



A miniDOAS instrument optimised for ammonia field-

measurements

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Abstract

- 15 We present a DOAS instrument, called "miniDOAS", optimised for optical open-path fieldmeasurements of ambient ammonia (NH₃) alongside nitrogen oxide (NO) and sulphur dioxide (SO₂). The instrument is a further development of the miniDOAS presented by Volten et al. (2012). Here, we use a temperature-controlled spectrometer, a deuterium light source and a modified optical arrangement. The system was set up in a robust, field-deployable,
- 20 temperature-regulated housing. For the evaluation of light spectra we use a new high-pass filter routine based upon robust baseline extraction with local regression. In order to fit differential absorption cross-sections to the measurements, multiple linear regression is performed including terms of an autoregressive-moving-average model. For NH₃ the instrument's precision is 0.8 to 1.4 %. Accuracy is larger than precision and derives from the
- 25 precision, uncertainty in DOAS absorption cross-sections (\pm 3 %) and an uncertain estimation of concentration offsets (c_0) present through the definition of reference spectrum I_0 . Accuracy will at minimum be approximately 0.3 µg m⁻³. The limit of detection against I_0 is around 0.2 µg m⁻³. Comparisons of miniDOAS measurements to those by NH₃ acid trap devices showed good agreement. The miniDOAS can be flexibly used for a wide range of field trials, such as
- 30 micrometeorological NH₃ flux measurements with approaches based upon horizontal or





vertical concentration gradients. Results from such applications, covering concentration dynamics of sub-ppb to ppm mixing ratios, are presented.

1 Introduction

- 35 Accurate, high time-resolution measurements of NH₃ for ambient concentration monitoring, source appointments and flux measurements are still a challenge due to the stickiness of this molecule and its interactions with inlet or instrument surfaces, water and aerosol particles (Parrish and Fehsenfeld, 2000). Differential optical absorption spectroscopy (DOAS) with open-path arrangement offers a contact-free in-situ way to determine ambient NH₃, which
- 40 features narrow absorption lines in the UV range between 200 and 230 nm. In this wavelength range, concentration determination by DOAS over path lengths up to 100 m is possible (Edner et al., 1993; Gall et al., 1991; Mount et al., 2002), but instrument performance can pose a challenge for scientific trials (Emmenegger et al., 2004; Mennen et al., 1996; Neftel et al., 1990). Volten et al. (2012) developed a "miniDOAS", for continuous, high time-
- 45 resolution NH₃ (combined with NO and SO₂) measurements. This system is currently being implemented in the Dutch air-monitoring network. It has been designed for the purpose of concentration monitoring, where the system can be set up in the protected environment of a monitoring station with solid installation, climate regulation and easy access to the miniDOAS on its breadboard. Collaborating with the developer group (RIVM, Bilthoven,
- 50 NL), we further developed this miniDOAS into an operational field measurement system. This was done in cooperation with the Swiss applied sciences institute NTB (Buchs, SG, CH). The focus was the design of a simple, reliable instrument, optimised for measurement campaigns, where the miniDOAS can be operated as stand-alone device.
- In this paper we present modifications and additions to the original RIVM model. These 55 include the simplification of the optical arrangement, introduction of another type of light source, a temperature-regulated spectrometer, a revolver for calibration cuvettes, a laser for light source - reflector alignment, a temperature-controlled, weather-resistant housing and stands for a stable field setup of instrument and reflector. Measurements related to NH₃ sources and sinks have to cover a large concentration range. We describe an advanced DOAS
- 60 data evaluation that ensures the validity of the concentration calculation over a wide range and we characterise instrument performance based on inter-comparisons with acid traps as well as parallel miniDOAS measurements. One application example of the new Swiss miniDOAS is the determination of NH₃ emissions from finite agricultural surfaces. We





present miniDOAS measurements resolving small and large NH₃ concentration gradients,
which can be used for emission determination, for example based on inverse dispersion modelling. Highlighted experiments comprise the determination of:

- gradients and emissions from field-application of cattle slurry
- gradients and emissions from a paddock grazed by dairy cattle
- gradients due to the emission from an artificial source along with elevated ambient

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SO₂ levels caused by the passage of the plume of the Holuhraun eruption of the Icelandic Bárðarbunga volcano in 2014 (Gauthier et al., 2015).

