



Global investigation of the Mg atom and ion layers using SCIAMACHY/Envisat observations between 70 and 150 km altitude and WACCM-Mg model results

M. P. Langowski^{1,2}, C. von Savigny², J. P. Burrows¹, W. Feng^{3,4}, J. M. C. Plane³, D. R. Marsh⁵, D. Janches⁶, M. Sinnhuber⁷, A. C. Aikin⁸, and P. Liebing¹

¹Institute of Environmental Physics (IUP), University of Bremen, Germany

²Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, Germany

³School of Chemistry, University of Leeds, UK

⁴National Centre for Atmospheric Science, University of Leeds, UK

⁵National Center for Atmospheric Research, Boulder, Colorado, USA

⁶Space Weather Lab, GSFC/NASA, USA

⁷Institut für Meteorologie und Klimaforschung – Atmosphärische Spurengase und Fernerkundung, KIT, Karlsruhe, Germany

⁸The Catholic University of America, Washington D.C., USA

Correspondence to: M. Langowski (langowskim@uni-greifswald.de)

Received: 19 December 2013 – Published in Atmos. Chem. Phys. Discuss.: 22 January 2014

Revised: 29 September 2014 – Accepted: 12 November 2014 – Published: 12 January 2015

Abstract. Mg and Mg⁺ concentration fields in the upper mesosphere/lower thermosphere (UMLT) region are retrieved from SCIAMACHY/Envisat limb measurements of Mg and Mg⁺ dayglow emissions using a 2-D tomographic retrieval approach. The time series of monthly mean Mg and Mg⁺ number density and vertical column density in different latitudinal regions are presented. Data from the limb mesosphere–thermosphere mode of SCIAMACHY/Envisat are used, which cover the 50 to 150 km altitude region with a vertical sampling of ≈ 3.3 km and latitudes up to 82°. The high latitudes are not observed in the winter months, because there is no dayglow emission during polar night. The measurements were performed every 14 days from mid-2008 until April 2012. Mg profiles show a peak at around 90 km altitude with a density between 750 cm⁻³ and 1500 cm⁻³. Mg does not show strong seasonal variation at latitudes below 40°. For higher latitudes the density is lower and only in the Northern Hemisphere a seasonal cycle with a summer minimum is observed. The Mg⁺ peak occurs 5–15 km above the neutral Mg peak altitude. These ions have a significant seasonal cycle with a summer maximum in both hemispheres at mid and high latitudes. The strongest seasonal variations

of Mg⁺ are observed at latitudes between 20 and 40° and the density at the peak altitude ranges from 500 cm⁻³ to 4000 cm⁻³. The peak altitude of the ions shows a latitudinal dependence with a maximum at mid latitudes that is up to 10 km higher than the peak altitude at the equator.

The SCIAMACHY measurements are compared to other measurements and WACCM model results. The WACCM results show a significant seasonal variability for Mg with a summer minimum, which is more clearly pronounced than for SCIAMACHY, and globally a higher peak density than the SCIAMACHY results. Although the peak density of both is not in agreement, the vertical column density agrees well, because SCIAMACHY and WACCM profiles have different widths. The agreement between SCIAMACHY and WACCM results is much better for Mg⁺ with both showing the same seasonality and similar peak density. However, there are also minor differences, e.g. WACCM showing a nearly constant altitude of the Mg⁺ layer's peak density for all latitudes and seasons.

1 Introduction

The amount of meteoric mass deposited daily on the Earth upper atmosphere is estimated to range from 2 to 300 tons (see, e.g. Table 1 of Plane, 2012, and references therein, and Feng et al., 2013; Marsh et al., 2013a and Gardner et al., 2014).

Since the number of extraterrestrial particles encountering the Earth's atmosphere is approximately inversely proportional, in a log–log scale, to the particle's size, the bulk of the daily meteoric mass flux is contributed mainly by particles in the 1–100 micrometre (in radius) size range (Ceplecha et al., 1998; Flynn, 2002; Mathews et al., 2001; Nesvorný et al., 2010, 2011a, b). Furthermore, most of the daily mass input originates from the sporadic meteor background, which is the interplanetary dust forming the Zodiacal dust cloud. The orbits of the meteoroids from that source are so evolved that they cannot be traced back to their original parent body (Brown and Jones, 1995; Janches et al., 2006; Fentzke and Janches, 2008). The constant bombardment of particles from the sporadic background contributes far more input than meteor showers (e.g. Murad and Williams, 2002), the latter being a time-limited (days to several weeks) enhancement of particles entering the atmosphere in parallel trajectories appearing to radiate from one point in the sky (Jenniskens, 2006).

When meteoroids enter the atmosphere at geocentric speeds between 11 to 72 km s⁻¹, they collide with air molecules, leading to frictional heating and deceleration. The meteoroids, consisting partly of metals, melt at their surfaces and metals are ablated. The ablation process depends on several factors, such as the entry velocity and angle of the meteoroid, the boiling point of the different constituents and the size of the meteoroid (see, e.g. McNeil et al. (1998) and Vondrak et al. (2008) for more details). For the micron-size particles of interest to this work, the ablation process occurs between 80 and 125 km altitude (Vondrak et al., 2008; Janches et al., 2009; Marsh et al., 2013a; Feng et al., 2013; Plane et al., 2014), resulting in the deposition of metallic atoms such as sodium (Na), iron (Fe), potassium (K) and magnesium (Mg) in the mesosphere and lower thermosphere (MLT).

The observation technique, used in this study, measures the number density of the metal atom and ion layers present in the MLT that are formed from the ablated material from the meteoroids. Once ablated the meteoric metals undergo chemical transformation (see, e.g. Plane, 2003). A fraction of the ablated metals in the ablation region (80 to 105 km altitude) is already in the ionized form. For the case of Mg⁺ this fraction is estimated to be negligibly small (Vondrak et al., 2008, Fig. 14). Mg⁺ is formed by charge exchange of Mg with the main ion constituents at this altitude, i.e. NO⁺ and O₂⁺. The dominant loss process for Mg is the reaction with O₃, which leads to stable oxides, hydroxides and carbonates as reservoir species. Mg⁺ is lost by reactions with O₃ but

also by reactions with N₂ and other trace gases (CO₂, H₂O) – see, e.g. Fig. 9 in Plane and Whalley (2012) for a schematic diagram of the most important reactions.

The metal molecules condense and form meteoric smoke particles (e.g. Hunten et al., 1980; Kalashnikova et al., 2000; Saunders and Plane, 2006). These meteoric smoke particles are thought to act as nucleation nuclei. Heterogeneous nucleation of clouds is thought to play an important role in the formation of noctilucent clouds (NLCs) (see, e.g. Rapp and Thomas, 2006) in the polar summer mesopause region and also in the formation of polar stratospheric clouds (PSCs) in the polar winter stratosphere (see, e.g. Voigt et al., 2005; Curtius et al., 2005). PSCs have an important role in the ozone chemistry and the depletion of stratospheric ozone. In a dynamical equilibrium of meteoroid input and the above-mentioned loss reactions, the neutral Mg layer is formed between 85 and 90 km altitude and the Mg⁺ layer is formed slightly above the Mg layer (see, e.g. Plane and Helmer, 1995; McNeil et al., 1998 and Plane and Whalley, 2012).

The MLT is not readily probed by in situ instrumentation, as balloons fly too low, and satellites have to fly higher because of the atmospheric drag that reduces the satellite's operation time. As a result, only rockets carrying in situ instrumentation are able to access this region (see Sect. 6 for references). These are, however, expensive and rare. Metal atoms and ions have very strong absorption coefficients and oscillator strengths (see, e.g. Kramida et al., 2012). As a result, although their density even in the peak region is only a few thousand particles per cubic centimetre at most (for Na, Fe, Mg, less for others), they are very strong emitters of resonance fluorescence.

Mg and Mg⁺ spectral lines are observed at wavelengths below 290 nm. This wavelength region is strongly affected by ozone absorption in the stratosphere, so that observations from ground are not possible. For this reason the knowledge of the Mg and Mg⁺ content in the MLT is poor.

In this study the dayglow emissions of Mg and Mg⁺, detected by the satellite experiment SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY) on Envisat (Environmental Satellite) are used. The Mg and Mg⁺ densities are retrieved by mathematical inversion of these measurements using a radiative transfer model. Mg and Mg⁺ profiles had already been retrieved from SCIAMACHY by Scharringhausen et al. (2008a, b). As a result of these investigations a novel optimized measurement mode for the purpose of better covering the peak region of Mg and Mg⁺ has been established, and the observations are used for this study.

The resulting new data products are compared in this study with other Mg and Mg⁺ measurements, as well as with WACCM-Mg simulations. WACCM-Mg combines different models: a Meteor Input Function model is coupled to a meteor differential ablation model, which provides the metal input in the MLT. The metal release into the upper atmosphere is then used as one input to simulations using the

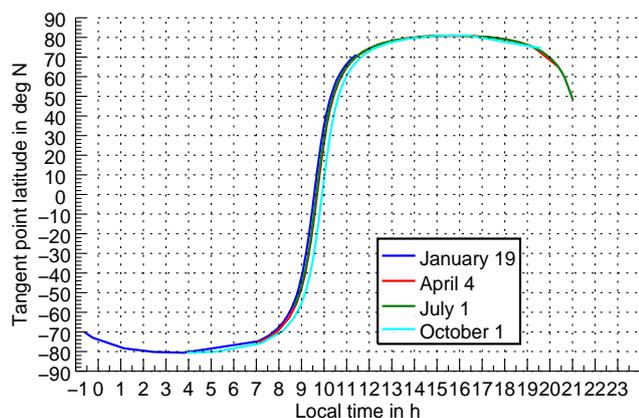


Figure 1. Local time at the tangent point of SCIAMACHY limb measurements at different latitudes for different seasons of the year.

Whole Atmosphere Community Climate Model (WACCM) (Marsh et al., 2013b) including a new chemistry model of Mg and Mg⁺ (Plane and Whalley, 2012). WACCM is a general circulation model that incorporates interactive chemistry for both neutral and ion species.

