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MAX-DOAS observations of the total atmospheric water vapour column and comparison with independent observations

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Abstract

We developed an algorithm for the retrieval of the atmospheric water vapour column from Multi-AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) observations in the yellow and red spectral range. The retrieval is based on the so called geometric approximation and does not depend on a-priori information, extensive radiative transfer simulations, or the construction of large look-up tables. Disturbances of the radiative transfer due to aerosols and clouds are simply corrected using the simultaneously measured absorptions of the oxygen dimer, O_4 . We applied our algorithm

- to MAX-DOAS observations made at the Max Planck Institute for Chemistry in Mainz, Germany, from March to August 2011 and compared the results to independent observations. Good agreement with Aerosol Robotic Network (AERONET) and European Centre for Medium-Range Weather Forecasting (ECMWF) H₂O vertical column densities (VCDs) is found, while the agreement with satellite observations is less good, most probably caused by the shielding effect of clouds for the satellite observations. Good
- ¹⁵ agreement is also found with near-surface in-situ observations, and it was possible to derive average daily H₂O layer heights (between 1.5 km and 3 km). MAX-DOAS measurements use cheap and simple instrumentation and can be run automatically. One important advantage of our algorithm is that the H₂O VCD can be retrieved even under cloudy conditions (except clouds with very high optical thickness).

20 1 Introduction

Water vapour is the most important natural greenhouse gas. Its atmospheric concentration increases strongly with temperature and the resulting increase in the atmospheric water vapour content is expected to further amplify climate change (water vapour feedback, see, e.g. Held and Soden, 2000, and references therein, Solomon et al., 2007). Water vapour is also important for meridional transport of latent heat, it determines the

²⁵ Water vapour is also important for meridional transport of latent heat, it determines the global distribution of clouds, and it plays an important role in many chemical reactions.





In contrast to most other greenhouse gases, the atmospheric water vapour distribution is highly variable. Thus measurements of atmospheric water vapour on various spatial and temporal scales are important.

There is a large variety of in-situ and remote sensing techniques for the measure-⁵ ment of water vapour that can be operated from different platforms (ground based, airborne, space borne). From these observations the water vapour concentration, altitude profiles, or (partial) columns can be retrieved. Here we present a new method for analysing the vertically integrated water vapour concentration, the so-called vertical column density (VCD), from Multi-AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) observations. The H₂O VCD is often referred to as total column precipitable water (expressed e.g. as g cm⁻²) in the meteorological literature: 1 g cm⁻² equals roughly 3.3 × 10²² molecules cm⁻².

MAX-DOAS instruments observe scattered sun light at various slant elevation angles and allow the retrieval of concentration profiles or column densities of several tropospheric trace gases, e.g. NO₂, HCHO or BrO (e.g. Hönninger et al., 2002; Van Roozendael et al., 2003; Wittrock et al., 2004; Wagner et al., 2004; Brinksma et al., 2008 and references therein). The first retrievals of H₂O concentration profiles were recently presented by Irie et al. (2011), using the H₂O absorption band at 506 nm. Here we follow a different strategy: our main aim is a simple and stable algorithm that does

- not depend on a-priori and external information. We use the H₂O absorption bands in the yellow and red spectral range, which are about one order of magnitude larger than those at 506 nm. Instead of retrieving a vertical concentration profile, our algorithm yields the integrated atmospheric column density. The information content of a column density is of course less than that of a vertical profile. However, as shown below, the
- H₂O VCD is highly correlated with the surface concentration. Furthermore, the H₂O VCD is a very useful quantity, e.g. for meteorological applications and the validation of satellite observations.





2 Instrument and data analysis

2.1 Instrument and measurement conditions

MAX-DOAS observations at the Max Planck Institute for Chemistry (MPIC) in Mainz, Germany (50.0° N, 8.27° E) were carried out from 19 March to 30 August 2011. The period of measurements covered different meteorological conditions, with temperatures 5 ranging from about 0 to 35°C and thus largely varying atmospheric H₂O VCDs. The measurements were performed using a Mini-MAX-DOAS instrument (Bobrowski et al., 2003; Ibrahim et al., 2010) covering the spectral range from 500 nm to 800 nm with a spectral resolution of about 1 nm (FWHM). Measurements were carried out between sunrise and sunset using an automated routine (based on the DOASIS software, see 10 Kraus, 2006) with typical integration times of about 1 min. Since the instrument was mounted directly in front of a window (see Fig. 1), the viewing angles were restricted by the roof (and also by opposite buildings) to a range between 15° and 70° (the selected sequence of elevation angles was 15°, 20°, 30°, 60°, 70°). The azimuth angle of the telescope was 74° with respect to north. Besides instrumental problems on several individual days and during a longer period between 5 May and 16 June, the instrument was operated almost continuously; in total more than 40 000 individual spectra were recorded.

2.2 Spectral analysis

- The measured spectra are analysed using the DOAS method (Platt and Stutz, 2008). Two separate wavelength intervals with relatively strong H₂O absorption bands were selected:
 - a. 608–680 nm. Besides the H_2O absorption, it also contains absorption bands of the oxygen molecule (O_2) and the oxygen dimer (O_4).
- b. 543–620 nm. Besides the H_2O absorption it also contains an O_4 absorption band.