2 Material and methods

2.1 The Swiss miniDOAS instrument

- 75 Figure 1 shows the main optical components of the Swiss miniDOAS version. The light source is a deuterium lamp (D2; Hamamatsu), where the light is 90° deflected and collimated by an off-axis parabolic mirror (EdmundOptics; custom-coated with an Al-based VUV-IR Mirror Coating), and directed to a hollow retro reflector (Newport UBBR2.5-5UV; not displayed) at distant location. Returned light is focussed by a parabolic mirror (Edmund
- 80 Optics, custom-coated with an Al-based VUV-IR Mirror Coating) and directed into the spectrometer with the possibility for remote-controlled calibration using a custom-tailored revolver equipped with cuvettes containing known amounts of calibration gas. We used cuvettes with pure N₂, NH₃ (275 ppm), NO (482 ppm) and SO₂ (29 ppm) (those three species in N₂). The D2 lamp exhibits superior UV performance, less noise and less visible light,
- 85 compared to the widely used xenon-type lamp (compare specifications at www.hamamatsu.com). An automated shutter (CVI rotor drive bi-stable flag shutter 04RDS501 with a custom made USB driver) in front of the spectrometer aperture was implemented for dark spectrum recording. The used spectrometer (OceanOptics QE65PRO; slit width 100 μm, grating #H7) features a thermo-electric temperature control and was
- 90 operated with -10 °C. A geometric cut-off, achieved by the tuning of the grating, prevents blooming due to high intensities potentially occurring with the spectrometer's charge-coupled device (CCD) array beyond 230 nm. Light beam adjustment using piezo-motors (Newport Picomotor) was implemented at three locations: two motors actuate the folding mirror and one moves the spectrometer along the optical axis into the "image distance". The instrument
- 95 is built into a robust, weather-proof, thermally insulated box. A pointing laser parallel to the light beam helps with the set-up of the box-reflector system. The box includes a ventilation





system, coupled to the breadboard temperature, keeping instrument temperature constant within a few degrees. Retro-reflectors are installed in a camera housing with heating to prevent from condensation. We equipped the instrument (as well as the reflector) with a solid,

100 custom-made tripod, where instrument and tripod can be connected directly into the breadboard. It is possible to mount the tripod on massive soil screws to ensure a stable field setup (Fig. 1).

In this article, we present measurements from two systems (models "S2" and "S5"). One experiment (W2, Sect. 2.3) includes measurements with an older version ("S1") where

105 another spectrometer (Avantes AvaSpec-2048x14 - same as in Volten et al. (2012)) had been used and where the box temperature was not controlled. Raw-data are recorded by a custom LabView (National Instruments) program, running on a notebook within the instrument. Light level is maximised by automatically adjusting the folding mirror or can be remotely adjusted. Quality parameters and preliminarily calculated concentrations are provided in real-time.

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2.2 DOAS concentration calculation

The DOAS principle is based on the linearization of the Lambert-Beer law (Platt and Stutz, 2008):

$$\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right)L_{path}^{-1} = \sum(-\sigma_i(\lambda)c_i) + P(\lambda), \tag{1}$$

- 115 where I_0 denotes the initial intensity of the light beam emitted by the light source and *I* is the radiation intensity of the beam after passing through a layer of thickness L_{path} (i.e. *I* is a typical measurement spectrum); λ = wavelength, *i* = index for a specific trace gas (here: NH₃, NO, SO₂), σ = absorption cross-section (of trace gas *i* with narrow-band absorption features), c = trace gas amount, *P* = broadband absorption structures; $\frac{I(\lambda)}{I_0(\lambda)}$ will be called I_{div} . Eq. 1
- 120 allows describing the light absorption as a linear combination of absorption cross-sections σ_i . c_i is consequently determined by multiple linear regression (Stutz and Platt, 1996). The crucial step of the DOAS evaluation is the distinction between broadband effects (*P*) on I_{div} and narrow-band absorption structures in σ_i . The purpose is the elimination of *P* by high-pass filtering of I_{div} while retaining the narrow-band features of σ_i (Platt and Stutz, 2008). The 125 absorption cross-sections fitted to the measurements were derived by calibration with a
- controlled gas cell or from literature. They are henceforth called differential absorption crosssections.





- The evaluated wavelength window covers 203.7 to 227.8 nm with 274 x 58 CCD pixels 130 (horizontal x vertically binned) across that range. In order to calculate I_{div} a measurement spectrum *I* (provided e.g. as 1 min mean) is required. Because the optical alignment of the miniDOAS limits the minimum reflector distance to 5 m, I_0 (Eq. 1) is arbitrarily defined as time-average of *I* during a confined period, assumed to be representative for the measurement situation. This I_0 will contain absorption from unknown amounts of the target trace gases (c_{0i})
- 135 present at the averaging time of I_0 . Any I evaluated against I_0 yields the concentration difference against c_{0i} . Once isolated, c_{0i} can be added to every c_i posteriori. Various ways to estimate c_{0i} are discussed in Sect. 3.2.3. One approach, chosen here, consists of intercomparison measurements with other systems, such as alpha samplers (Tang et al., 2001) distributed along L_{path} .
- 140 The applied DOAS routine is similar to that used by Volten et al. (2012). However, the concentration calculation was further adapted to meet our requirements for a robust and efficient high-pass filtering of I_{div} and linear response over a wide ambient concentration range. For high-pass filtering we employ local regression (Cleveland et al., 1988; Jacoby, 2000) by using a combination of local polynomial regression ("loess" method; R Core Team,
- 145 2014) and robust baseline extraction ("rfbaseline" method; R Core Team, 2014; Ruckstuhl et al., 2012): a smoothed (loess, alpha = 0.15) baseline (rfbaseline, alpha = 0.13) of I_{div} (denoted as $\langle I_{div} \rangle_{lowp}$) yields $\hat{I}_{div} = I_{div} / \langle I_{div} \rangle_{lowp}$. The step is iterated a second time (loess alpha = 0.2): $\tilde{I}_{div} = \hat{I}_{div} / \langle \hat{I}_{div} \rangle_{lowp}$. The alpha parameter defines the running window used for local regression as a fraction of all investigated CCD pixels. The rfbaseline method is based on
- 150 robust local regression with asymmetric outlier weighing in order to extract the baseline signal from a series of data points (Ruckstuhl et al., 2012). \tilde{I}_{div} (representing the high-pass filtered I_{div}) features two properties: first, the involved low-pass filter can account for the shape of P encountered with our instrument to ensure a statistically valid DOAS evaluation (Stutz and Platt, 1996). Second, $\langle \hat{I}_{div} \rangle_{lowp}$ acts as a baseline to the regions of narrow-band
- 155 absorption. Each measurement I is corrected with a dark spectrum, recorded with blocked spectrometer inlet. Pixels at the far end of the CCD, where no light should be received by the grating, are used to map the influence of stray-light within the detector cell. This offset due to stray-light is assumed to show a uniform distribution across the CCD array and is considered for further calculations.





