M., Sokolov, A. O., Ravegnani, F., Yushkov, V. A., and Ulanovskiy, A. E.: A chemi-

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luminescent balloon-type Nitrogen Dioxide Meter for Tropospheric and Stratospheric Investigations (NaDA), *Instrum. Exp. Tech.*, 48(3), 400–405, 2005.

Steinbacher, M., Zellweger, C., Schwarzenbach, B., Bugmann, B., Ordoñez, C., Prevot, A. S. H., and Hueglin, C., Nitrogen dioxide measurements at rural sites in Switzerland: bias of conventional measurements techniques, *J. Geophys. Res.*, 112, D11307, doi:10.1029/2006JD007971, 2007.

Wendel, G. J., Stedman, D. H., and Cantrell, C. A.: Luminol-based nitrogen dioxide detector, *Anal. Chem.*, 55, 937–940, 1983.

White, E. H., Zafiriou, O., Kägl, H. H., and Hill, H. M.: Chemiluminescence of luminol: the chemical reaction, *J. Am. Chem. Soc.*, 86, 940–941, 1964.

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3, 2805–2832, 2010

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Table 1. Chemical compounds and concentrations used in the aquatic solution of luminol. The second column shows the optimal concentration range for the chemical compounds. The concentrations that are applied in this paper are shown in the third column. The standard solutions have a higher than optimal concentration for potassium hydroxide, which is chosen to compensate for the effect of acidification by carbon dioxide. See Sect. 3 for more details.

Chemical compound	Optimal concentration range	Standard concentration
Luminol	1×10^{-4} – 2×10^{-4} M	1×10^{-4} M
Sodium sulphite	0.01–0.02 M	0.02 M
Potassium hydroxide	0.01–0.016 M (pH: 12–12.2)	0.03 M (pH: 12.5)
Sodium EDTA	2×10^{-4} M	2×10^{-4} M
Triton X100	0.02% v/v	0.02% v/v
Ethanol	0.05% v/v	0.05% v/v

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Fig. 1. The outside of the NO₂ sonde. On the right side a picture is shown of the inside of the NO₂ sonde, which is painted black so ambient light is absorbed. On the left side a ready-to-use NO₂ sonde.

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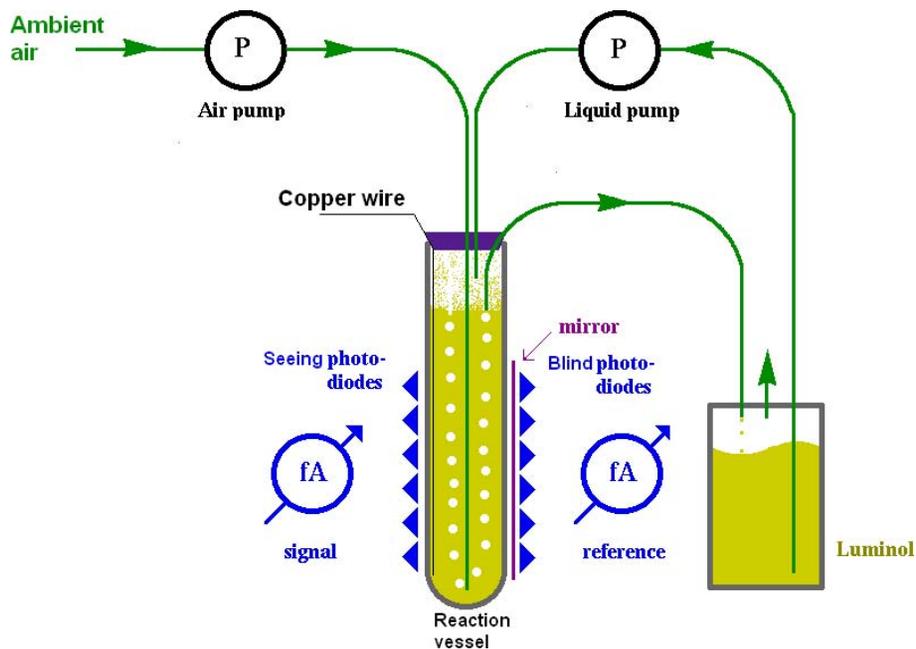


Fig. 2. The design of the NO_2 sonde. The liquid pump moves the luminol solution to the reaction vessel in the centre. The Teflon air pump forces the air into the reaction vessel. The NO_2 in the air reacts with the luminol, and the emitted photons are detected by an array of silicon photodiodes (the “seeing” photodiodes). An aluminium mirror is placed on the opposite site to reflect the emitted photons back to the seeing photodiodes. An identical array of photodiodes, the “blind” array, is mounted behind the aluminium foil to measure – and correct for – dark current and temperature changes. A copper wire is mounted in the reaction vessel to prevent electrostatic build-up.