In addition to the reference spectra for these species and ozone (see Table 1), a Fraunhofer reference spectrum, a Ring spectrum (calculated from the Fraunhofer reference spectrum) and a low order polynomial were included in the spectral analysis (using the WinDOAS software, Fayt and van Roozendael, 2001). A spectrum measured at 70° elevation angle on 26 March 2011 at 13:13 (SZA = 52.3°) was used as Fraunhofer reference spectrum for the whole experiment. The wavelength calibration was performed

based on a high resolution solar spectrum (Kurucz et al., 1984). Typical fit results are shown in Fig. 2. The output of the spectral analysis is the slant column density (SCD), which is the in-

tegrated trace gas concentration along the effective light path through the atmosphere. Besides H₂O, the SCDs of O₂ and O₄ are also used for further processing (see below). From the spectral analysis, the uncertainty of the retrieved SCDs are also determined; for the SCDs of H₂O, O₂, and O₄ it is typically < 10 %.

Since a measured spectrum is used as Fraunhofer reference, the retrieved results represent the difference of the SCDs between the measurement at low elevation angle α and the Fraunhofer reference spectrum, the so called differential SCD or DSCD:

 $\mathsf{DSCD}_{\alpha} = \mathsf{SCD}_{\alpha} - \mathsf{SCD}_{\mathsf{Fraunhofer}}$

Because H₂O and O₄ are retrieved in both spectral ranges, a decision had to be made
 which analysis should be used for further processing. To answer this question, we compared the results of both spectral ranges. They are very similar, but small differences were also found, especially with respect to the scatter of subsequent data points on clear days. For such conditions, it is expected that the diurnal variation of the retrieved DSCDs should show a smooth behaviour. The results for one selected clear day are
 shown in Fig. 3. For H₂O less scatter is found for the wavelength interval 608–680 nm. In contrast, for O₄ less scatter is found for the wavelength interval 543–620 nm. The

respective retrieval results are used in the following.



(1)



2.3 Conversion to the atmospheric vertical column density (VCD)

From the retrieved DSCDs, the vertically integrated trace gas concentration, the so called vertical column density (VCD) is calculated according to the following formula (Wagner et al., 2010):

$$5 \quad \text{VCD}_{\alpha,\beta} = \frac{\text{DSCD}_{\alpha} - \text{DSCD}_{\beta}}{\text{AMF}_{\alpha} - \text{AMF}_{\beta}}$$

Here $DSCD_{\alpha}$ and $DSCD_{\beta}$ refer to the retrieved DSCDs for low (α) and high (β) elevation angles (Eq. 1) of an individual elevation sequence. AMF_{α} and AMF_{β} are the respective air mass factors (AMF). The air mass factor describes the ratio between the SCD and VCD:

10 AMF = SCD/VCD

15

The AMFs used in this study are calculated by the so called geometric approximation (Brinksma et al., 2008; Zieger et al., 2011). For MAX-DOAS observations of tropospheric trace gases, the geometric approximation of the AMF is determined from simple geometric considerations:

 $AMF_{aeometric} = 1/sin(\alpha)$

The geometric approximation is adequate for measurements, for which the effective atmospheric light path through the trace gas layer can be well described by a straight

²⁰ line. This is typically fulfilled for measurements at large wavelengths and for low aerosol loads. While the first condition is fulfilled for our MAX-DOAS measurements, the effect of aerosol scattering can potentially have a strong influence on some days (for more details see Sect. 2.4).

The VCDs of H₂O and O₄ retrieved from the 6 different combinations of low (15°, 20°, 30°) and high elevation angles (60°, 70°) are shown in Fig. 3. Both for H₂O and O₄,

(2)

(3)

(4)



the VCDs for the different combinations show similar values. Nevertheless, for further processing of the H_2O VCDs we used the combination of 20° and 70°, because the resulting VCDs typically showed the lowest scatter. Of course, for future studies using different azimuth and elevation angles, other combinations of elevation angles might 5 be favourable.

Note that the O_4 VCD is usually expressed in the unit [molec² cm⁻⁵], because the equilibrium constant between O_4 and $(O_2)_2$ is not known. Therefore the O_4 VCD usually refers to the integrated quadratic O₂ concentration (see also Greenblatt et al., 1990).

Since the H₂O absorption fine structure is not fully resolved by our measurements, the H₂O SCDs derived from the spectral analysis are not a linear function of the true at-10 mospheric H₂O SCDs. We correct this "saturation effect" by simulating the non-linearity as described in Wagner et al. (2003). In the following, the corrected H₂O DSCDs are used for the determination of the H₂O VCD (Eq. 2). It should, however, be noted that for the H₂O VCDs retrieved from our observations, the saturation effect is typically well below 10% (see bottom panel of Fig. 3).

15

2.4 Radiative transfer simulations

In this section we investigate the validity of the geometric approximation for our MAX-DOAS retrievals. For this purpose we performed radiative transfer simulations using the Monte-Carlo-model MCARTIM (Deutschmann et al., 2011).

- For all simulations, we used a H_2O profile with a scale height of 2 km and an O_4 20 profile with a scale height of 4 km. The assumption of a scale height of 2 km for the H_2O profile is confirmed by the comparison of the retrieved H₂O VCDs and simultaneous in-situ measurements of the H₂O concentration at the surface (see Sect. 3.7). To study the effect of aerosols, we assumed different aerosol extinction profiles and calculated
- the respective AMFs of H_2O and O_4 for various combinations of elevation angles (EA), 25 relative azimuth angles (RAZI) and solar zenith angles (SZA). The results for a SZA of 50° are shown in Fig. 4 (similar results are found for other SZA). In the upper part of the figure, the AMFs simulated for EA of 20° and 70° are shown. The bottom part



shows the ratio of the AMF differences (20° minus 70°) between the radiative transfer simulations and the geometric approximation. Deviations of this ratio from unity reflect systematic errors caused by the geometric approximation.