- 160 Fitting the differential absorption cross-sections with ordinary least-square (OLS) optimisation often leaves some degree of auto-correlation in the residual spectrum. Concentrations estimated with such properties are biased and resulting standard errors can be too small (Platt and Stutz, 2008). In order better account for auto-correlation, we include terms of an auto-regressive moving-average (ARMA) regression model (Brockwell and
- 165 Davis, 2002; R Core Team, 2014) in our fitting procedure. The terms of the ARMA models are allowed to contain solely up to two orders, resulting in a total of 5 parameter combinations. The best model for each spectrum is selected using the corrected Akaike information criterion (Brockwell and Davis, 2009). Volten et al. (2012) consider potential wavelength drift with the detector by searching for the best correlation of the DOAS fit when
- 170 shifting over the CCD array. Since we use a thermoelectrically cooled spectrometer, which does not show major systematic CCD pixel drift, we restrict this step to shifts of ± 1 pixel.

2.3 Field experiments

As a demonstration of applications for the miniDOAS instrument, exemplary results obtained 175 from five experiments with a focus on NH_3 are presented (Table 1). Two experiments (R1 and HAFL) focused on inter-comparisons. During R1, two miniDOAS systems were operated in parallel. At the HAFL trial, the same systems were inter-compared to impinger NH3 measurements. With W2, W3 and R3 horizontal and vertical concentration gradients are presented. These experiments investigated NH₃ gradients related to emissions from slurry 180 application (W2) and from an artificial NH₃ source (W3) as well as from a paddock grazed by dairy cattle (R3). These gradients can be used to determine the associated NH_3 emissions by means of inverse dispersion models, such as with backward Lagrangian Stochastic (bLS; Flesch al., 2004)dispersion "WindTrax", et modelling (e.g. www.thunderbeachscientific.com) or e.g. with the "FIDES" model (Loubet et al., 2010). In

the following the experimental setups are briefly outlined.

2.3.1 Inter-comparison with impingers

A comparison between impingers and miniDOAS was performed indoors in the auditorium of the agricultural school HAFL in Zollikofen, Switzerland. The NH₃ concentrations were modulated by ventilation that is scaled with the CO₂ concentration in the room and is switched of during night-time. Two miniDOAS systems were placed in the diagonal of the





room with a path length of 56 m. 12 impingers were evenly distributed on both sides along the miniDOAS beams.

195 2.3.2 Parallel miniDOAS measurements and NH₃ emissions from grazing cattle

The French program BTéP (Emissions gazeuses au Bâtiment, sTockage, Epandage et Pâturage des systèmes bovins laitiers) is devoted to investigate NH₃ emissions along the production chain of a dairy system. One aspect was the determination of NH₃ emissions during grazing. Measurements took place in May 2015 at the "Institut de l'Elevage"

Monvoisin – BP 85225 35652 Le Rheu Cedex Brittany in France. Before the grazing period the miniDOAS systems were run side-by-side (Experiment R1) and in parallel alpha passive samplers (Tang et al., 2001). To estimate NH₃ emissions under grazing conditions the miniDOAS systems were located up- and downwind at the edges of the grazed paddock of about 0.5 ha (Fig. S1, Supplement). We tentatively calculated NH₃ emissions based on bLS and miniDOAS. Details about the used bLS approach are documented by Häni et al. (2016).

2.3.3 Emissions from slurry field application

The site Witzwil (46°59'06''N, 7°04'32''E) is located on the Swiss Plateau 431 m a.s.l. The experiment took place on a 18 ha flat grassland field that was cut end of August and treated
with Glyphosate on September 6th 2014 to prepare a no-till sawing. On September 1st 14:00 cattle slurry was applied to a circular plot with a radius of 19 m (Fig. S2, Supplement). Moderate easterly winds prevailed. The miniDOAS S1 was placed east of the circle to monitor the inflow NH₃ concentration and S2 was placed 5 m downwind of the circle. For comparison, NH₃ emissions were derived from bLS-impinger measurements as well as from 1HF-impinger measurements at the plot centre. Details about these methods and the

experiment can be found in Häni et al. (2016).