In Sects. 2 and 3 the SCIAMACHY/Envisat satellite observations and the Mg and Mg⁺ density retrieval are briefly described. In Sects. 4 and 5 the results obtained for Mg and Mg⁺ are presented and discussed. In Sect. 6 these findings are compared to other measurements. In Sect. 7 the WACCM-Mg model simulations of Mg and Mg⁺ are introduced and the model simulations are compared with the SCIAMACHY data set. In Sect. 8 a possible connection between Mg and Mg⁺ results and NLCs is discussed. Finally, Sect. 9 summarizes the results obtained in this study.

2 Instrument and algorithm

SCIAMACHY, a satellite-borne grating spectrometer on Envisat, was launched by ESA (European Space Agency) on 28 February 2002 (see, e.g. Burrows et al., 1995; Bovensmann et al., 1999). Envisat flies in a sun-synchronous orbit with a 10:00 a.m. descending node. The duration of one orbit is roughly 100 min (≈ 15 orbits a day). Note that the local time of SCIAMACHY limb observations changes with latitude. It is ≈ 11 a.m. at 60° N and 9 a.m. at 60° S and, as shown in Fig. 1, varies strongly in the vicinity of the poles. The highest latitude covered by SCIAMACHY limb observations of scattered light is $\approx 82^\circ$.

Data from SCIAMACHY's limb MLT mode with tangent altitudes between ≈ 50 and ≈ 150 km covered in 30 consecutive ≈ 3.3 km steps are used in this study. Dependent on latitude, consecutive limb measurements have a latitudinal separation of up to 8°, because nadir measurements are performed between two MLT measurements. However, there is also a small latitude offset between MLT measurements in

two consecutive orbits, to improve the meridional sampling for zonal averages.

MLT measurements were performed from mid-2008 until the loss of contact to Envisat in April 2012. They were performed roughly every 2 weeks for 15 consecutive orbits, which corresponds to 1 day of consecutive measurements. This means that measurements on 84 single days were performed, which is roughly a quarter year of single day data. This is much less than 4 years of single day data, and there are no continuous daily observations in the MLT mode. Apart from a few days, where some orbits are missing in the data, all longitudes are equally covered (sampling every $\approx 24^\circ$ of longitude).

The 2-D retrieval algorithm uses all measurements of one orbit and retrieves the metal density from each emission line of the species on a latitude and altitude grid. For averaged data, a reference orbit for geolocations is used, which is formed from the geolocations of the data that are averaged. Measurements with similar latitudes and local times as the measurements of the reference orbit are averaged. For Mg the spectral line at 285.2 nm is used. For Mg⁺ the spectral lines at 279.6 nm and 280.4 nm are used. A comprehensive discussion of the algorithm was provided by Langowski et al. (2013), who also present an extensive discussion of systematic and statistical errors and, e.g. also explain why only data for altitudes above 70 km altitude are used in this study.

An improvement compared to the analysis described by Langowski et al. (2013) is achieved by correcting the measured spectra for the polarization response of the instrument. This is briefly discussed in Sect. 3. As the main focus of this study is on the results of the retrieval algorithm, this discussion is kept short and more details can be found in Langowski (2015).

The first measurements at the start of the sunlit part of each orbit (high/mid northern latitudes) are contaminated by solar stray-light, which can be seen in the dark signal measurement at 350 km tangent altitude. We, therefore, exclude these measurements and also adjacent measurements, for which the contamination cannot be clearly excluded. When using the remaining measurements, some of the features similar to the ones resulting from this error source are still observed. However, these features are not dependent on the orbit phase like the ones resulting from the stray-light contamination, but only appear at latitudes $> 78^\circ$ N, and it is not clear whether these features are real or not (see discussion of Fig. 21 at the end of Sect. 7.2).

The actual latitude grid for calculating the density has a larger extent than the shown results. This is because the outermost latitude intervals have been cut off to reduce edge effects, which may, however, affect the neighbouring latitudes. In Sect. 8, where near-polar effects are discussed, fewer data are cut off.

3 Polarization correction

SCIAMACHY is sensitive to the polarization of the incoming radiation. This was known before launch and wavelength-dependent correction parameters were measured. The majority of backscattered radiation from the Earth's atmosphere is produced by Rayleigh scattering, which polarizes the incoming unpolarized solar radiation. The resonance fluorescence process of metals results in non-zero polarization of radiation even if the incoming beam is unpolarized, depending on the change of angular momentum between the electronic states that are involved in the fluorescence process. The polarization of the resonance fluorescence process of metals is well described by Hamilton (1947) and can also be found in Chandrasekhar (1960) with a slightly different nomenclature in the used formulas.

The incoming solar radiation is assumed to be unpolarized, which means that the parallel and perpendicular intensity components are equal in any observation plane. Following Chandrasekhar, 1960 (Eq. (259), p. 51), the incoming radiation components parallel and perpendicular to the scattering plane are transformed as follows:

$$\begin{pmatrix} I_{\parallel\text{out}} \\ I_{\perp\text{out}} \end{pmatrix} = \left(\frac{3}{2} E_1 \begin{pmatrix} \cos^2\theta & 0 \\ 0 & 1 \end{pmatrix} + \frac{1}{2} E_2 \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \right) \begin{pmatrix} I_{\parallel\text{in}} \\ I_{\perp\text{in}} \end{pmatrix}. \quad (1)$$

The parallel component is dependent on the scattering angle θ , which leads to non-zero polarization, if $E_1 \neq 0$. The parameters (E_1, E_2) are (1,0) for Mg at 285.2 nm, (0.5,0.5) for Mg^+ at 279.6 nm and (0,1) for Mg^+ at 280.4 nm. The coordinate system independent degree of polarization P is

$$P = \sqrt{\left(\frac{I_{\parallel\text{out}} - I_{\perp\text{out}}}{I_{\parallel\text{out}} + I_{\perp\text{out}}} \right)^2},$$

and the polarization direction is perpendicular to the scattering plane.

The response of SCIAMACHY depends on the polarization state of the radiation, so that an accurate absolute calibration requires the effect to be corrected for. Until recently, this was not possible because the available set of calibration data for the polarization sensitivity which is provided with the Level 1 data suffered from severe errors, in particular for the limb measurement geometry, and studies for an improvement of this effect in the calibration are still being done (see, e.g. Krijger et al., 2014 and Liebing et al., 2013).

From in-flight data it is possible to derive polarization sensitivities in the wavelength range below 300 nm by comparing measured reflectances with the ones calculated by a vector radiative transfer model (SCIATRAN 3.1, see, e.g. Rozanov et al., 2014) and then fitting the differences to the expected polarization. The results of this fit have been applied here together with Eq. (1) and a transformation to the SCIAMACHY polarization reference frame.

To derive the polarization sensitivities an ozone profile has to be assumed. The error due to the unknown actual ozone distribution is estimated to be quite large. This is why a consistency check to this approach has been performed here. Assuming the unpolarized Mg^+ line at 280.4 nm (D_1 line) to

yield exact results, a correction factor for the line at 279.6 nm (D_2 line) can then be determined requiring that the density retrieved from both Mg^+ lines match. Assuming that the polarization sensitivity does not change between 280 and 285 nm wavelength, a correction factor for Mg can be calculated knowing that the degree of polarization P_{D_2} of the D_2 line is just half of the degree of polarization P_{Mg} of the Mg line.

In cases where the Mg^+ signal is not dominated by noise, the results from both methods agree with each other well for Mg. Similarly, the Mg^+ density retrieved from both lines, using the updated polarization correction for SCIAMACHY, is in good agreement. We, therefore, conclude that the polarization correction for the 280–285 nm region improved the calibration of the data considerably.

4 Seasonal variations of Mg

The seasonal variation of Mg and Mg^+ density on a latitude and altitude grid is investigated. Prior to averaging, measurements at night or those having noise peaks in the investigated spectral region, caused by highly energetic particles hitting the detector (e.g. in the Southern Atlantic Anomaly region), are removed from the data set by filtering. The limb spectra of up to 15 daily single orbits are zonally averaged before running the retrieval algorithm, to improve the signal to noise ratio. To further reduce the noise in the results, data for individual months are averaged for the entire measurement period.

The retrieval algorithm calculates the density on an altitude and latitude grid with 40 equidistant day-side latitude intervals between 82° S and 82° N and 80 altitude intervals with 1 km thickness between 70 and 150 km. Additionally, there are latitude intervals for the part of the orbit, where the satellite moves northwards (see Fig. 1), to overcome ambiguities of identical latitudes but different local time at high latitudes.

The monthly averaged results for Mg are shown in Fig. 2. Mg shows a peak at around 90 km with densities up to 1500 cm^{-3} . There is a strong month-to-month variability in the latitudinal distribution. The annual mean results for Mg are shown in Fig. 3. In the annual mean, the density at low latitudes is higher than at the high latitudes in the peak region. At the highest southern latitude covered there an increased density above 100 km, which, however, is most likely explained by the fact that at this latitude the number of measurements is smaller and the statistical error thus larger.

Figure 4 shows the seasonal variation of the vertical profile for low, mid and high latitudes, and Fig. 5 shows the seasonal and latitudinal variation of the vertical column density (VCD). The month-to-month variations are large, and thus the error on the estimate of the amplitude of seasonal variations for mid latitudes is relatively large. The seasonal variation of the Mg peak altitude is estimated to be less than 5 km.