For aerosol-free conditions, the VCDs retrieved using the geometric approximation
 underestimate the true atmospheric VCDs by about 10% and 30% for H₂O and O₄, respectively. However, in the presence of aerosol scattering, the underestimation can become much stronger, especially for small relative azimuth angles. This underestimation is caused by the additional aerosol scattering which leads to a decrease of the direct light path through the trace gas layer and thus to a reduced AMF for low elevation angles. Because of the higher atmospheric scale height, this effect has a stronger influence on the O₄ AMFs.

2.5 Correction using observations of the oxygen dimer O₄

20

As demonstrated in the previous section, the errors of the H_2O VCD due to the geometric approximation can be quite large, especially for high aerosol loads and for mea-

¹⁵ surements made at small relative azimuth angles (in our measurements, small relative azimuth angles occur in late morning).

One possibility for correcting these errors would be to use appropriate AMFs derived from radiative transfer simulations instead of AMFs calculated by the geometric approximation. However, such calculations are complicated because typically the atmospheric aerosol extinction profile is not known, and clouds also strongly affect the atmospheric radiative transfer.

Because of these difficulties, we followed a different approach: we continued using the geometric approximation, but in order to correct for the effects of aerosols (and clouds) we used the simultaneously retrieved O_4 VCDs (also based on the geometric approximation). Since the atmospheric O_4 VCD is almost constant (small changes of

²⁵ approximation). Since the atmospheric O_4 VCD is almost constant (small changes of a few percent are caused by variations of temperature and pressure), deviations of the retrieved O_4 VCD indicate deviations of the geometric approximation from the true atmospheric AMFs.





We calculated a correction factor F_{corr} containing two terms:

- The first term is the ratio of the retrieved O₄ VCD and the true atmospheric O₄ VCD (for our measurement location we calculated a O₄ VCD of 1.3×10^{40} molec² cm⁻⁵ from typical temperature and pressure profiles).
- The second term accounts for the general difference in sensitivity of MAX-DOAS retrievals using the geometric approximation for H_2O and O_4 . For low aerosol loads and/or large relative azimuth angles, the ratio of the respective sensitivities for H_2O and O_4 (see Fig. 5) is about 1.25. Thus for the correction factor F_{corr} we obtain

$$F_{\rm corr} = 1.25 \cdot \frac{O_4 \, \rm VCD_{\rm geometric}}{O_4 \, \rm VCD_{\rm true}}$$

The final H_2O VCD product from our MAX-DOAS observations is determined from the H_2O VCD_{geometric} (Eq. 2) retrieved using the geometric approximation by multiplication with this correction factor:

$$H_2O VCD = F_{corr} \cdot H_2O VCD_{geometric}$$

For most cases shown in Figs. 4 and 5, the H₂O VCDs retrieved in this way will be close to the true atmospheric H₂O VCDs. However, for observations with high aerosol load (especially for small relative azimuth angles), large deviations from the true atmospheric H₂O VCD can occur (see Fig. 5). To avoid such errors in the final H₂O data
set, we excluded all measurements, for which the difference of the retrieved O₄ VCD from the true O₄ VCD exceeded ±30 %. Using this criterion, not only measurements affected by high aerosol loads, but also by clouds (see below) are identified and removed. Of course, the threshold of 30 % is chosen rather arbitrarily (from visible inspection of measurements affected by cloud and aerosol effects). Future studies might use more sophisticated selection criteria.



(5)

(6)



From all measurements (elevation sequences), 54 % fulfilled the O_4 criterium while 46 % showed deviations > 30 % and were omitted. Here it is interesting to note that the fraction of skipped measurements is very similar for measurements under clear skies and thin clouds (for details of the cloud classification see Sect. 2.6), while most of the seasurements under "thick" clouds are removed by this criterion.

The processing steps described in this section are illustrated for one clear and one cloudy day in Fig. 6. On the clear day, strong deviations from the geometric approximation are present for the morning observations (made at small relative azimuth angles). On the cloudy day, strong deviations from the geometric approximation occur, which are caused by the diffusing screen effect and the multiple scattering effect of clouds

- ¹⁰ are caused by the diffusing screen effect and the multiple scattering effect of clouds (for details see Sect. 2.6). After correction using the measured O_4 VCDs (Eq. 6), part of these deviations is corrected. In the final H_2O VCD data set (bottom panel of Fig. 6) the observations not fulfilling the O_4 criterion are removed, and the remaining data show a consistent diurnal cycle.
- In Fig. 7 the daily averaged H_2O VCDs during the whole measurement period are shown. The blue symbols show measurements that fulfil the O_4 criterion; the red symbols show measurements that do not fulfil the O_4 criterion. As expected, the latter show much larger scatter than the measurements that fulfil the O_4 criterion.

2.6 Effects of clouds

Like aerosols, clouds can also strongly affect the atmospheric radiative transfer and thus the MAX-DOAS observations. Two main effects are especially important for MAX-DOAS observations: the so called diffusing screen effect and the multiple scattering effect (see Wagner et al., 2011).