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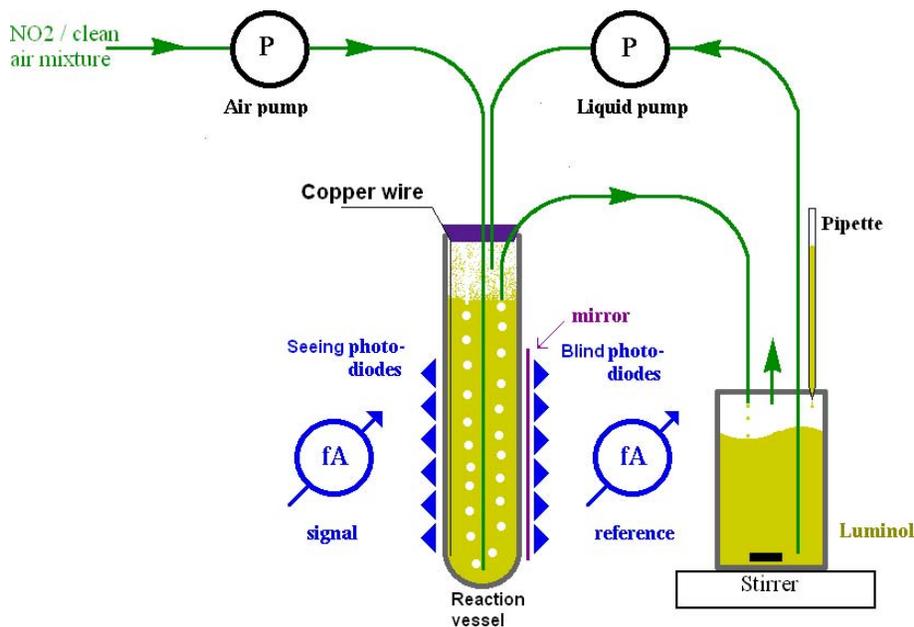


Fig. 3. Set-up for optimizing the luminol solution. On the top right side of the luminol container a pipette is illustrated. With the pipette some liquid can be added to the luminol container to change the concentration of one of the components of the luminol solution. A stirrer mixes the solution. NO₂ was supplied from a gas cylinder (10 ppmv NO₂ in N₂), and diluted with CO₂-free air to a concentration of 1.4 ppmv.

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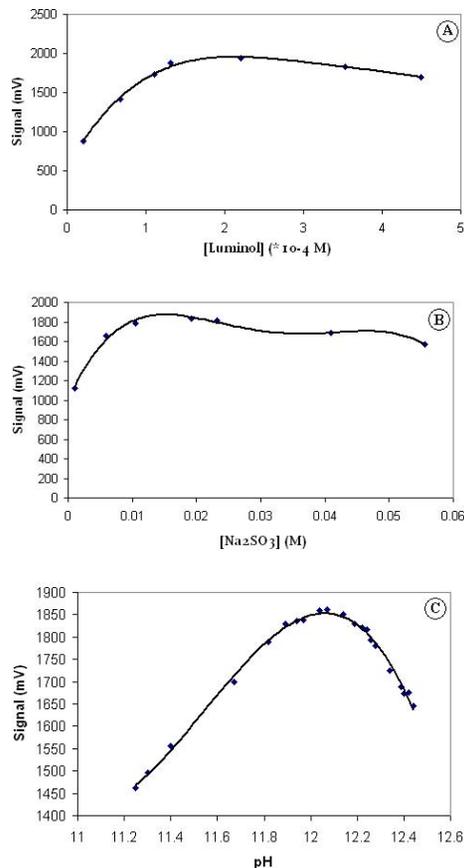


Fig. 4. Optimum concentration experiment for luminol **(A)**, Na₂SO₃ **(B)** and KOH **(C)**. **(A and B)** show signal (mV) versus concentration (M=mol/l), **(C)** shows signal (mV) versus pH value. A constant concentration of 1.4 ppmv NO₂ is used. The blue points represent the average signal over 15 min. The black line is a 4th order polynomial fit. The optimal concentration ranges are shown in Table 1.