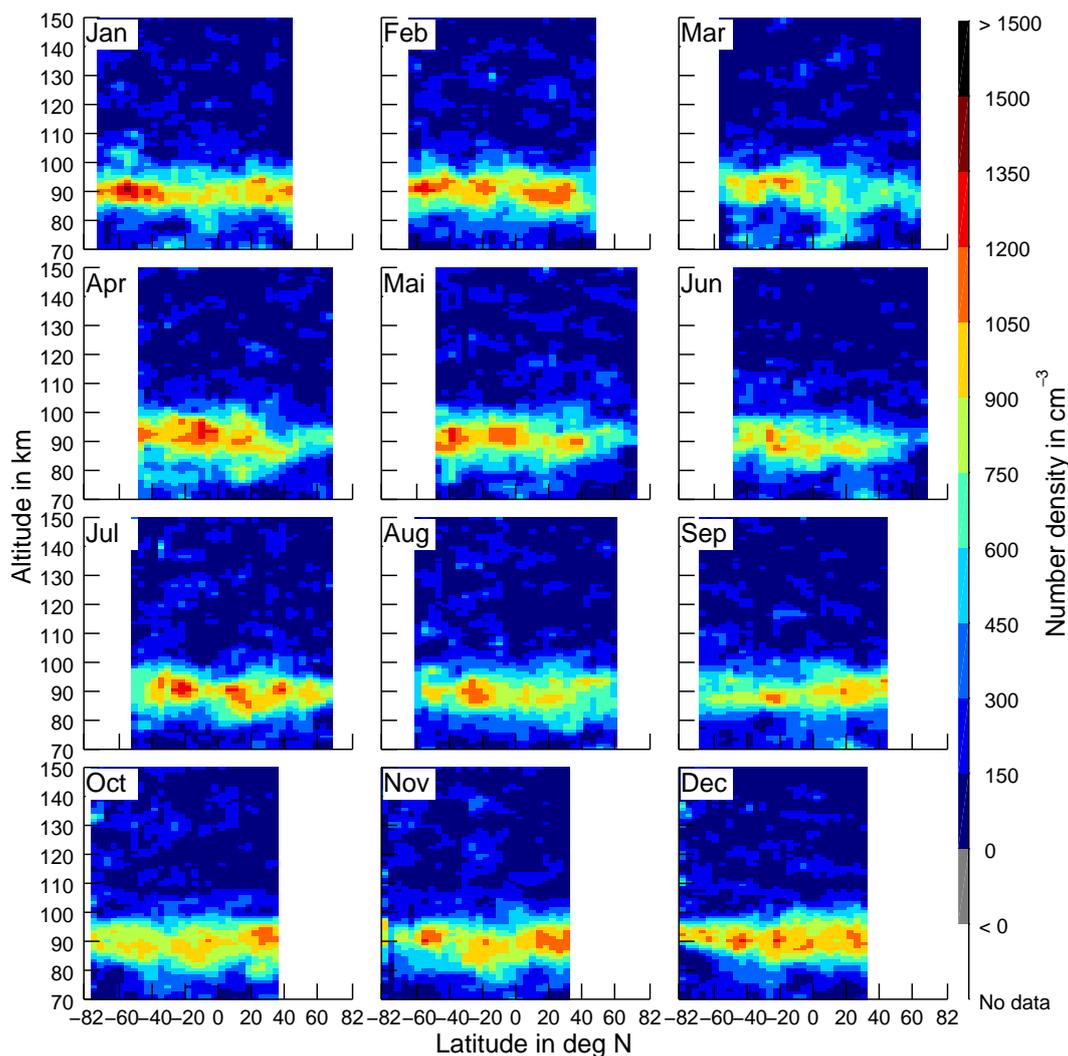


Figure 2. Latitudinal variation of monthly (averaged over all January, February, etc. results from 2008–2012) and zonally averaged Mg density profiles retrieved from the 285.2 nm line. The Mg layer peaks at around 90 km altitude and has a FWHM of about 15 km.

The VCD of Mg varies between $0.5 \times 10^9 \text{ cm}^{-2}$ and $3.5 \times 10^9 \text{ cm}^{-2}$ and is around $1.75 - 2.5 \times 10^9 \text{ cm}^{-2}$ for most latitudes and times. The VCD between 40° N and 40° S is higher than for higher latitudes, which are only covered in the hemispheric summer and show a summer minimum, which, however, is only clearly observed in the Northern Hemisphere. The seasonal variation is small compared to the mean of the VCD. This relatively small variation is required to retrieve the correct mean value, because of non-linearities in the retrieval, as comprehensively discussed and explained by Langowski et al. (2013).

5 Seasonal variations of Mg^+

For Mg^+ the same approach for data averaging is used as described for Mg in Sect. 4. For Mg^+ there are two spectral

lines, one at 279.6 nm and the other one at 280.4 nm. Both emission lines yield very similar results and only the results for the 280.4 nm line are shown here. This line is not affected by polarization-related issues, but has the larger statistical error. Mg^+ density is independently retrieved from both lines. The differences in the peak region are lower than 25%.

The density on an altitude and latitude grid for the monthly averaged results is shown in Fig. 6. The Mg^+ density peaks at altitudes in the range of 95–105 km with peak values of 500–4000 cm^{-3} . The peak density shows a seasonal variation with a summer maximum between $25\text{--}45^\circ$ in both hemispheres. In summer the highest peak altitude is roughly at 45° (N and S). It occurs around 105 km, which is up to 10 km higher than the lowest peak altitude at the equator and higher than that at the high-latitude region. There is a minimum at the equator and also a second maximum in peak altitude in the mid latitudes

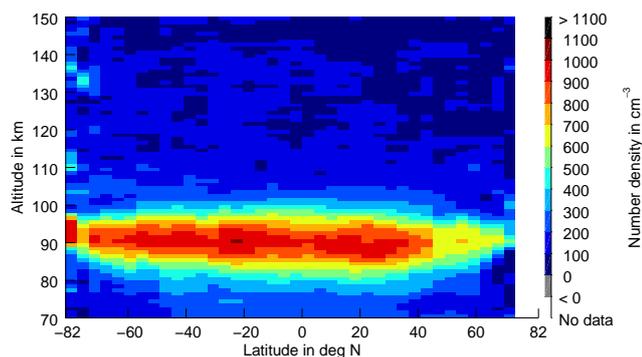


Figure 3. Latitudinal variation of Mg profiles averaged over all available data for the years 2008–2012. Note that only between 45° N and S do measurements from all 12 months contribute to the averages, while for high latitudes there is only summer coverage and/or near-terminator measurements.

in the winter hemisphere, which, however, is more variable than the one in the summer hemisphere.

The latitudinal variation of Mg^+ is also seen in the average over all available measurements in 2008–2012, which is shown in Fig. 7. The latitudinal dependence of the peak altitude seems to be symmetric to the equator. However, there is an asymmetry in the peak density, with larger density for the Northern Hemisphere (NH) than for the Southern Hemisphere (SH). However, this effect is compensated by a broader profile in the SH, so that the differences in the VCD are smaller.

A reason for this may be Lorentz force induced transport processes together with the very different mapping of geomagnetic coordinates to geographic coordinates (the magnetic south pole at around 65°S is further away from the geographic pole than the magnetic north pole at around 82° N).

At the upper vertical profile edge up to 110 km the density is higher at mid latitudes than at the equator, which can be explained by the density maximum at mid latitudes being also at higher altitudes, than at the equator. However, above 110 km altitude this behaviour is reversed and the equatorial density is larger than the density at mid latitudes. This may be explained by enhanced vertical upward transport in the equatorial region, which will be discussed in Sect. 7.2.

Figure 8 shows the seasonal variation of the vertical Mg^+ profile for low, mid and high latitudes, and Fig. 9 shows the corresponding VCD. In each of the latitude regions, a maximum in peak altitude is found during summer in the corresponding hemisphere. The VCD varies between $1 \times 10^9 \text{ cm}^{-2}$ and $6 \times 10^9 \text{ cm}^{-2}$. A seasonal cycle with a summer maximum is observed and the strongest variations are observed at latitudes between 20° and 40°.

Figure 10 shows the ratio of Mg^+ and Mg VCD. The ratio is in between 0.5 and 5. The seasonal variability of the ratio follows the one of Mg^+ , as Mg (beside for northern high latitudes) does not show a strong seasonal variability.

6 Comparison to other measurements

Mg and Mg^+ cannot be observed from the ground, because the wavelengths of the lines are below 300 nm and the emission signal is absorbed strongly by ozone in the stratosphere. As a result, only few measurements are available and rely on observations from sounding rockets and satellites. The first rocket-borne ion mass spectrometer measurement of metal ions was reported by Johnson and Meadows (1955) (May 1954, White Sands) and enhanced ion signals between 93 and 124 km were found. According to Grebowsky and Aikin (2002) approximately 50 flights of rocket-borne mass spectrometers had been made until 2002, probing the region between 80 and 130 km altitude. Results of these flights for Mg^+ can, e.g. be found in Istomin (1963), Narcisi and Bailey (1965), Narcisi (1971), Aikin and Goldberg (1973), Philbrick et al. (1973), Zbinden et al. (1975), Herrmann et al. (1978), Kopp and Herrmann (1984), Kopp et al. (1985b, a), Kopp (1997) and Roddy et al. (2004). Date, local time, latitude and reference publications of these and other rocket flights can also be found in Table 1 of Grebowsky et al. (1998). Figure 11 shows reproduced plots of vertical number density profiles of Mg^+ . The original sources of the data for these plots are listed in Table 1.

A disadvantage for the comparison with the new data set presented in this study is that most of these measurements were performed during special events having E_s layers (sporadic electron layers), aurora, meteor showers, stratospheric warmings or NLCs present. Sporadic Mg^+ layers often occurred between 105–110 km and/or at around 120 km altitude. The Mg^+ peak altitude in most of these measurements can be found between 90 and 95 km altitude and the full width at half maximum (FWHM) of the layers is on the order of 5–10 km, but sometimes the FWHM is only 1 km.

When comparing in situ mass spectrometer measurements with satellite remote sensing results, it has to be noted that the in situ measurements are localized and limited to the direct vicinity of the rocket. In contrast, remote sensing techniques typically cover a large volume with horizontal distances along and perpendicular to the viewing direction of several hundreds of kilometres. This results in smoother layers with a larger FWHM for the remote sensing method. Still, the width of the Mg^+ layers as well as the peak density presented in this study are in good agreement with the in situ rocket measurements. However, the strong latitudinal dependence of the peak altitude observed in Fig. 8 as retrieved from SCIAMACHY measurements is not found in the in situ rocket data.