2.3.4 Artificial gas release

On September 22nd an artificial gas-release source was installed on the dead grass canopy at
 Witzwil. The source consisted of a grid of 36 critical orifices (100 µm diameter, stainless steel, LenoxLaser, USA) in order to release gas at a known mass-flow rate. The grid was designed to approximate a circular area with a radius of 10 m, i.e. an area of 314 m² (see Fig. S3, Supplement). The orifices were placed equidistant to each other and were radially





connected to a distribution unit at the centre with eight 6 mm (OD) PA (Legris, Parker Hannifin) tubes. Gas-supply was regulated by a mass-flow controller (red-y smart controller, Voegtlin Instruments, Switzerland). Grid pressure was monitored to guarantee constant overpressure. 4.97 % NH₃ in N₂ gas standard (5.0, CarbaGas, CH) was used with a release rate of 10 nl min⁻¹ corresponding to an average emission rate of 369.5 µmol s⁻¹ over a circular area with a radius of 10 m. For this experiment we used three miniDOAS systems, placed downwind of the source at a distance of 3 meters from the edge of the source and the S1 device measured upwind of the source. The heights of the 72 m miniDOAS paths were 0.42,

3 Results and discussion

1.22 and 3.2 m above ground.

235 **3.1 Differential absorption cross-sections**

The differential absorption cross-sections used for our evaluation (Fig. 2b) were obtained by calibration with a flow cuvette, similar as in Volten et al. (2012). Calibration spectra are treated exactly the same way as regular measurement spectra to provide the differential absorption cross-sections for the determination of c_i. The NH₃ absorption cross-section by
Cheng et al. (2006) (from the UV/VIS Spectral Atlas; Keller-Rudek et al., 2013) was compared to the differential cross-sections from our calibration after convolution of the literature values to the spectrometer's CCD resolution (Fig. 2a). Calibrations were within ± 3 % of the differential absorption cross-section derived from Cheng et al. (2006) (Fig. 2b).

Figure 2c shows I_0 and I with absorption by NH₃, NO and SO₂. The applied high-pass filter represents a baseline to narrow-band absorption (Fig. 2d). This individually for NH₃, NO, SO₂ (Fig. 2b), but also for all three gases combined. As a result, differential absorption crosssections are independent from the magnitude of absorption (or the ambient concentration for a given L_{path}) (Fig. 3). For verification, \tilde{I}_{div} was calculated for NH₃ with simulated spectra using the absorption cross-section by Cheng et al. (2006), based on ambient concentrations of 10,

250 100 and 1000 ppb across $L_{path} = 75$ m. Resulting NH₃ differential cross-sections, evaluated with the rfbaseline high-pass filter, were equivalent over the entire concentration range, demonstrating that the procedure provides robust results over a wide range of ambient concentrations (Fig. 3). For comparison, a running mean based high-pass filter yields NH₃ differential cross-sections that slightly depend on the amount of absorption. In this case a non-





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The rfbaseline method (Sect. 2.2) is conducted with one-sided outlier weighting. Situations resulting in apparent negative concentrations (meaning *I* exhibits less narrow-band absorption than I_0) are assessed this way with a higher uncertainty. Consequently, using the rfbaseline-based low-pass requires that I_0 is ideally taken during periods with lowest expected concentrations by all three gases.

3.2 Instrument performance

3.2.1 Field operation

- Under a range of ambient air temperatures between -10 to 30 °C, the temperature inside the
 miniDOAS box can be kept constant (here at 35 °C) within 3 °C, while the spectrometer keeps its temperature set to -10 °C. Feasible L_{path} range between 10 to 100 m as the optical arrangement limits the minimum reflector distance whereas light loss due to increasing beam diameter and O₂ / O₃ absorption restricts the maximum distance due to the associated deterioration of the precision of concentration calculation. The usual spectrometer integration
 time for a single spectrum is between 20 to 150 ms. With the stable mounting of instrument
- and reflector, measurement uptime close to 100 % is possible and is primarily limited by fog episodes.

3.2.2 Filters and multiple linear fit

- Figure 4 demonstrates the presence of non-random noise structures in I_{div} . I_{div} experiences broadband deformation (*P*) to various degrees (in the order of a few per-cent at maximum), changing on timescales of hours to days. This can be caused by Rayleigh and Mie extinction, broadband-like absorption by gases and further detrimental instrumental effects, such as unevenly distributed stray-light within the spectrometer cell. Depending on the interaction of
- 280 the low-pass filter with unfavourable combinations of strong *P*-deformation and noise might lead to auto-correlation structures in the residuum spectrum. Figure 4 demonstrates three different cases with the focus on NH₃ in order to highlight features and limitations of the concentration calculation. Small differences between the concentration and associated standard error from the ARMA and an OLS fit, respectively, become evident. We regard the
- 285 advantage of the applied ARMA model over the OLS regression as twofold: first, autocorrelation structures in the residual spectrum can impose features resulting in artefact concentration values when using the OLS regression. ARMA regression yields slightly more