The diffusion screen effect describes the fact that under cloudy skies a substantial fraction of the photons received by the MAX-DOAS instrument has been directly scattered from the cloud bottom (instead from air molecules). This effect is especially important at large wavelengths and leads to both, a slight increase of the sensitivity for





trace gases below the cloud, and a loss of sensitivity for trace gases above the cloud bottom.

Thus for trace gases like H_2O and O_4 , for which a considerable fraction of the total atmospheric column usually resides above the cloud bottom, the diffusing screen ef-

- ⁵ fect typically leads to an underestimation of the true atmospheric column density. The strength of this underestimation depends on the altitude of the cloud bottom and is in general larger for O_4 than for H_2O because of the larger scale height of O_4 . In Fig. 8 results from radiative transfer simulations of the diffusing screen effect for H_2O and O_4 are shown (similar to the simulations of the aerosol effects shown in Figs. 4 and 5).
- ¹⁰ These simulations are performed for an assumed cloud with vertical thickness of 1 km and an optical thickness of 5. The cloud bottom is assumed to be at 3, 6, or 10 km. In the upper row of Fig. 8 the ratio of the simulated AMF differences ($20^{\circ}-70^{\circ}$) and those from the geometric approximation is shown. Values < 1 indicate an underestimation and > 1 an overestimation of the true atmospheric VCDs. For H₂O only low clouds
- ¹⁵ lead to a systematic underestimation of the true VCD. For high clouds the increase of the direct light path below the cloud is the dominant effect and even causes a slight overestimation. In contrast, for O₄, low and mid level clouds cause a systematic underestimation of the true O₄ VCD of up to 50 %. The bottom row of Fig. 8 shows the ratio of the deviations of geometric approximations for H₂O and O₄ (similar to Fig. 5). For all scenarios, values > 1 are found indicating that the diffusing screen effect leads to an
 - overestimation of the H_2O VCD retrieved by Eq. (6).

Multiple scattering becomes important for vertically extended clouds with large optical depth. Under such conditions, the light path lengths inside the clouds can become very long (up to more than 100 km, e.g. Erle et al., 1995; Wagner et al., 1998; Winterreth et al., 1990). Since a substantial fraction of H O and O, is turisally present

²⁵ terrath et al., 1999). Since a substantial fraction of H₂O and O₄ is typically present inside the cloud, the respective absorptions can become strongly increased compared to clear sky conditions. Especially in the case of rapidly varying cloud cover, the multiple scattering effect can lead to strong positive or negative deviations of the retrieved H₂O VCD from the true atmospheric VCDs. Examples of both cloud effects (diffusing





screen effect and multiple scattering effect) are shown in Fig. 9 (details will be discussed in Sect. 2.6.1). The influence of clouds on the VCDs of H_2O and O_4 can also be seen in Fig. 6 (right panel).

Characterisation of cloud properties during the measurement period

- ⁵ We performed a simple characterisation of the influence of clouds based on the measured MAX-DOAS spectra. The results of this characterisation are verified using satellite images from the MODIS instrument (from the AERONET Data synergy tool, http://aeronet.gsfc.nasa.gov/cgi-bin/bamgomas_interactive). Three categories are distinguished (see also Wagner et al., 2011):
- 10 a. clear skies
 - b. thin clouds (main effect is the diffusing screen effect)
 - c. thick clouds (main effect is the multiple scattering effect)

To assign a given measurement to one of the three categories, we used the following quantities: the retrieved DSCDs of H₂O, O₄, and O₂, the measured (relative) radiance, and a colour index (here we use the ratio of the measured radiances at 510 nm and 780 nm). Note that we slightly modified the procedure described in Wagner et al. (2011), because in this study the MAX-DOAS observations were made at another set of elevation angles and for a different spectral range.

- Clear sky conditions are indicated by a smooth temporal variation of the measured radiance, the colour index, as well as the DSCDs of H_2O , O_4 , and O_2 . One example for a (mostly) clear day (23 March 2011) is shown in Fig. 9 (left). While the diurnal variations of the DSCDs of H_2O and O_4 still show some scatter, the radiance, the colour index, and the O_2 DSCDs show a rather smooth variation (except towards the end of the day). At the bottom of Fig. 9 satellite images from the MODIS instrument are
- ²⁵ shown, indicating mostly clear skies around Mainz (blue circle) for 23 March 2011.





In the right part of Fig. 9 an example of a mostly cloudy day is shown (27 April 2011). Between about 09:00 and 15:00 UTC the DSCDs of H_2O , O_4 and O_2 as well as the radiance and the colour index show rapid temporal variations indicating the presence of "thin" clouds (diffusing screen effect). Around 15:30 UTC a strong increase is found

⁵ for the measured DSCDs, indicating strongly enhanced multiple scattering caused by "thick" clouds. The presence of an optically thick cloud is confirmed by the minimum of the measured radiance. Also in the MODIS image on that day an extended cloud system is seen.

According to these findings, we categorised measurements (by visual inspection) as 10 cloudy (thin or thick clouds), for which the measured radiance, the colour index and the DSCDs of H_2O , O_4 and O_2 show rapid temporal variations. If at least the radiance and the colour index show a smooth temporal variation, the measurements are categorised cloud free. If the measured DSCDs of H_2O , O_4 and O_2 show a strong enhancement compared to clear sky conditions, the measurement is categorised as being affected 15 by a "thick" cloud (multiple scattering effect).