In addition to the in situ measurements with rockets, there are also airglow measurements available from rockets, the space shuttle and satellites. However, to retrieve density information from this method radiative transfer models as well as inversion techniques and computational power are needed. As a result, slant column information rather than profiles has been retrieved and made available in the first remote sens-

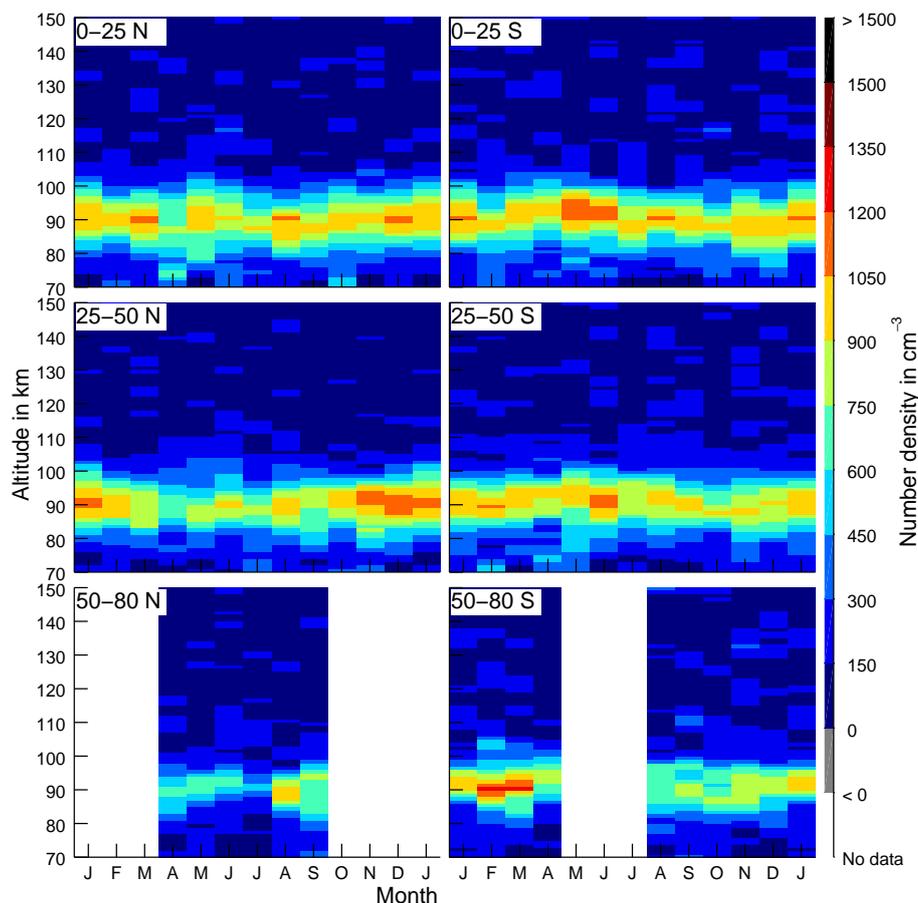


Figure 4. Seasonal variation of the vertical Mg profile for different latitudinal zones (left: Northern Hemisphere (NH), right: Southern Hemisphere SH, top: low latitudes, middle: mid latitudes, bottom: high latitudes). The peak altitude is at 90 km for all latitudes with variations of ± 5 km. The month-to-month variations in peak altitude and density are bigger than any seasonal variations.

Table 1. Original sources and geolocations of plots in Fig. 11.

No.	Lat	Long	Date	Original reference	Taken from
1	mid N	U.S.S.R.(Eur)	15 June 1960	(Istomin, 1963)	(Istomin, 1963)
2	30 N	86 W	31 October 1963	(Narcisi and Bailey, 1965)	(Narcisi and Bailey, 1965)
3	30 N	86 W	12 April 1967	(Narcisi, 1971)	(Grebowsky and Aikin, 2002)
4	30 N	86 W	12 April 1967	(Narcisi, 1971)	(Grebowsky and Aikin, 2002)
5	8 N	77 E	19 March 1970	(Aikin and Goldberg, 1973)	(Aikin and Goldberg, 1973)
6	8 N	77 E	19 March 1970	(Aikin and Goldberg, 1973)	(Aikin and Goldberg, 1973)
7	8 N	77 E	9 March 1970	(Aikin and Goldberg, 1973)	(Aikin and Goldberg, 1973)
8	8 N	77 E	10 March 1970	(Aikin and Goldberg, 1973)	(Aikin and Goldberg, 1973)
9	30 N	86 W	20 November 1970	(Philbrick et al., 1973)	(Grebowsky and Aikin, 2002)
10	40 N	9 E	14 December 1971	(Zbinden et al., 1975)	(Zbinden et al., 1975)
11	38 N	75 W	12 August 1976	(Herrmann et al., 1978)	(Kopp, 1997)
12	51 N	93 W	24 February 1979	(Kopp and Herrmann, 1984)	(Kopp, 1997)
13	67 N	20 E	30 November 1980	(Kopp et al., 1985b)	(Kopp, 1997)
14	67 N	20 E	13 August 1978	(Kopp et al., 1985a)	(Kopp, 1997)
15	38 N	75 W	1 July 2003	(Roddy et al., 2004)	(Roddy et al., 2004)
16	± 20 N	all	15 October–29 November 1999	(Minschwaner et al., 2007)	(Minschwaner et al., 2007)

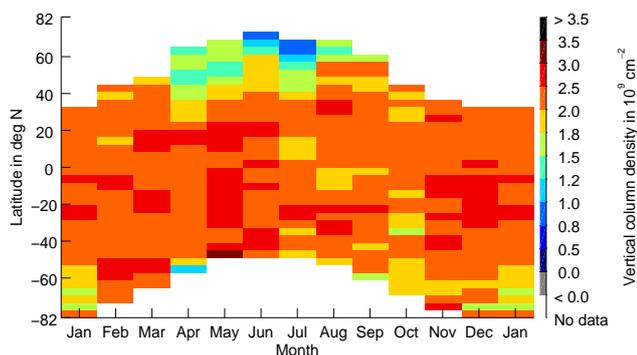


Figure 5. Seasonal variation of the Mg vertical column density (VCD) between 70 km and 150 km for different latitudinal regions. The VCD varies between $0.5 \times 10^9 \text{ cm}^{-2}$ and $3.5 \times 10^9 \text{ cm}^{-2}$. No clear seasonal cycle is observed. Variations between consecutive days with measurements (at least 14 days difference) are even higher than the inter-monthly variations.

ing studies (see, e.g. Boksenberg and Gérard, 1973 or Gérard and Monfils, 1974). In Anderson and Barth (1971) (summer, $\approx 40^\circ \text{ N}$) the region up to 106 km altitude is scanned during a sporadic E_s layer event, and the peak altitude of the Mg^+ was not observed during this flight, i.e. it was higher than 106 km. No Mg signal above the instrumental noise was observed in these spectra.

The region above the peak altitude from 150 km up to the F-layer and above was investigated by Gérard and Monfils (1978), Fesen and Hays (1982a), Mende et al. (1985), Gardner et al. (1995) and Gardner et al. (1999) and typically shows less than $100 \text{ cm}^{-3} \text{ Mg}^+$ ions at 150 km altitude. This is in good agreement with the profiles described in Sect. 5. In some cases a higher density is observed in the profiles retrieved from the SCIAMACHY limb observations. This is explained by retrieval artifacts on the edge of the retrieval grid and vertical constraints tuned for the main peak. These effects result in small oscillations, compared to the main peak, in regions with lower density. Since these artifacts appear at the upper edge of the profile it also implies that there is a significant density above the highest tangent altitude for Mg^+ .

In Minschwaner et al. (2007) a combined NO and Mg^+ retrieval for satellite limb measurements is shown, which is in good agreement with the results in Sect. 5 in terms of the Mg^+ concentrations at peak altitude and at the upper edge of the profile. However, the Mg^+ peak altitude is at 90 km. Taking into account the coarser sampling (every 7 km), higher statistical errors and a tangent height offset ($\pm 4 \text{ km}$) in Minschwaner et al. (2007), the agreement is reasonable. Accurate tangent height determination was an issue for SCIAMACHY, too. Offsets of a similar magnitude were initially observed for SCIAMACHY data products (see, e.g. von Savigny et al., 2005). However, this error source was minimized and the tangent height knowledge was improved to $\pm 200 \text{ m}$

(von Savigny et al., 2009). The NO band emission, which overlaps with the Mg^+ lines and the Mg line, is of the same order of magnitude as the Mg^+ lines in the study by Minschwaner et al. (2007) and even bigger than the Mg emission, which made a NO correction necessary. The SCIAMACHY MLT data set does not show these strong NO lines at 280 and 285 nm. NO in this region is very sensitive to solar activity. Results on NO retrievals from the same SCIAMACHY level 1 data set as used in this study are reported by Bender et al. (2013). Only at high latitudes in summer and winter and from late 2011 to 2012 do the results of Bender et al. (2013) show NO density of the same magnitude as the equatorial density plot for NO in Minschwaner et al. (2007). However, we did not observe clear NO signals in the vicinity of the Mg/ Mg^+ lines during this period.

A time series of Mg^+ vertical columns covering several years and retrieved from SBUV nadir measurements was presented by Joiner and Aikin (1996). These measurements were performed approximately 1 day per month, with a spectral resolution of 1.13 nm and a spectral sampling every 0.2 nm (compare to SCIAMACHY with $\approx 0.22 \text{ nm}$ resolution and sampling every $\approx 0.11 \text{ nm}$). The results in Joiner and Aikin (1996) are in very good agreement with the results obtained in this study, especially when comparing Figs. 10 and 11 in Joiner and Aikin (1996) with Fig. 9 in this study. Figs. 12 and 13 show redrawn VCD time series from different sources for a quick and easy comparison of the results of Mg^+ and Mg (see the original sources for more details).

Mg was also investigated in Joiner and Aikin (1996). However, the average VCD for these profiles, where the signal was significant, is $4 \times 10^{10} \text{ cm}^{-2}$, which is a factor of 10 more than the VCD in Fig. 5. These large discrepancies must be investigated in the future.