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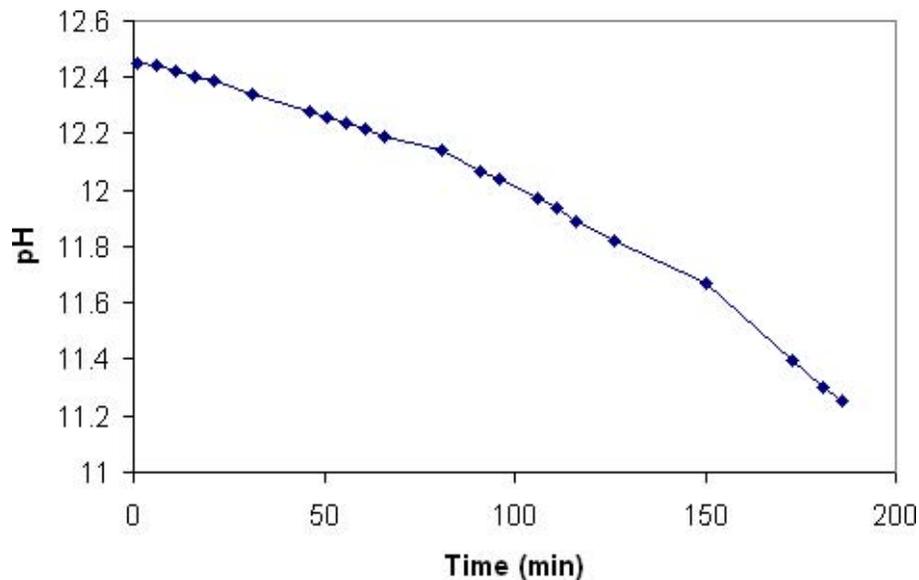


Fig. 5. The pH as function of time. Acidification is caused by CO_2 , see Sect. 3.2. The measurement points are connected with straight lines.

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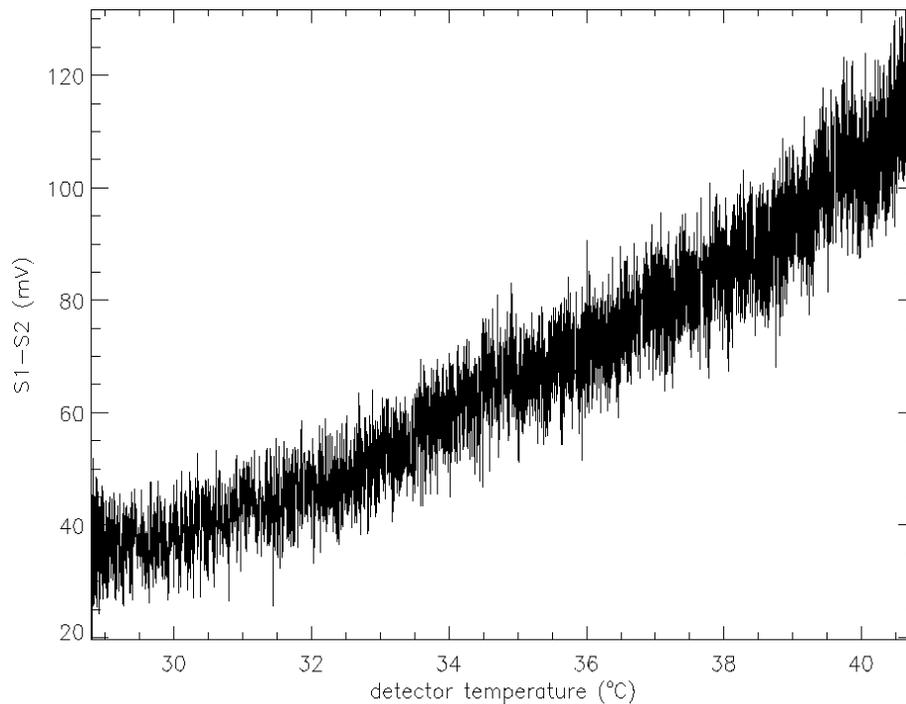


Fig. 6. The difference $S1-S2$ between the signals measured by the seeing and blind detector arrays, using water and ambient air, as a function of the detector temperature. The signal represents the offset O in Eq. (4), for which the NO_2 measurements need to be corrected.