robust results for all three gases. Second, the concentration standard error, as a result of the ARMA fit, tends to be larger than that from OLS and better approximates the fit's uncertainty.
We checked potential interference by rotating sealed cuvettes (N₂, NH₃, NO, SO₂) into the beams of two instruments. The largest effect was observed from SO₂ on NO with up to -15 %. The effect of SO₂ on NH₃ was at most -2 %. An example is given in the supplemental material (Table S1). Results differ between instruments and depend upon the used reference spectra. As supporting information the concentration standard errors do indicate the fit's uncertainty. Possible interferences are negligible under most atmospheric circumstances

3.2.3 miniDOAS inter-comparison

During experiment R1 two miniDOAS models (S2 and S5) were operated in parallel under identical conditions for four days. For a direct comparison, the differential absorption crosssections from individual calibrations were adjusted in order to match the literature-derived cross-section (Sect. 3.1). Applied corrections were -1.3 and 2.5 % for instrument S2 and S5, respectively. Figure 5 shows the time series of NH₃ concentrations and the scatter between both instruments. The time series was characterised by easterly winds at the beginning and towards the end, where advected NH₃ from a nearby stable produced elevated and fluctuating

305 concentrations. During the period in-between, westerly winds with low and constant concentrations prevailed.

The ranges of the standard errors for all three gases were assessed from 1 min averaged spectra (also see Fig. S4, Supplement). Median standard errors were 0.06 μ g m⁻³ NH₃ (interquartile: 0.05 to 0.09), 0.33 μ g m⁻³ NO (0.24 to 0.41) and 0.18 μ g m⁻³ SO₂ (0.14 to 0.22).

- 310 Calculations based on 30 min averaged spectra yielded similar ranges. This suggests that the uncertainty of the concentration calculations was influenced by non-random spectral structures. The concentration differences between S2 and S5, evaluated with half-hourly means, were of a similar magnitude as the associated standard errors, demonstrating that the concentration standard errors from the multiple linear fit are a suitable measure for the
- 315 precision of concentration calculation (Stutz and Platt, 1996). Fig. 6 shows the relationship of the standard error to the concentration level. This indicates that the precision of NH₃ depended on instrumental features and was 0.8 to 1.4 %.

The NH_3 inter-comparison time series and regression of S2 onto S5 (Fig. 5) reveal the consistency between both instruments, which further consolidates the precision analysis. The

320 instruments show very good agreement with only minor deviations caused by episodes of drift





between both instruments. The slope of S2 onto S5 is one and the intercept is practically zero. Overall, the NH₃ limit of detection (LOD) against c_{0i} for 1 to 30 min concentrations, approximated as three times the median standard error, is 0.2 µg m⁻³. In general, the system's precision is at minimum the LOD µg m⁻³ or roughly 1.4 % the NH₃ concentration (Fig. 6).

- The exact determination of c_{0i} is a challenge. Measurement inter-comparisons with other systems can constrain c_{0i}. As such comparison systems are mostly point-location measurements, it is necessary that horizontal gradients are small within the miniDOAS path and are representatively cached by the point measurements. For the results presented in Fig. 5, c_{0,NH3} = 1.92 µg m⁻³ was derived from parallel measurements with three alpha sampler batches
 distributed along L_{path}. In principle, there are alternative ways to approximate c_{0,NH3} as
 - follows:

a) During long-term concentration monitoring, periods with lowest ambient concentrations reflect conditions closest to zero. For example, NH₃ can be very low during or after rainfall and under cool temperatures and in a well-mixed boundary layer.

b) I_0 could be recorded at very remote places, where it is a safe assumption to find extremely low ambient concentrations. An NH₃-free situation could also be attempted by construction of a "giant denuder" with NH₃ scrubbing, where I_0 is recorded within the denuder tunnel.

c) $c_{0,\text{NH3}}$ could be derived from fitting a baseline to I_0 allowing for the quantification of narrow-band absorption. This can be done using our data filtering approach (Sect. 2.2). Since

- 340 the signal-to-noise ratio with the baseline and I_0 is inevitably larger than with I and I_0 , this approach yields results with limited accuracy. The absorption present in I_0 , used for R1, was analysed using the rfbaseline method to derive a new I_0 without narrow-band absorption structures. This yielded $c_{0,NH3} = 1.93 \ \mu g \ m^{-3}$ - similar to the inter-comparison with alpha samplers. However, the statistical uncertainty from this analysis is high (NH₃ standard error =
- 1.35 μg) and the result is sensitive to the rfbaseline filter width.
 Although miniDOAS determines SO₂ and NO besides NH₃, the system is optimised for the latter. SO₂ and NO absorption signatures are considered and their c₀ does not have to be known for an accurate NH₃ determination. c_{0i} represents a constant, reflecting the ambient concentration during I₀ definition. It does not affect the linearity or precision of the calculation. In case of NH₃, c₀ from any of the discussed approaches is expected accurate at best by 0.3 µg m⁻³, which represents the absolute limit to accuracy. Assume an NH₃ analysis, based on 1 to 30 min averages, yields 5 µg m⁻³, representing a typical ambient concentration in agricultural areas. While the precision is approximately 0.2 µg m⁻³, the accuracy will be





 $0.65 \ \mu g \ m^{-3}$, given by 0.2 (precision) + 0.3 (c_0) + 3 % (differential absorption cross-section) x 355 5 $\mu g \ m^{-3}$.