Satellite measurements with long time series and daily coverage are available from GOME and GOME-2 in nadir mode and from SCIAMACHY in nadir and nominal limb mode. All three instruments have a similar spectral resolution. The VCD of Mg and Mg^+ was retrieved from the GOME data set by Correia et al. (2008, 2010) and Correia (2009). Figures 1 and 2 in Correia et al. (2008) show Mg and Mg^+ VCD for 1996 and 1997 as well as the Mg^+ to Mg ratio for latitude intervals from $0\text{--}10^\circ$ and $30\text{--}40^\circ$ for both hemispheres. For the low latitudes, where there is less seasonality, the VCD for Mg^+ is about $6\text{--}7 \times 10^9 \text{ cm}^{-2}$, which is higher than in Fig. 9. The Mg density is about $3 \times 10^9 \text{ cm}^{-2}$, which is similar to that in Fig. 5. In the equatorial region the Mg column agrees better, and a higher VCD in the nadir results for Mg^+ can be explained by the thermospheric part of Mg^+ which is not part of the VCD in Fig. 9. At mid latitudes Mg^+ shows a strong seasonal cycle with a summer maximum in Correia et al. (2008). This seasonality is quite symmetric for both hemispheres with higher VCD in the SH. Furthermore, the summer maximum at mid latitudes does not exceed the VCD at low latitudes. For Mg a summer maximum is observed, which is more pronounced in the SH. The Mg^+ to

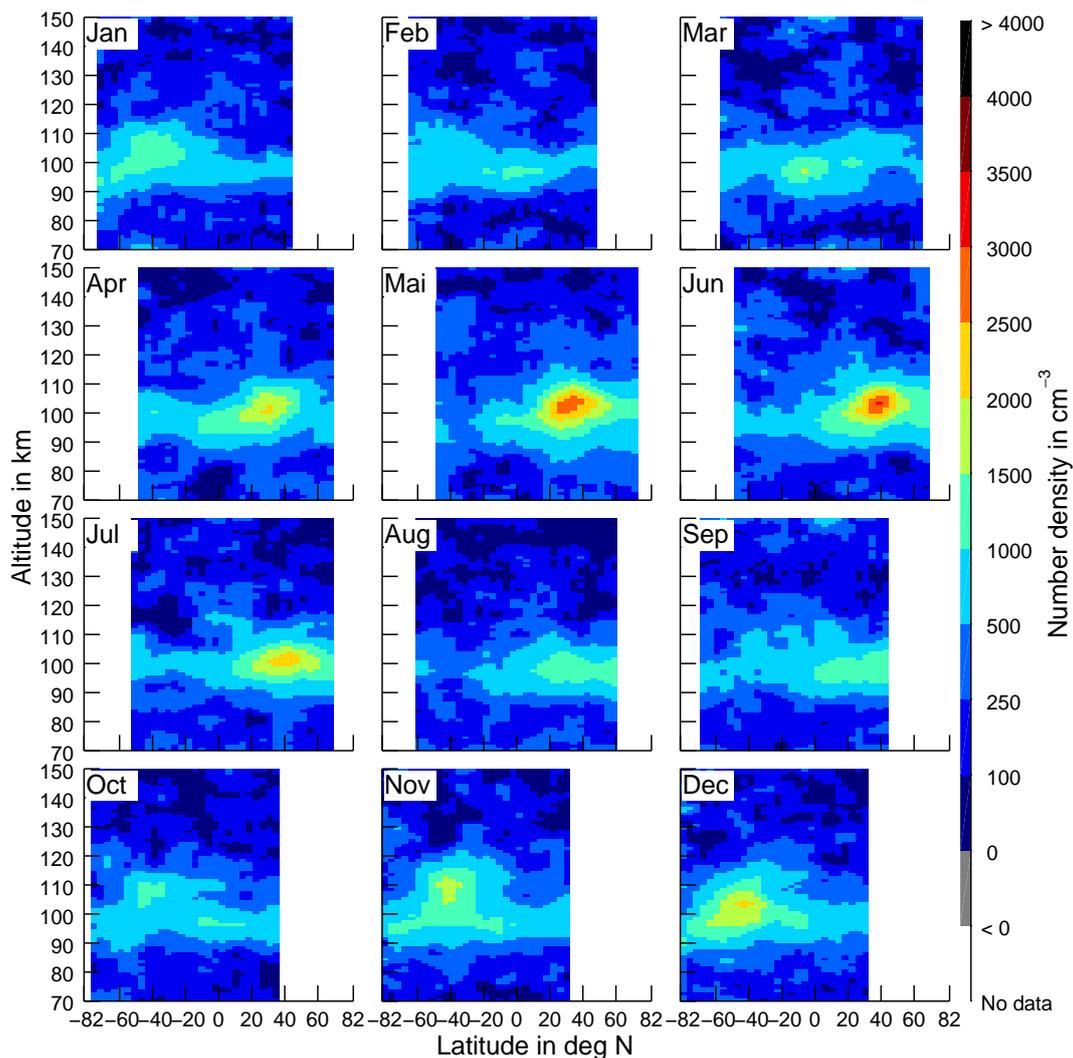


Figure 6. Latitudinal variation of monthly and zonally averaged Mg^+ profiles (for the years 2008–2012) retrieved from the Mg^+ line at 280.4 nm. Mg^+ shows a seasonal cycle with a summer maximum, which is especially pronounced in the region between 25° and 45° latitude in the summer hemisphere. Furthermore, in this region the peak altitude is about 105 km, which is up to 10 km higher than at the equator or at the poles.

Mg VCD ratios in Correira et al. (2008) are in good agreement with our results shown in Fig. 10.

The nominal limb mode data set, covering the tangent height range from the surface up to 92 or 105 km (only until early 2003), respectively, combined with the nadir mode data set from SCIAMACHY from 2002 to 2007 was investigated in Scharringhausen et al. (2008a, b) and Scharringhausen (2007). The peak region for the ions could not be fully resolved with the nominal limb mode. However, qualitatively the agreement between the results by Scharringhausen (2007) (page 69 and 70) and the results from this study for the ions is quite good, showing a similar seasonal cycle in the NH, which, however, shows up to a factor 3–4 larger density and the highest density at high latitudes, and not at mid latitudes. In the SH the seasonal cycle was not

identified well in Scharringhausen (2007), which agreed with the results similar to Fig. 9 when using the pre-flight polarization correction (not shown), which we now found to be wrong (see Sect. 3).

At the very beginning of the Scharringhausen VCD data set in 2002 (e.g. Figs. 69 and 70 in Scharringhausen, 2007) slightly higher VCD for both species are observed than for the other years. This may come from increased NO signals near the Mg and Mg^+ lines during solar maximum. Another reason for the higher Mg^+ VCD in 2002 may also be related to the change of the maximum tangent altitude from 105 to 92 km.

More differences between our retrievals and the results by Scharringhausen (2007) can be found in the Mg data. This is because the data product retrieved using the Mg line is more

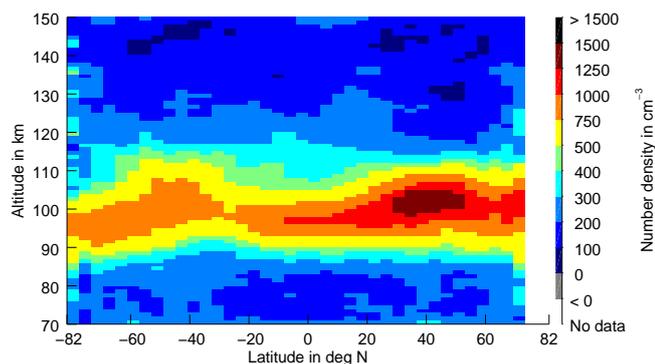


Figure 7. Latitudinal variation of Mg^+ profiles averaged over all available data for 2008–2012 for the Mg^+ line at 280.4 nm.

affected by the radiative transfer improvements made in this study than the product retrieved using the Mg^+ lines. For example, there was no correction of the Ring effect, the filling in of Fraunhofer lines by inelastic Raman scattering in the Earth's atmosphere (Grainger and Ring, 1962), in Scharringhausen (2007), which led to high density below 80 km and a density maximum at the lower edge of the retrieval boundaries at 70 km. This inelastic scattering contribution additionally adds a seasonal variation to the data set.

Furthermore, the Mg line at 285.2 nm is much more affected by self-absorption of the emission, which was not considered in Scharringhausen (2007), so the Mg VCD was smaller than reported here. However, most of the important findings from the further analysis of the Scharringhausen data set are only weakly affected by these differences and are still valid.

In summary, it can be concluded that the Mg/Mg^+ results presented here are often in good agreement with previous satellite and rocket instruments. The most striking difference to previous measurements is the strong latitudinal dependence of the peak altitude of Mg^+ with differences of up to 10 km for different latitudes.

7 Comparison of Mg and Mg^+ observed by SCIAMACHY and modelled with WACCM

7.1 WACCM-Mg model

The first global 3-D model of magnesium, which is similar to other metals (e.g. Na in Marsh et al. (2013a), Fe in Feng et al. (2013) and K in Plane et al. (2014)), is used to investigate several important questions: for example what injection rate of Mg via the ablation of interplanetary dust particles is needed to explain the absolute Mg and Mg^+ densities; how well can Mg^+ – the only atomic ion to be observed on a global scale – be modelled; and is the coupling of long-range transport and chemistry in the MLT region correctly captured?

WACCM is a high-top chemical-dynamical model, which simulates the altitudes from the Earth's surface up to 140 km (Garcia et al., 2007; Marsh et al., 2007, 2013b). Here we use the specified dynamics SD-WACCM, which is nudged by the GEOS5 meteorological data set (including temperature, specific humidity, horizontal winds, see Suarez et al., 2008) below 60 km. This is the same version used by Feng et al. (2013), Marsh et al. (2013a) and Plane et al. (2014), who successfully incorporated iron, sodium and potassium chemistry into WACCM.

Here we develop a global model of meteoric magnesium in the atmosphere by combining three components: a treatment of the injection of meteoric constituents into the atmosphere (Feng et al., 2013; Marsh et al., 2013a; Plane et al., 2014), a description of the neutral and ion–molecule chemistry of magnesium in the mesosphere and lower thermosphere (Whalley and Plane, 2010; Plane and Whalley, 2012) and WACCM. The Mg meteoroid injection function (MIF) has a similar seasonal variability as those of Fe and Na. The minimum of the MIF occurs in the spring with an ablation flux of $1300 \text{ atoms cm}^{-2} \text{ s}^{-1}$, and the maximum occurs in the autumn with $2400 \text{ cm}^{-2} \text{ s}^{-1}$ (both at high latitudes). The average flux is $\approx 1850 \text{ cm}^{-2} \text{ s}^{-1}$, which sums up to 32.5 kg d^{-1} over the entire planet. Magnesium constitutes 9.6% of chondritic meteorites by mass, so the equivalent interplanetary dust particle mass is 0.338 t d^{-1} . This is an extremely low number, which indicates that Mg ablates relatively inefficiently from meteoroids.