According to this characterisation scheme, 20% of all measurements were made under clear sky conditions and 74% and 6% were made under thin and thick clouds, respectively. While the first part of the time series (March–May) had many (partly) clear days, the second part (June–August) was mostly cloudy.

20 3 Comparison with independent data sets

In this section, the H_2O VCDs retrieved from the MAX-DOAS observations are compared to other data sets:

- a. H₂O VCDs from the ERA-Interim reanalysis data set of the ECMWF
- b. H₂O VCDs from AERONET measurements also made at MPIC, Mainz
- $_{25}$ c. H₂O VCDs from satellite observations of the GOME-2 instrument on METOP





d. H₂O surface concentrations measured by the air quality network of the federal state of Rhineland-Palatinate in a suburb of Mainz

In the following sub-sections these data sets are briefly described, followed by a comparison of time series and correlation analyses.

5 3.1 ECMWF model data

The H₂O VCD simulation data used in this study are based on the total water column output of the ERA-Interim reanalysis data set (Dee et al., 2011) provided by the ECMWF. We used the output on a regular 0.25/0.25 degree grid for every 6-h model output between March and May 2011. For the comparison, the region between 7.75 and 8.25° E and between 49.75 and 50.25° N was averaged.

3.2 AERONET observations

 H_2O VCDs are retrieved from direct sun radiometry in the 940-nm solar absorption channel employed in the Aerosol Robotic Network (AERONET, http://aeronet.gsfc. nasa.gov/). The Mainz AERONET site at the MPIC is shown at http://aeronet.gsfc. nasa.gov/new_web/photo_db/Mainz.html. Information on the AERONET observational network can be found in Holben et al. (2001). Details on the H₂O retrieval are given e.g. in Schmid et al. (1996) and Smirnov et al. (2004).

In this study we use the Level 2.0 data. Typical integration times are 2 to 15 min. AERONET direct sun measurements are even possible during rather short cloud-free

- 20 periods. Here it is interesting to note that such conditions are often characterised as cloudy by our cloud algorithm (see Sect. 2.6.1), because they are associated with rapid fluctuations of the measured quantities. Since the MAX-DOAS retrieval of the H₂O VCD is based on subsequent observations made at different elevation angles, under partly clear conditions the MAX-DOAS observations are more likely affected by clouds than the direct our AEDONET.
- the direct sun AERONET observations.





3.3 Satellite observations

Several H₂O VCD products retrieved from UV-visible satellite instruments have been developed during the past years (Noël et al., 1999; Casadio et al., 2000; Maurellis et al., 2000; Lang et al., 2003; Wagner et al., 2003). In this study we use the retrieval developed at the University of Heidelberg and the MPIC (Wagner et al., 2003, 2006). Details of this retrieval are given in EUMETSAT (2009) (http://atmos.caf.dlr.de/gome/ product_h2o.html). This retrieval consists of two steps: First the slant column densities of H_2O and O_2 are analysed in the red part of the spectrum (614–682 nm). In a second step the H₂O VCD is derived from the H₂O SCD using a "measured" AMF based on the simultaneously measured O_2 SCD. For the comparison with MAX-DOAS results, 10 observations of the GOME-2 instrument on METOP are used, which cover the location of the MAX-DOAS instrument (EUMETSAT, 2005). GOME-2 has a ground pixel size of $80 \times 40 \text{ km}^2$, global coverage is achieved after 1.5 days. The overpass time of GOME-2 is about 09:30 LT (local time). The satellite data are cloud screened by applying a threshold for the O₂ absorption. It should, however, be noted that in individual cases, 15

the shielding effect of clouds can still be substantial for the atmospheric H_2O column.

3.4 In-situ observations

20

Routine observations of temperature and relative humidity (1 h averages) are performed by the federal state of Rhineland-Palatinate in a suburb of Mainz, about 3.5 km north of the MAX-DOAS instrument (Landesamt für Umwelt, Wasserwirtschaft

- und Gewerbeaufsicht Rheinland-Pfalz, http://www.luft-rlp.de). Using the Clausius-Clapeyron relationship, we calculated the water vapour concentration from both measured quantities. Since these in-situ observations provide the near-surface H₂O concentration and not the H₂O VCD, no direct comparison with the MAX-DOAS results
- ²⁵ is possible. Nevertheless, from the correlation analysis of both quantities, information on the agreement of the relative temporal variation can be obtained (see Sect. 3.6).





In addition, the ratio of the H_2O VCD and the H_2O concentration can be determined which provides information about the H_2O scale height (see Sect. 3.7).