3.3 Ammonia field experiments

3.3.1 Concentration inter-comparison

The miniDOAS systems have been compared to conventional impinger systems (Häni et al., 2016) in an indoor experiment (HAFL, Sect. 2.3). The two systems were independently calibrated, which allows for an independent concentration (Table 2). For the impinger-results the precision is indicated as the standard error of the mean value. For the miniDOAS the precision is indicated as the standard deviation of the 1 min values during the corresponding intervals. The measurements in the HAFL auditorium showed small differences between

365 miniDOAS and impingers. These were smaller than the precision of both systems (10 %) when the ventilation of the room was switched of (after 18:00). The first two intervals showed larger differences, but they were within the precision of the measurements. However, they might reflect the existing inhomogeneity of the concentration field in the room.

370 **3.3.2** Gradients and emissions due to grazing cattle

From 13.5 to 19.5.2015 miniDOAS S2 was located at the SW side of the field and S5 in the centre (Fig. S1, Supplement). 26 cows grazed the SW quarter of the field from the morning of 18.5 until early afternoon on 19.5. As the wind direction during this period tended to be between SW and WNW, S2 represented the inflow concentration and S5 measured an outflow concentration influenced by the NH₃ emission caused by the cows grazing on the pasture. A systematic increase of the horizontal gradient, from the beginning of grazing until the early afternoon next day (when the miniDOAS systems were moved), was recorded (Fig. 7). This emission gradient increased from below the LOD up to 6 ug m⁻³. From May 21st 2015 onwards, S2 was located at the NW edge and S5 at the SE border of the entire field while the cattle grazed at the entire paddock. Again, elevated emission gradients were observed. During

the period before grazing (13th to 18th), smaller gradients were present probably due to a combination of NH₃ advection from surrounding sources and deposition over the investigated field. We used the gradients for a first emission calculation by bLS when the cattle was on pasture. The emissions were generally below 1 ug m⁻² s^{-.1}. They peaked characteristically when the wind blew from a direction where the downwind miniDOAS had a larger





concentration footprint within the grazed area, showing that the determination of small emissions with miniDOAS from grazed systems is possible. A more detailed analysis of these structures, including a more comprehensive estimation of NH₃ emissions due to the excrements of the grazing cows, is beyond the scope of this paper and will be presented elsewhere.

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3.3.3 Gradients and emissions after slurry field-application

During the Witzwil experiment (W2) miniDOAS was employed to measure horizontal NH₃ gradients following the application of cattle slurry to an experimental plot of 1250 m². 395 Application of slurry causes strong emission peaks that typically decrease with half times between less than one to several hours (Häni et al., 2016; Sintermann et al., 2011a; Sommer et al., 2003). Figure 8 shows the horizontal gradients developing between up- and downwind miniDOAS. The according gradient was elevated by up to 800 µg m⁻³ (1 min averages), featuring the characteristic quick decline approximated by a bi-exponential decay over time

400 (Sintermann et al., 2011a). The gradients were used for emission determination based on inverse dispersion modelling (compare Loubet et al., 2010) with a bLS model (Flesch et al., 2004). Cumulated emissions compare excellently with those derived from impinger concentration measurements in conjunction with bLS as well as with an integrated horizontal flux (IHF) approach (Denmead, 1995). Details of this experiment are described in Häni et al. 405 (2016).

3.3.4 Artificial source and volcano plume

As part of the trials at the Witzwil site, the emission of an artificial NH₃ source of 20 m diameter was measured with four miniDOAS systems: three were put downwind in a vertical profile (W3, Sect. 2.3) and one system upwind of the source. The extraordinary and 410 unplanned passage of a huge SO₂ plume, caused by the eruption of the Icelandic Bárðarbunga volcano (Gauthier et al., 2015; Umweltbundesamt, 2014), occurred at the same time as the artificial source was in operation. The SO₂ concentrations by the miniDOAS agreed well with those recorded by the monitoring stations of the Swiss national air pollution network (Fig. 9).

415 The time shift between different stations reflects the passage of the plume over Switzerland. This is indirect evidence that the SO₂ calibration of the miniDOAS system was reliable.





Figure 9 shows the concentrations of NH_3 and SO_2 until 10:00, the period of the 22^{nd} September before the SO_2 plume arrived. During this period only two systems were in operation. The NH_3 concentration shows an emission profile. Figure 9 also shows the passage

420 of the SO₂ plume combined with the artificial release of NH₃. The release caused a strong emission gradient whereas the SO₂ concentrations were equal within the miniDOAS precision, or even tended towards a deposition profile.