The peak ablation height is at around 95 km. The fluxes are obtained by scaling the Mg MIF to match the observed Mg^+ column density (not to the Mg column density, as Mg^+ is better known from earlier satellite studies). This requires dividing the Mg ablation flux by a factor of 15, relative to that of Na (Marsh et al., 2013a). Since the relative chondritic abundance of Mg is 16 times that of Na, this means that the ablation fluxes of Mg and Na are similar in the model. Similarly, when modelling the Fe layer using WACCM, (Feng et al., 2013) had to reduce the Fe MIF relative to Na by a factor of 4. The most likely explanation is that more extreme differential ablation is occurring. As shown in (Vondrak et al., 2008) – see Fig. 12 – the more refractory elements such as Mg and Fe ablate less efficiently than Na from slow meteoroids with entry speeds below 20 km s^{-1} .

The MIF used in the present study was calculated from an astronomical dust model where the average speed is around 30 km s^{-1} – see (Feng et al., 2013) and (Marsh et al., 2013a) for further details. Hence, one implication of these relatively small injection rates of Mg and Fe is that a significant fraction of meteoroids enter the atmosphere from near-prograde orbits, with speeds close to the minimum of 12 km s^{-1} .

Tables 2–4 list the Mg chemical reactions and their rate coefficients added to the standard chemistry scheme in this study. A schematic diagram of the Mg^+/Mg chemistry appears as Fig. 9 in Plane and Whalley (2012). An important magnesium reservoir on the underside of the

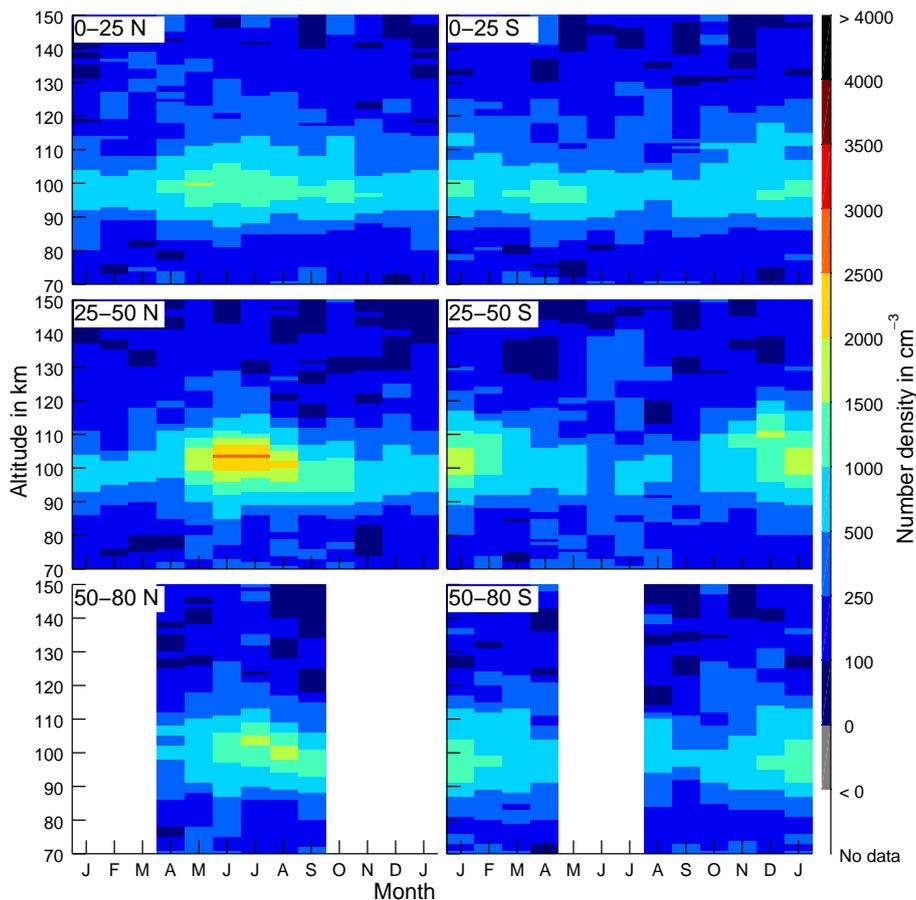


Figure 8. Seasonal variation of the vertical profile of Mg^+ (280.4 nm line) for different latitudinal zones (left: NH, right: SH, top: low latitudes, middle: mid latitudes, bottom: high latitudes), averaged over all available observations in 2008–2012. For all these latitudinal zones a seasonal cycle in the peak altitude with a summer maximum and a winter minimum can be observed. The seasonal variations are similar or larger than the month-to-month variations. The maximum peak altitude is 5–10 km higher than the minimum peak altitude. For mid latitudes, the peak altitude in the winter hemisphere is still higher than the peak altitude at the equator (see also Fig. 6).

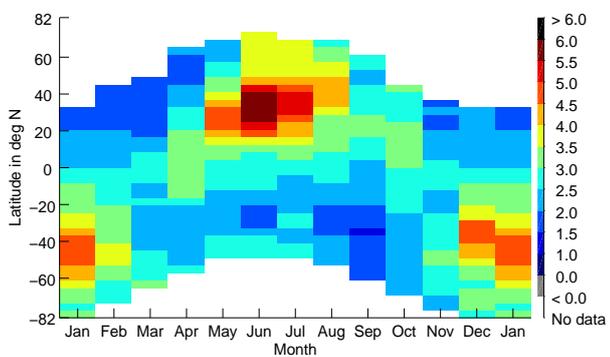


Figure 9. Seasonal variation of the Mg^+ vertical column density (VCD) between 70 km and 150 km and for different latitudinal regions, retrieved from the 280.4 nm line. A clear seasonal cycle with a summer maximum can be observed. The summer maximum in the NH has higher values compared to the one in the SH. The highest variability can be found between 25° and 50° in both hemispheres.

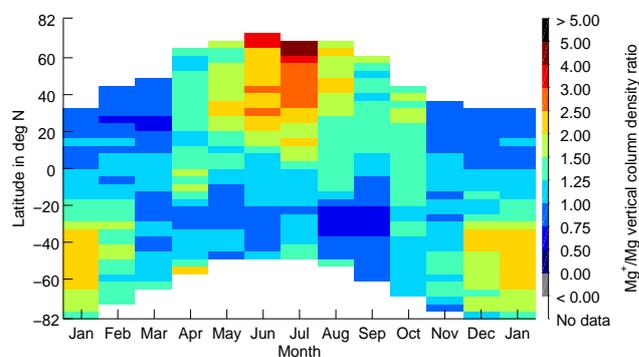


Figure 10. Seasonal variation of the Mg^+ to Mg ratio for different latitudes. The ratio varies between 0.5 and 5 and shows a summer maximum, which is in good agreement with Correira et al. (2008).

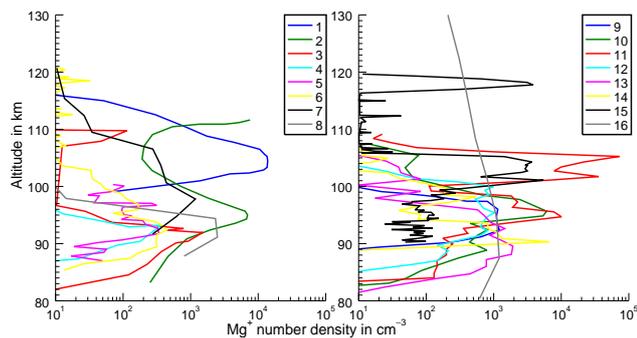


Figure 11. Measurements of the vertical Mg^+ number density profile mentioned in the text and listed in Table 1. Note that the data points are redrawn from the original figures, and not all details of the original figures may be captured.

Table 2. Magnesium photolysis chemistry added into WACCM.

No.	Reaction	Rate/ s^{-1}	Reference
J1	$\text{Mg} + h\nu \rightarrow \text{Mg}^+ + \text{e}^-$	$j_1 = 4 \times 10^{-7}$	Swider (1984)

Mg layer is $\text{Mg}(\text{OH})_2$. This is reduced back to Mg via MgOH by reaction with H atoms (R12a). The subsequent reaction with H atoms (R12b) is most likely faster than R12a, and so the reaction rate is not explicitly listed in Table 3 (Plane and Whalley, 2012). The polymerization of MgO_2H_2 to form meteoric smoke is parametrized by a dimerization rate coefficient (reaction R13 in Table 3). This reaction should be essentially at the high-pressure limit even in the upper mesosphere because of the large number of atoms in the dimer and the large binding energy (268 kJ mol^{-1} , calculated at the B3LYP/6-311+g(2d, p) level of electronic structure theory using the Gaussian 09 program suite; Frisch et al., 2009). The capture rate coefficient is then increased to $9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to account for the concentration of other metallic species (e.g. NaHCO_3 , FeOH) with which MgO_2H_2 can also polymerize.

The model was run for the period 2004 to 2011, when the GEOS5 analysis data are available. To derive the modelled climatologies of temperature, Mg and other chemical constituents, we use the model output from 2005 to 2011.