3.5 Comparison of time series

In Fig. 10, the diurnal variation of the H₂O VCDs from the different data sets (MAX-DOAS, AERONET, satellite, ECMWF) is shown for selected days. For the MAX-DOAS data, error bars are also presented, which indicate the relative deviation of the retrieved O₄ VCDs from the true value (see Sect. 2.5). The first day (25 April 2012) was a mainly clear day. The H₂O VCDs retrieved from MAX-DOAS show only little scatter, and good agreement is found between all data sets. The second day (29 April 2012) was a mostly cloudy day, but again little scatter of the MAX-DOAS data and good agreement between

- all data sets is found (also the MAX-DOAS error bars are small). It should be noted that only few AERONET retrievals were possible on that day, because they can only be performed when the sun is visible. The third and fourth days were also mainly cloud covered. However, on these days the scatter of the MAX-DOAS data is larger than on
- ¹⁵ the two first days, indicating that the cloud effects and/or their temporal variation were stronger. The increased scatter of the MAX-DOAS data is well reflected in the larger error bars. This indicates that the deviation of the measured O₄ VCD from the true value is a good measure for the accuracy of the H₂O VCDs retrieved from MAX-DOAS. Also the agreement with the other data sets is worse compared to the first two days.
- ²⁰ In Fig. 11 the time series of daily averaged values of the H₂O VCDs from the different data sets are shown. The first (19 March–4 April) and second part (17 June–30 August) of the measurement time series is displayed in two separate sub-plots. Overall, the agreement of the temporal patterns and the absolute values is good. However, especially for (partly) cloudy days the H₂O VCDs retrieved from satellite observations are
- ²⁵ often lower than from the other data sets. This underestimation is mainly caused by the shielding effects of the atmospheric column below the clouds.





3.6 Correlation analyses of daily average values

In this section, correlation analyses using an orthogonal linear regression (Cantrell, 2008) for daily average values of the different data sets are presented and discussed. Figure 12 presents the results for MAX-DOAS and ECMWF data. Overall good agree-

- ⁵ ment is found with a coefficient of determination (r^2) of 0.92 and a slope of 1.06. Similar results are obtained if only MAX-DOAS observations for clear sky conditions or for thin clouds are considered. For MAX-DOAS observations under thick clouds the agreement is worse ($r^2 = 0.66$).
- In Fig. 13 results for the correlation analyses between MAX-DOAS and AERONET data are shown. Again, overall good agreement is found with a coefficient of determination (r^2) of 0.80 and a slope of 1.07. If only MAX-DOAS data for clear sky conditions are considered, a better correlation ($r^2 = 0.90$) is found, and if only MAX-DOAS data under thin clouds are considered, a slightly worse correlation ($r^2 = 0.77$) is found. These findings are probably related to the fact that the AERONET H₂O VCDs are retrieved from
- direct sunlight, which is not visible for cloudy conditions. For MAX-DOAS observations under thick clouds, only few coincident data pairs are available and the correlation is worse ($r^2 = 0.47$).

In Fig. 14 results for the correlation analyses between MAX-DOAS and satellite data are shown. Compared to the previous comparisons, the correlation is worse ($r^2 = 0.53$).

- ²⁰ This can mainly be attributed to the strong influence of clouds on the satellite data. Note that the satellite criterion for clear sky observations also includes measurements with small, but obviously not negligible cloud influence. If clear sky observations are selected according to the more strict MAX-DOAS cloud determination scheme, the agreement improves ($r^2 = 0.71$).
- ²⁵ In Fig. 15 results for the correlation analyses between the H₂O VCDs from MAX-DOAS and the H₂O concentration measured at the surface are shown. Although different quantities are compared, a linear correlation can in principle be expected, because the overall shape of the water vapour concentration profile is mainly determined by the





Clausius-Clapeyron relationship and the atmospheric lapse rate. This expectation is confirmed by the rather good correlation between both data sets ($r^2 = 0.84$). Similar agreement is found for MAX-DOAS observations under clear skies and thin clouds. As in the previous examples, worse correlation is found for thick clouds ($r^2 = 0.54$).

5 Correlation analyses between the external data sets

Besides the correlation analyses between MAX-DOAS observations and the external data sets, correlation analyses between the different external data sets were also performed. The results are summarised in Table 2. Very good correlation between AERONET and ECMWF ($r^2 = 0.93$) as well as ECMWF and in situ data ($r^2 = 0.90$) is found. For the comparison of ECMWF and satellite data the correlation is worse ($r^2 = 0.70$). However, if only clear sky measurements (according to the MAX-DOAS observations) are selected, the correlation between ECMWF and satellite data improves again ($r^2 = 0.81$), indicating that a substantial fraction of the satellite observations is affected by cloud shielding.

15 3.7 Determination of H₂O layer height

From the MAX-DOAS H_2O VCDs and the H_2O concentration [H_2O] measured at the surface, a layer height can be calculated:

 $L = \frac{\text{VCD}_{\text{H}_2\text{O}}}{[\text{H}_2\text{O}]}$

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This layer height *L* can be interpreted as the scale height (i.e. the altitude at which the
 H₂O concentration has decreased to 1/e of the value at the surface) of an exponentially decreasing concentration. Such an exponential profile is not an unrealistic assumption because of the Clausius-Clapeyron relationship and the decreasing temperature with increasing altitude.



(7)

In Fig. 16 the layer height *L* derived from MAX-DOAS and in situ measurements is shown. In addition, the layer height calculated from the H_2O VCD and the H_2O surface concentration, both taken from the ECMWF model, is also shown. It shows good agreement with the layer height determined from MAX-DOAS and in-situ observations. During the first part of the MAX-DOAS measurements slightly lower values are found

⁵ During the first part of the MAX-DOAS measurements slightly lower values are found (minimum: 1.5 km, maximum: 2.8 km) than during the second part (minimum: 1.5 km, maximum: 3.2 km). The day-to-day variation is typically of the order of about 1 km. The average layer height for all pairs of MAX-DOAS and in-situ measurements is 2.15 km. The respective average value for the ECMWF data is 2.08 km.