This episode provides an additional field test for NH_3 -SO₂-NO cross-interference. Figure 9 demonstrates how the determination of NH_3 and SO₂ does not interfere with one another.

425 While NO seemed to show no apparent vertical emission or deposition profile, it looks like deviations in the NO signal between instruments and over time occurred primarily due to the presence of large amounts of SO₂. Also, a slight interference of NH₃ on NO was observed for one of the three instruments, consistent with the findings presented in Sect. 3.2.2. The standard error-range as a result of the ARMA fit, however, well reflected this uncertainty.

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4 Conclusions and outlook

We have presented a further development of the miniDOAS by Volten et al. (2012) into a stand-alone, field-applicable system for NH₃ measurements, combined with NO and SO₂ determination. Furthermore, we developed a DOAS data evaluation procedure involving robust baseline local regression and fitting with an ARMA regression model. This guarantees the linearity of the spectral evaluation over a wide concentration range. The instrument and its performance have been tested and evaluated in field campaigns. This miniDOAS can be used

for a wide range of trials, such as flux measurements with approaches based upon horizontal or vertical concentration gradients. We have highlighted examples of miniDOAS application

- 440 for such trials. The involved micrometeorological flux methods can comprise mass balance, aerodynamic gradient (see Wichink Kruit et al., 2010) and inverse dispersion modelling techniques (e.g. this study). The fact that miniDOAS determines SO₂ and NO alongside NH₃ might be used in emission studies relying on the tracer-ratio method, where NO or SO₂ could be released with known source strength in order to explore the concentration-to-emission
- relationship and relate that to the miniDOAS NH₃ measurement. For NH₃, the instrument has a precision down to the LOD of 0.2 μ g m⁻³ (against c_{0i}) or 1.4 %. Concentration differences between approximately 0.3 μ g m⁻³ NH₃ (upper estimate of 95 % confidence) up to more than 1000 μ g m⁻³ can be resolved, which renders the miniDOAS an exceptionally flexible instrument available for studies investigating strong NH₃ emissions as well as small fluxes.





- 450 Concentration gradient measurements involving two or more miniDOAS instruments have to be used for flux measurement approaches. Then, the determination of the gradient requires precision but not accuracy if c_0 was defined under identical conditions. The low LOD might allow for bi-directional flux monitoring based on the aerodynamic gradient method (Flechard and Fowler, 1998), e.g. over semi-natural and natural ecosystems. A typical setup would
- 455 involve miniDOAS measurements at two heights, e.g. at 0.5 and 2 m over a short canopy. Characteristic turbulent transfer velocities between those two heights are in the order of 0.014 to 0.087 m s⁻¹ (calculated under neutral stratification, $u_* = 0.05$ to 0.3 m s⁻¹, $z_0 = 1$ to 2 cm). A minimum resolvable NH₃ concentration gradient of 0.3 µg m⁻³ would then yield a flux LOD of 4 to 26 ng m⁻² s⁻¹ deposition or emission. Such measurements would help to improve the
- 460 characterisation of compensation points (Massad et al., 2010). One major advantage of the open path miniDOAS over closed-path systems and filter packs is the inlet-free in-situ determination of ambient concentrations. This makes the NH₃ measurement insensitive against NH₃ volatilisation from aerosol particles (e.g. at inlet filters) or the interaction of gaseous NH₃ with water molecules and any kind of instrumental surface (Sintermann et al.,
- 465 2011b and references therein). The miniDOAS offers full potential for source appointments where strong NH₃ dynamics have to be considered. Additional instrumental improvements could include an optimisation of the light signal capture in terms of stability and stray-light minimisation within the spectrometer. A better stray-light performance and higher wavelength pixel-resolution over the considered UV window (e.g. using an optimised grating) will further
- 470 enhance miniDOAS performance.

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585 Tables

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Table 1: Overview of experimental trials as examples for miniDOAS application.

-	Experiment:	W2	W3	R1	R3	HAFL
590	Site	Witzwil, CH; 46°59'06''N, 7°04'32''E, grassland	Witzwil, CH; 46°59'06''N, 7°04'32''E, grassland with dead canopy	Rennes, FR; 48°07'02''N, 1°47'50''E , paddock before grazing	Rennes, FR; 48°07'02''N, 1°47'50''E, paddock during grazing	auditorium HAFL closed room with passive ventilation
	Measurement period	1.9 - 2.9. 2014	22.9. 2014	7.5 11.5. 2015	18.5 19.5. 2015	11.6 12.6. 2015
595	Subject of investigation	NH ₃ emissions from cattle slurry application	NH ₃ emissions from release- grid; Bárdarbunga SO ₂ plume	miniDOAS concentration inter- comparison	NH ₃ emissions from paddock grazed by dairy cattle	miniDOAS & impinger inter- comparison at a high concentration level
600	Approach	horizontal concentration gradients + bLS & IHF	horizontal & vertical concentration gradients+ bLS & mass balance method	miniDOAS & alpha samplers	horizontal gradients + bLS	12 Impingers parallel on miniDOAS path
	$L_{\text{path}}\left(\mathbf{m}\right)$	80	76	60	60	60
	Measurement height (m)	1.25	0.4, 1.22, 3	1.25	1.25	1.25