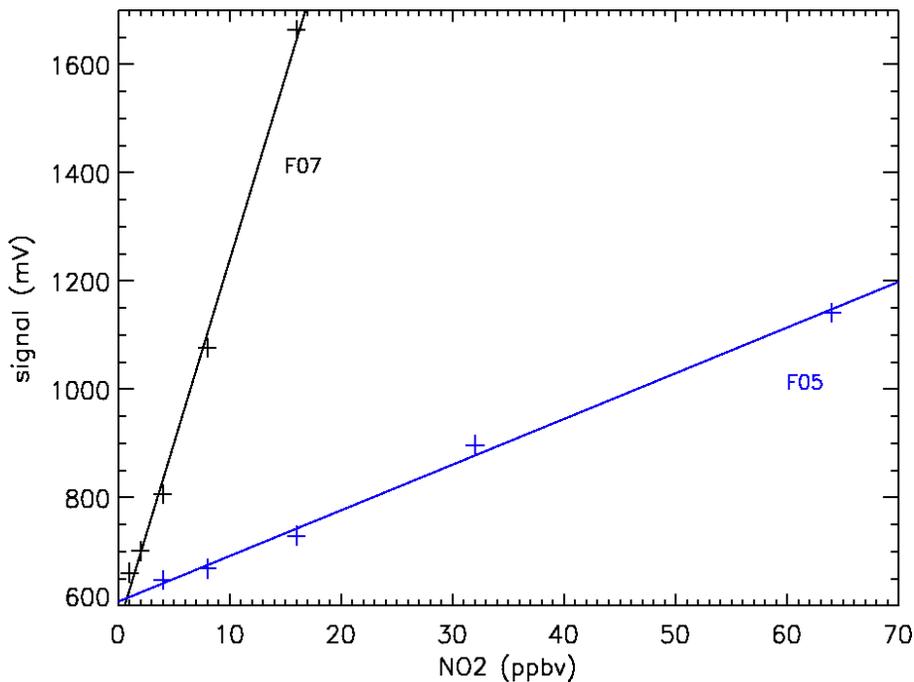


Fig. 7. The signal of the NO₂ sonde detectors as a function of the amount of NO₂ for two different versions of the detector, F05 and F07. F05 is designed for laboratory studies, and is less sensitive, allowing larger NO₂ concentrations. The solid lines are linear least-squares fits.

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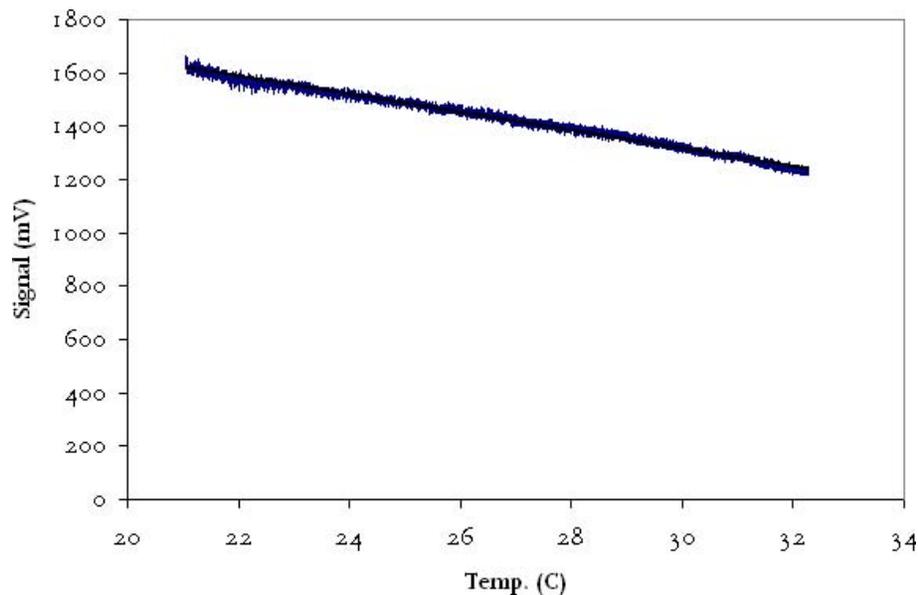


Fig. 8. Signal (mV) of the seeing photodiodes as a function of temperature ($^{\circ}\text{C}$) in the luminal solution, for a constant amount of NO_2 (blue). The black line represents a linear fit through the measured points. The signal decreases with 2.0% per degree Celsius.