10 4 Conclusions

We developed an algorithm for the retrieval of the atmospheric water vapour column density from MAX-DOAS observations in the yellow and red spectral range. There the H₂O absorption is much stronger than at shorter wavelengths, leading to increased sensitivity. Our algorithm is based on measurements from only two elevation angles and thus has the potential to yield a rather high temporal resolution (of the order of minutes or less). The retrieval is based on the application of the simple geometric approximation and does not depend on a-priori information, extensive radiative transfer simulations, or the construction of large look-up tables. Disturbances of the radiative transfer due to aerosols and clouds are simply corrected using the simultaneously measurement errors. In addition to the H₂O retrieval, we also developed a simple cloud characterisation scheme based on quantities derived from the MAX-DOAS observations.

We applied our retrieval scheme to MAX-DOAS observations made at the Max Planck Institute for Chemistry in Mainz, Germany from March to August 2011. MAX-DOAS measurements were performed and analysed for about 40 000 single measurements made on 111 days.





We compared the H_2O VCDs retrieved from the MAX-DOAS observations with independent data sets. In addition to the H_2O VCDs from AERONET measurements, satellite observations, and ECMWF model simulations, H_2O concentrations measured at the surface were also considered. Good agreement with AERONET and ECMWF

- ⁵ H₂O VCDs was found with coefficients of determination (r^2) between 0.77 and 0.92 and regression slopes between 0.90 and 1.09. For the comparison with ECMWF data, the agreement for MAX-DOAS observations under thin clouds and clear sky conditions is very similar. This indicates that our algorithm is well suited for observations under cloudy skies (except optically thick clouds). For the comparison with AERONET data the agreement for observations under clear sky conditions is substantially better than
- for cloudy observations, mainly because AERONET observations are only possible if direct sunlight can be observed.

For the comparison with satellite observations, less good agreement is found (r^2 between 0.53 and 0.77, slopes of the regression lines between 0.99 and 1.25); underestimation of the satellite data can be mainly attributed to the shielding effect of clouds.

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For the comparison with the H_2O concentration measured at the surface good correlation was found (r^2 between 0.79 and 0.88), but a quantitative comparison of the different quantities would require profile information. Nevertheless, from the time series of MAX-DOAS H_2O VCDs and the H_2O surface concentration we derived a characteristic layer height. Typical values are between 1.5 and 3 km, the average value during the whole time series is 2.1 km. Good agreement with layer heights calculated from ECMWF data is found.

MAX-DOAS observations of the H₂O VCD use cheap and simple instrumentation, ²⁵ which can be operated automatically. Our retrieval algorithm is fast and robust and can yield the H₂O VCD and associated uncertainties in near real time, even under cloudy conditions (except for optically thick clouds). In addition to the H₂O VCD, other trace gases (e.g. NO₂) or aerosol properties can in principle be simultaneously retrieved from the MAX-DOAS observations. In the future, MAX-DOAS measurements should use





optimised viewing angles: zenith observations should be included, and small relative azimuth angles should be avoided (the telescope should be directed to the north in the Northern Hemisphere).

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Table 1. Settings used for the spectral analysis.

Spectrum	Source	Preparation								
(A) Analysis in the red spectral range (608–680 nm)										
H ₂ O cross section	HITRAN data base (Rothman et al., 2005)	convolution to match spectral resolution of the instrument								
O ₂ cross section	HITRAN data base (Rothman et al., 2005)	convolution to match spectral resolution of the instrument								
O₄ cross section Ring spectrum	Greenblatt et al. (1990) interpolation calculated from Fraunhofer reference spectrum using the DOASIS software (Kraus, 2006)									
Polynomial of 4th order										
(B) Analysis in the yellow spectral range (543–620 nm)										
H ₂ O cross section	HITRAN data base (Rothman et al., 2005)	convolution to match spectral resolution of the instrument								
O ₂ cross section	HITRAN data base									
	(Rothman et al., 2005)	convolution to match spectral resolution of the instrument								
O_4 cross section	(Rothman et al., 2005) Greenblatt et al. (1990)	convolution to match spectral resolution of the instrument interpolation								
O_4 cross section O_3 cross section	(Rothman et al., 2005) Greenblatt et al. (1990) 221 K, (Burrows et al., 1999)	convolution to match spectral resolution of the instrument interpolation convolution to match spectral resolution of the instrument								
O_4 cross section O_3 cross section Ring spectrum	(Rothman et al., 2005) Greenblatt et al. (1990) 221 K, (Burrows et al., 1999) calculated from Fraunhofer reference spectrum using the DOASIS software (Kraus, 2006)	convolution to match spectral resolution of the instrument interpolation convolution to match spectral resolution of the instrument								



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Table 2. Results of selected correlation analyses between the different external data sets. Also the average ratios of individual data pairs $\langle A/B \rangle$ and the ratio of the averages $\langle A \rangle/\langle B \rangle$ are shown.

Data sets	Quantity	Condition	r ²	Slope	$\langle A/B \rangle$	$\langle A \rangle / \langle B \rangle$
ECMWF versus satellite	H ₂ O VCD	Clear according to satellite	0.70	0.96	1.22	1.05
ECMWF versus satellite	H ₂ O VCD	Clear according to MAX-DOAS	0.81	0.86	1.04	0.90
ECMWF versus satellite	H ₂ O VCD	Cloudy according to satellite	0.40	1.70	1.70	1.51
ECMWF versus AERONET	H ₂ O VCD		0.93	1.03	1.07	1.07
ECMWF versus in-situ	H ₂ O concentration		0.90	1.01	1.01	1.00

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Fig. 1. Instrumental set-up at the Max Planck Institute for Chemistry, Mainz, Germany. A Mini-MAX-DOAS instrument was placed in front of a window. It was protected from rain by the roof of the building. But this roof also restricted the highest possible elevation angle to 70°. The lowest elevation angle (15°) was determined by the height of opposite buildings.