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Table 2: Comparison between impinger systems and the miniDOAS systems S2 and S5 at the HAFL auditorium

Time	Impinger (µg m ⁻³)	Impinger standard error (µg m ⁻³)	miniDOAS (mean value S2 and S5) (µg m ⁻³)	miniDOAS standard deviation (µg m ⁻³)
11.06.15 12:30 - 16:00	75.0	6.6	71.4	8.6
11.06.15 16:00 - 18:00	77.9	4.7	73.6	6.7
11.06.15 18:00 - 20:00	84.0	2.4	83.9	6.8
11.06.15 20:00 - 22:00	91.7	2.2	94.1	2.5
11.06.15 22:00 - 24:00	97.0	1.6	97.8	1.1
12.06.15 00:00 - 02:00	98.7	1.8	99.6	0.8
12.06.15 02:00 - 04:00	101.5	2.7	102.5	1.2

Figures



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Figure 1: Swiss miniDOAS scheme and field setup of three instruments (retro-reflectors and shutter not shown).







Figure 2: miniDOAS calibration and literature-derived absorption cross-sections, including example data evaluation steps; a): absorption cross-section by Cheng et al. (2006) including convolution to the CCD pixel resolution, b): differential absorption cross-sections (obtained from *Ĩ_{div}* by instrument S5 calibration, performed with a cuvette concentration of 191.9 mg NH₃ m⁻³) and compared to literature values for NH₃ as shown in a), c): spectrum *I*₀ and *I* including simulated absorption by NH₃ alone and all three gas species combined, d): different evaluation steps for *I_{div}* using the combined spectrum from c).











Figure 4: UV-spectra from concentration evaluation for three cases: a) a relatively high NH₃ concentration (10.26 μg m⁻³), b) a small concentration (0.39 μg m⁻³) and c) a concentration value close to zero; three different evaluation steps are shown: *I*_{div}, DOAS differential optical density and residuum spectrum; the difference between ARMA regression and OLS regression is also highlighted; residuals from the OLS fit exhibit significant degrees of autocorrelation down to lags of 7, 5, 4 pixel, for cases a), b), c), respectively, whereas the ARMA model fit successfully considered this auto-correlation.







Figure 5: Concentration inter-comparison of two miniDOAS instruments (S2, S5) operated in

640 parallel during experiment R1; a) time series ($c_{0,NH3} = 1.92 \ \mu g \ m^{-3}$ was added, determined by parallel measurements with three alpha samplers, distributed along the DOAS path; shaded areas show the concentration standard error-range for 30 min time resolution), b) regression (Deming method; Linnet, 1990) of 5 min averages (n = 1086; without $c_{0,NH3}$); slope and intercept are given with 95% confidence interval limits; crosses in the scatterplot reflect the range of calculated concentration ± standard error).







Figure 6: NH₃ standard error vs. NH₃ concentration (instruments S2 and S5); coloured circles represent 1 min averages, gray circles display concentration differences between instrument
S2 and S5 for half hourly means (Δ₃₀= |S2 - S5|) of the individual 1 min values; regression was carried out with the Deming method (Linnet, 1990).



Figure 7: Horizontal NH₃ gradients and derived emissions from grazing experiment R2 (Table 1); black/grey open symbols show the period without cattle on the investigated pasture, black/grey filled symbols highlight the period with cattle grazing on subplot or the entire field (see Fig. S1, Supplement), red symbols show emissions; concentrations were calculated like in experiment R1; gradient uncertainty range (grey lines) represents the maximum limit of 95 % confidence; the grey band indicates $0 \pm 0.2 \ \mu g \ m^{-3}$ (LOD); the data gap was caused by power supply interruption and translocation of instruments.







Figure 8: Horizontal NH₃ gradients by miniDOAS and cumulated NH₃ emissions (coloured) caused by slurry application to grassland (W2, Table 1); emissions were determined by miniDOAS/bLS and impinger/bLS as well as impinger/IHF (see Sect. 2.4 and Häni et al., 2016); gradient uncertainty range (grey) represents the upper limit of 95 % confidence.







Figure 9: Episode of NH₃, SO₂ and NO concentrations during NH₃ gas release experiment (W4, Table 1) coinciding with a SO₂ peak due to the passage of the plume from the Icelandic Bárðarbunga volcano (Gauthier et al., 2015; Umweltbundesamt, 2014); miniDOAS

670 Bárðarbunga volcano (Gauthier et al., 2015; Umweltbundesamt, 2014); miniDOAS concentrations (coloured) are shown as 5 min running mean ± standard error (*c*_{0i} not included; data gaps from the topmost miniDOAS instrument result from low light due to software crashes); in grey: concentrations from the Swiss air quality monitoring network (www.empa.ch/nabel).

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