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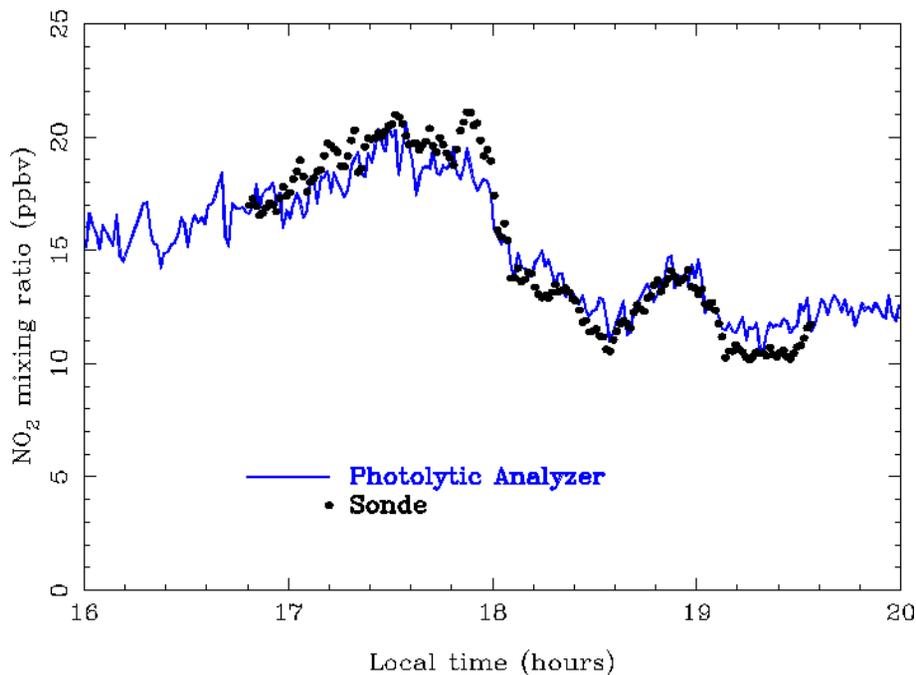


Fig. 9. NO₂ concentration measurements by the NO₂ sonde (black dots) compared with those by the M200E photolytic analyzer (blue line). Measurements were taken during the evening rush-hour in Bilthoven, The Netherlands.

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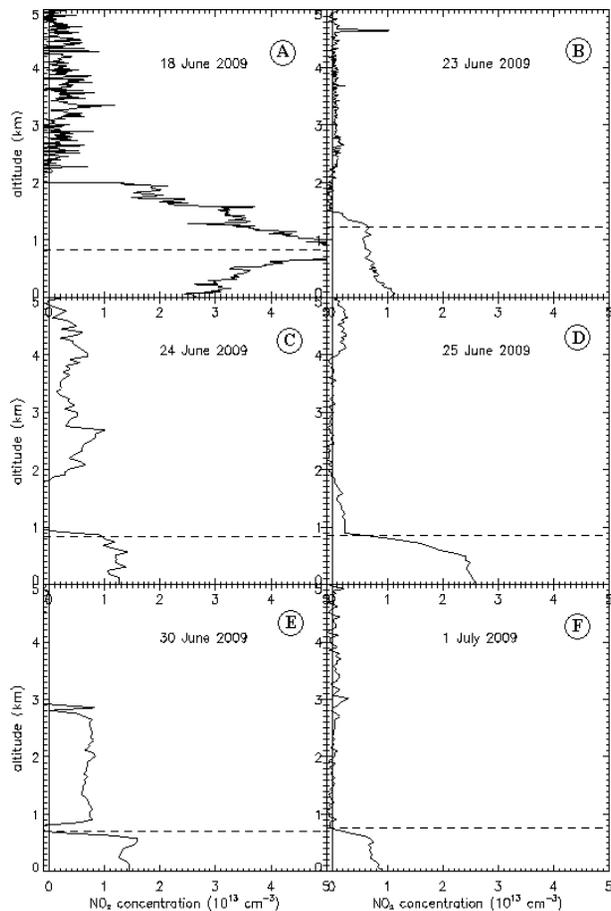


Fig. 10. Six vertical NO_2 profiles measured during CINDI June/July 2009. On the x-axis the NO_2 number density (10^{13} cm^{-3}) and on the y-axis the altitude (km). The dashed horizontal lines indicate the boundary layer height above Cabauw around 10:30 UT, measured by the KNMI Ceilometer.