7.2 Comparison of WACCM model and SCIAMACHY measurements results

Figure 14 shows the monthly mean results for 7 yr of WACCM simulations of Mg from 2005 to 2011 and Fig. 15 shows the same for Mg^+ . Figure 16 shows the VCD for both Mg and Mg^+ . Mg shows a clear seasonal cycle with a winter maximum which is most pronounced at the poles. The peak altitude is nearly constant, but small seasonal variations can be found. For example, in February the peak altitude at the poles is roughly 85 km, while it is 5 km higher at 90 km

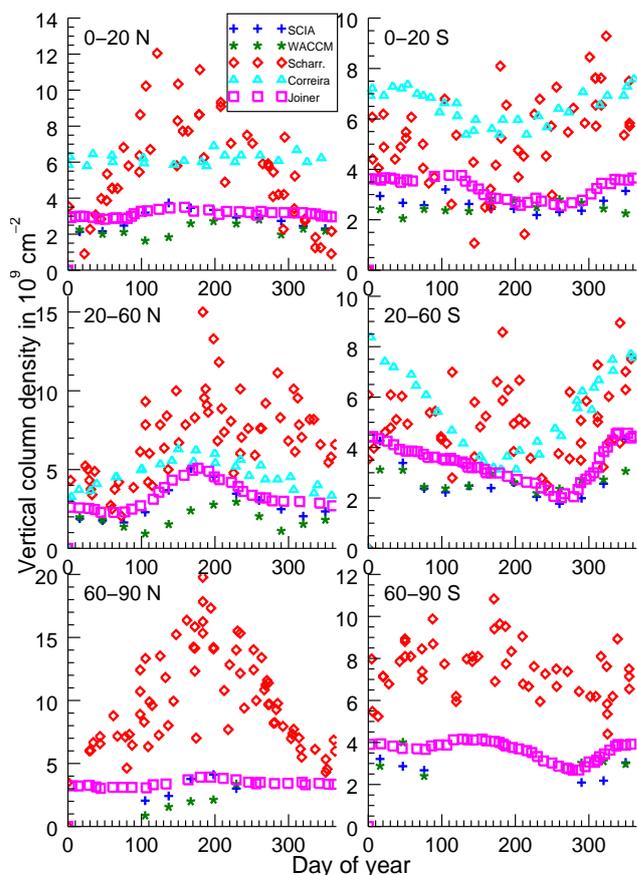


Figure 12. Mg^+ VCD results for different latitudinal regions and from different sources. The left column shows the NH and the right column the SH. From top to bottom results for low, mid and high latitudes are shown. Note that different sources originally used different time periods. The data used are from SCIAMACHY (blue) and WACCM (green) from this work (0–20° N/S, 20–60° N/S, 60–90° N/S, WACCM data co-located to SCIAMACHY coverage), from (Scharringhausen, 2007) (Figs. 7.3 and 7.4, red), from (Correira et al., 2008) (Fig. 1, cyan) and (Joiner and Aikin, 1996) (Figs. 10 and 11, magenta).

in the equatorial region. Mg^+ shows a seasonal cycle with a summer maximum. In addition, there is an increased Mg^+ density at the poles, even in the winter hemisphere. The Mg^+ peak altitude is close to 95 km and shows no strong variation with latitude and time. The seasonal variations in the VCD profiles for Mg and Mg^+ are very similar to Na and Na^+ profiles (Fig. 3 in Marsh et al., 2013a) and Fe and Fe^+ in Feng et al. (2013).

The geophysical behaviour of the Mg and Mg^+ layers can be explained as follows: the abundance of Mg atoms in the layer is governed by the injection flux of Mg atoms, as well as chemical loss and transport through diffusion and advection. The column injection flux of Mg atoms has a seasonal cycle with an autumn maximum most pronounced at the poles where the autumn Mg column injection rate is roughly twice

Table 3. Neutral chemistry of magnesium added into WACCM.

No.	Reaction	Rate/cm ³ molecule ⁻¹ s ⁻¹	Reference
R1	Mg + O ₃ → MgO + O ₂	$k_1 = 2.3 \times 10^{-10} \exp(-139/T)$	Plane and Helmer (1995)
R2	MgO + O → Mg + O ₂	$k_2 = 6.2 \times 10^{-10} \times (T/295)^{0.167}$	Whalley and Plane (2010)
R3	MgO + O ₃ → MgO ₂ + O ₂	$k_3 = 2.2 \times 10^{-10} \exp(-548/T)$	Plane and Helmer (1995)
R4	MgO ₂ + O → MgO + O ₂	$k_4 = 7.9 \times 10^{-11} \exp(T/295)^{0.167}$	Whalley and Plane (2010)
R5	MgO + H ₂ O + M → MgO ₂ H ₂ + M	$k_5 = 1.1 \times 10^{-26} \times (T/200)^{-1.59}$	Rollason and Plane (2001)
R6	MgO ₃ + H ₂ O → MgO ₂ H ₂ + O ₂	$k_6 = 1.0 \times 10^{-12}$	Rollason and Plane (2001)
R7	MgO + O ₂ + M → MgO ₃ + M	$k_7 = 3.8 \times 10^{-29} \times (T/200)^{-1.59}$	Rollason and Plane (2001)
R8	MgO + CO ₂ + M → MgCO ₃ + M	$k_8 = 5.9 \times 10^{-29} \times (T/200)^{-0.86}$	Rollason and Plane (2001)
R9	MgCO ₃ + O → MgO ₂ + CO ₂	$k_9 = 6.7 \times 10^{-12}$	Plane and Whalley (2012)
R10	MgO ₂ + O ₂ + M → MgO ₄ + M	$k_{10} = 1.8 \times 10^{-26} \times (T/200)^{-2.5}$	Plane and Whalley (2012)
R11	MgO ₄ + O → MgO ₃ + O ₂	$k_{11} = 8.0 \times 10^{-14}$	Plane and Whalley (2012)
R12a	MgO ₂ H ₂ + H → MgOH + H ₂ O	$k_{12} = 1.0 \times 10^{-11} \times \exp(-600/T)$	Plane and Whalley (2012)
R12b	MgOH + H → Mg + H ₂ O	faster than R12a	see text
R13	MgOH + MgOH → Mg ₂ O ₂ H ₂	$k_{13} = 9.0 \times 10^{-10}$	see text
R14	MgO ₃ + H → MgOH + O ₂	$k_{14} = 2.0 \times 10^{-12}$	Plane and Whalley (2012)
R15	MgO ₃ + O → MgO ₂ + O ₂	$k_{15} = 1.0 \times 10^{-13}$	Plane and Whalley (2012)

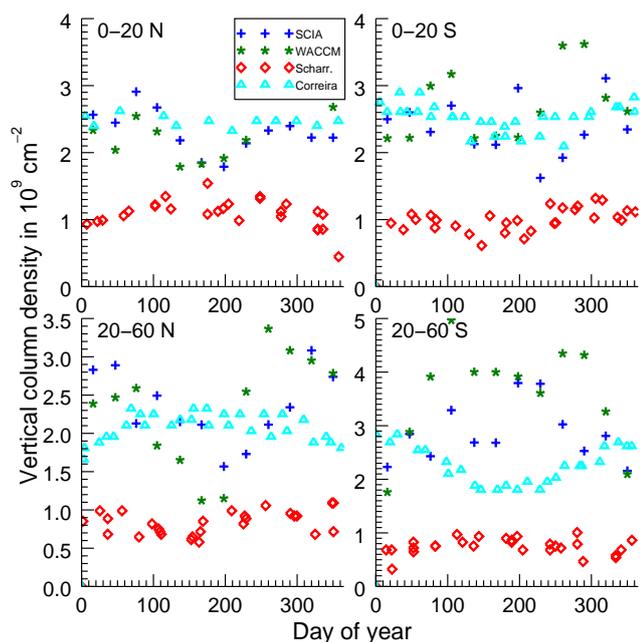


Figure 13. Mg VCD results for different latitudinal regions and from different sources. The left column shows the NH and the right column the SH. From top to bottom results for low, mid and high latitudes are shown. Note that different sources originally used different time periods. The data used are from SCIAMACHY (blue) and WACCM (green) from this work (0–20° N/S, 20–60° N/S, 60–90° N/S, WACCM data co-located to SCIAMACHY coverage), from (Scharringhausen, 2007) (Figs. 7.3 and 7.4, red) and from (Correira et al., 2008) (Fig. 1, cyan).

as large as in the spring minimum. The vertical distribution of the metal's injection has a maximum at around 90 km altitude (see, e.g. Vondrak et al., 2008, Fig. 11). However, the actual height and shape of this injection is not that relevant, as the neutral Mg layer is governed by an ion–molecule cycle on the top-side, and a neutral cycle on the bottom-side, which are fast compared to vertical transport.

The strongest loss processes are the charge transfer reactions of neutral Mg with NO⁺ and O₂⁺ (R28 and R29 in Table 4), which occur mainly at the top of the layer above 90 km, where the concentrations of NO⁺ and O₂⁺ are large, as well as the reaction with O₃ (R1 in Table 3), which has a nearly exponentially increasing density towards lower altitudes, which leads to the largest loss rate at the centre and the bottom of the Mg profile. The ozone reaction is fast and several percent of the Mg atoms are converted into MgO within a second. However, this is countered by the reaction of MgO and O to form Mg (R2) and also by reaction R12 on the underside of the layer, which results in a nearly constant amount of Mg atoms in the Mg layer over the diurnal cycle, although the density of the reaction partners, e.g. ozone, varies by a factor of 10 between day and night.

There is also the dissociative recombination of Mg-containing ions (R22–R27) on the upper side of the layer, which produces Mg, but is less important for the formation of the Mg layer than the reactions of O and H with neutral reservoir species. More details on the neutral chemistry of Mg, which in summary is complex and does not have only one dominant reservoir species, are discussed by (Plane and Whalley, 2012). The seasonal cycle is thus a complex coupling of photochemistry involving O, H, O₃ and H₂O and transport (mainly vertical, but horizontal convergence/divergence is also significant at high latitudes). For