Fig. 2. Typical result of the DOAS fit in both spectral windows. Shown are the cross-sections (red) scaled to the respective absorption in the measured spectrum (black). Observations are from 4 April 2011, 08:28 UTC, for an elevation angle of 15° and a solar zenith angle of 58.3°.



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Fig. 3. DSCDs (**A** and **B**) and VCDs (**C**, **D** and **E**) of H_2O and O_4 retrieved on a clear day (23 March 2011) in the yellow spectral range (left) and red spectral range (right). The VCDs are calculated from different combinations of high and low elevation angles using the geometric approximation. For H_2O a saturation correction (see text) was applied.







Fig. 4. Results of radiative transfer simulations for H_2O (scale height of 2 km, left) and O_4 (scale height of 4 km, right) for different aerosol loads. Top: AMFs for an elevation angle of 20° as function of the relative azimuth angle. Middle: AMFs for an elevation angle of 70° as function of the relative azimuth angle. Bottom: ratio of simulated AMF-differences (20° minus 70°) and those using the geometric approximation. This ratio describes the underestimation of the true VCDs by retrievals based on the geometric approximation. The aerosol layer was assumed to have constant extinction between the surface and 1 km. The solar zenith angle is 50°.







Fig. 5. Ratio of the relative deviation of the geometric approximation for H_2O and O_4 (see Fig. 4 bottom). A value of 1.25 is used to correct the retrieved H_2O VCDs (see text).











Fig. 7. Daily averaged H_2O VCDs derived from MAX-DOAS observations. Blue symbols indicate measurements which fulfil the O_4 criterion; red symbols indicate measurements which do not fulfil the O_4 criterion (see text).













Fig. 9. Diurnal variation of the retrieved DSCDs of H_2O , O_4 and O_2 as well as the measured (relative) radiance and colour index for a mostly clear day (23 March 2011, left) and a mostly cloudy day (27 April 2011, right). In the bottom, satellite images from the MODIS instrument are shown. Note that for the DSCDs of H_2O and O_2 different y-scales for both days are used. The MODIS overpass times are 23 March 2011 at 11:00 LT; 27 April 2011 at 09:55 LT. (AERONET Data synergy tool, http://aeronet.gsfc.nasa.gov/cgi-bin/bamgomas_interactive.)







Fig. 10. Diurnal variation of the H_2O VCD from the different data sets for selected days. The error bars of the MAX-DOAS data indicate the relative deviation of the measured O_4 VCD from the true atmospheric value. On the two cloudy days in the bottom part of the figure the scatter of the MAX-DOAS data is rather large indicating a strong cloud effect and/or rapid variation of the cloud properties. The increased scatter is well represented by the enhanced values of the error bars.













Fig. 12. Correlation analyses of daily average H₂O VCDs from MAX-DOAS and ECMWF data. **(A)** All MAX-DOAS data. **(B)** MAX-DOAS observations for clear sky. **(C)** MAX-DOAS observations for thin clouds. **(D)** MAX-DOAS observations for thick clouds. ECMWF are averages during daytime (06:00, 12:00, 18:00 UTC). The symbols $\langle A/B \rangle$ and $\langle A \rangle/\langle B \rangle$ indicate the average of ratios of individual data pairs and ratio of averages, respectively. All values in units of molec cm⁻².



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Fig. 13. Correlation analyses of daily average H₂O VCDs from MAX-DOAS and AERONET data. **(A)** All MAX-DOAS data. **(B)** MAX-DOAS observations for clear sky. **(C)** MAX-DOAS observations for thin clouds. **(D)** MAX-DOAS observations for thick clouds. The symbols $\langle A/B \rangle$ and $\langle A \rangle / \langle B \rangle$ indicate the average of ratios of individual data pairs and ratio of averages, respectively. All values in units of molec cm⁻².





Fig. 14. Correlation analyses of daily average H₂O VCDs from MAX-DOAS and satellite data. The satellite data include only measurements for mostly clear sky. **(A)** All MAX-DOAS data. **(B)** MAX-DOAS observations for clear sky. **(C)** MAX-DOAS observations for thin clouds. **(D)** MAX-DOAS observations for thick clouds. The symbols $\langle A/B \rangle$ and $\langle A \rangle/\langle B \rangle$ indicate the average of ratios of individual data pairs and ratio of averages, respectively. All values in units of molec cm⁻².







Fig. 15. Correlation analyses of daily average H₂O VCDs from MAX-DOAS and the H₂O concentration measured at the surface. (A) All MAX-DOAS data. (B) MAX-DOAS observations for clear sky. (C) MAX-DOAS observations for thin clouds. (D) MAX-DOAS observations for thick clouds. The symbols $\langle A/B \rangle$ and $\langle A \rangle/\langle B \rangle$ indicate the average of ratios of individual data pairs and ratio of averages, respectively. H₂O concentrations are in molec cm⁻³ and H₂O VCDs in units of molec cm^{-2}