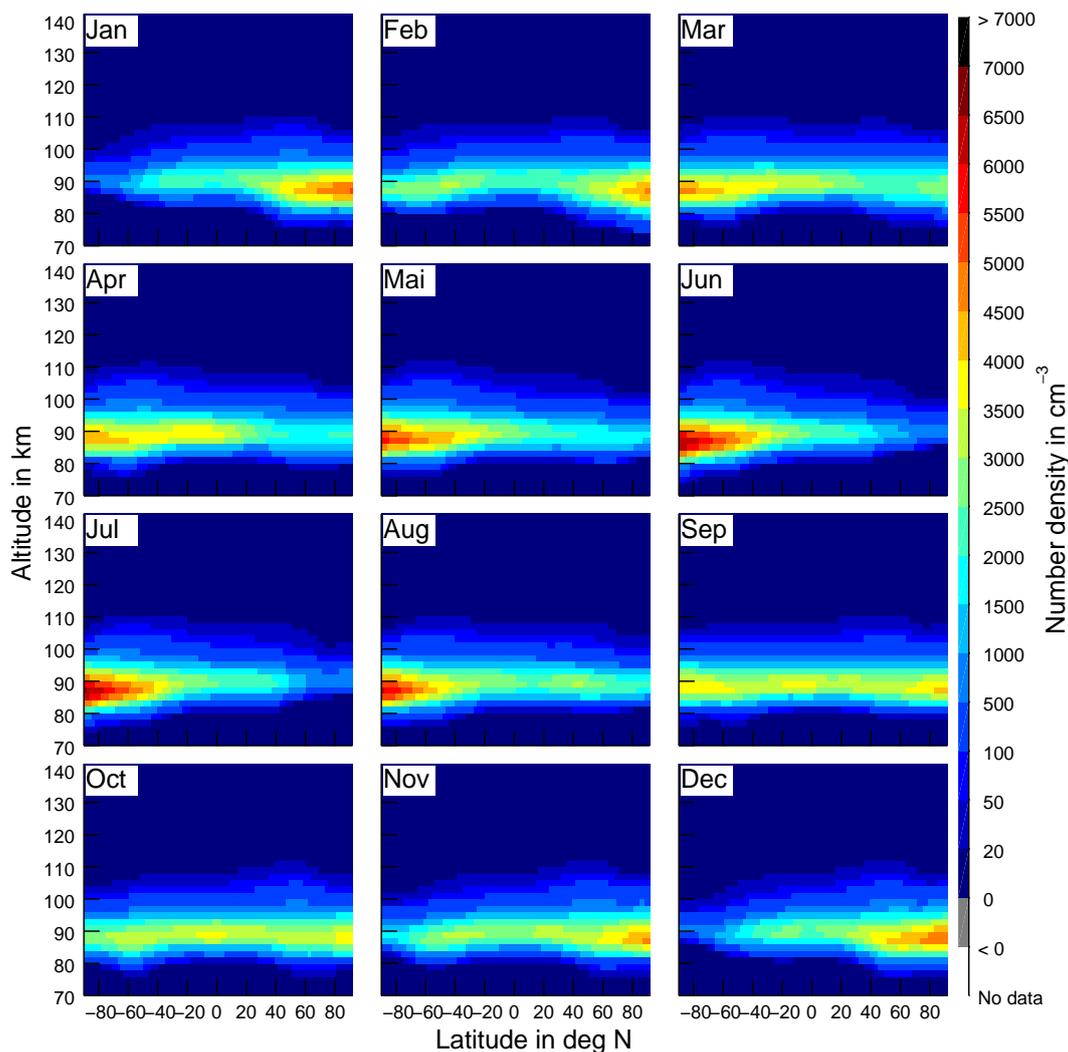


Figure 14. Monthly mean WACCM results for Mg averaged over 7 yr from 2005 to 2011. The model results show a clear seasonal cycle with a winter maximum, most pronounced at high latitudes.

mid and low latitudes this complex chemistry leads to a low seasonal variation of Mg, which is observed in both SCIAMACHY and WACCM data. Horizontal transport processes are important at high latitudes. At winter high latitudes, which are not observed by SCIAMACHY, WACCM shows a maximum for Mg, which is caused by the convergence of the meridional circulation over the polar vortex. At the summer pole the transport due to the meridional circulation reduces the Mg density.

The seasonal cycle of the Mg^+ layer is more easily explained than that of the Mg layer, and is mainly driven by the availability of the charged main atmospheric constituents NO^+ and O_2^+ for charge exchange reactions. The Mg^+ maximum thus can be found in summer, particular at high latitudes. A summarizing schematic diagram of the neutral and ionized magnesium chemistry is shown in Fig. 9 of (Plane and Whalley, 2012).

In contrast to the SCIAMACHY measurements, which are made at one particular local time, daily averaged output is used for WACCM in Figs. 14–16. We also co-located the WACCM data set to SCIAMACHY local time and latitudinal coverage, but found only small differences to the non co-located daily average mean of WACCM (not shown). There is a diurnal variation of the vertical column density in the WACCM data, but nearly no diurnal variation for the vertical profile shape. Figures 17 and 18 show the direct comparison of SCIAMACHY and WACCM annual means for Mg and Mg^+ . We used the co-located data for both plots, since these are the only plots with significant differences between not co-located daily means and co-located data, for latitudes higher than 40° . Figures 19 and 20 show the comparison for the equatorial vertical profile only.

The peak density of Mg for WACCM in the global annual mean profile is higher than for SCIAMACHY. How-

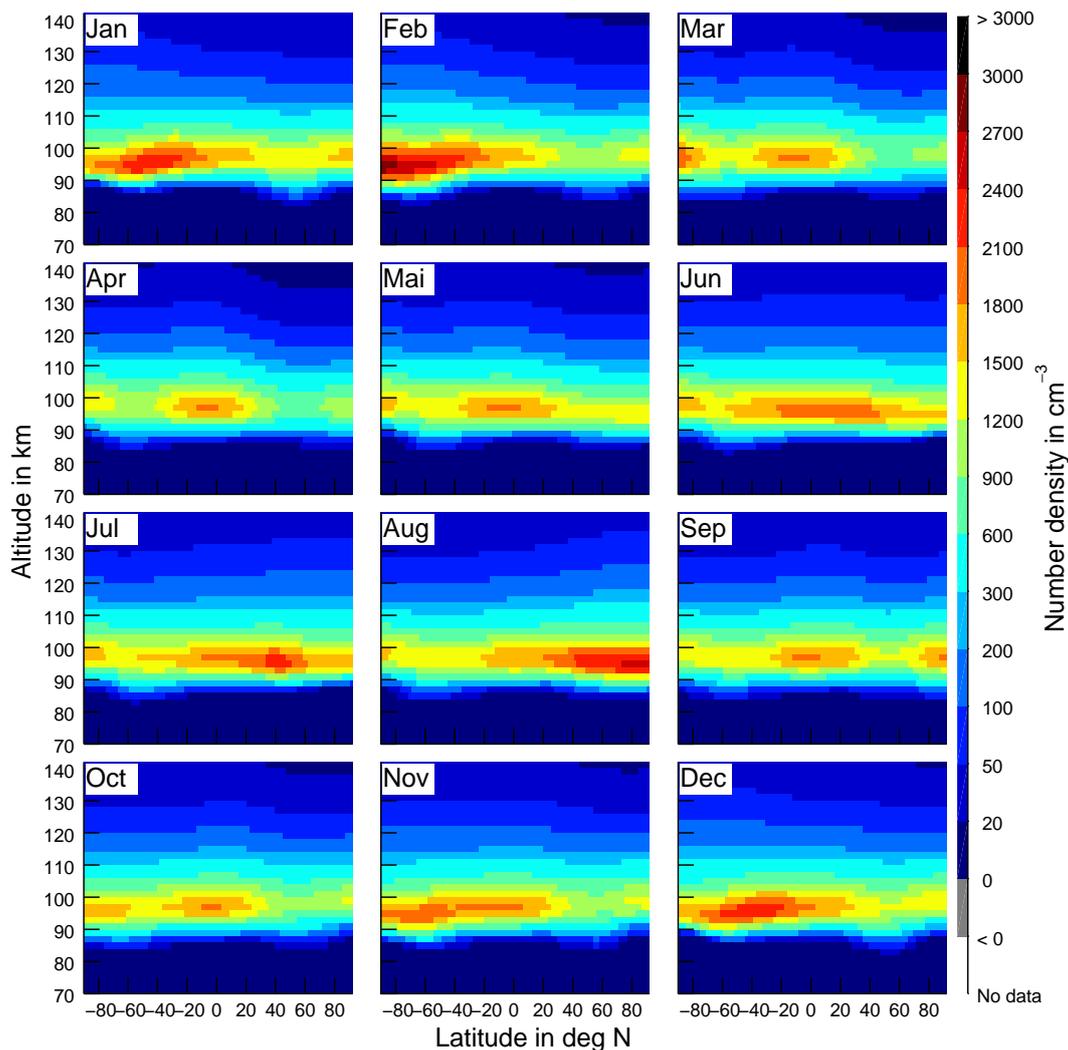


Figure 15. Monthly mean WACCM results for Mg^+ averaged over 7 yr from 2005 to 2011. The model results show a clear seasonal cycle with a summer maximum, most pronounced at high latitudes. There is also a second smaller maximum at high latitudes for the winter hemisphere.

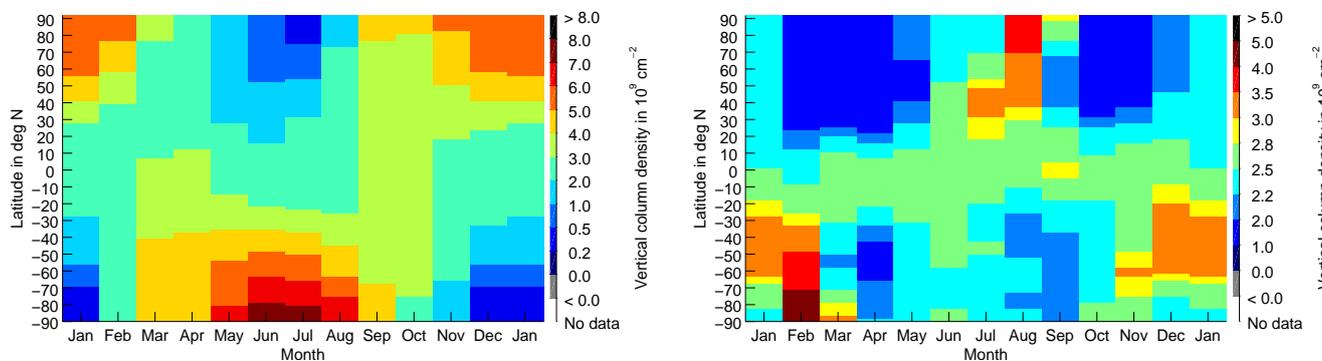


Figure 16. WACCM VCD timelines for different latitudes for Mg (left) and Mg^+ (right). Mg VCD varies between $0.5 \times 10^9 \text{ cm}^{-2}$ and $8 \times 10^9 \text{ cm}^{-2}$ and shows a clear seasonal cycle with a winter maximum, which is most pronounced at the poles. Mg^+ VCD varies from $1 \times 10^9 \text{ cm}^{-2}$ to $5 \times 10^9 \text{ cm}^{-2}$, with most VCD values between $2 \times 10^9 \text{ cm}^{-2}$ and $3 \times 10^9 \text{ cm}^{-2}$. A clear seasonal cycle with a summer maximum for Mg^+ is observed. SCIAMACHY results of VCD are shown in Figs. 5 and 9.

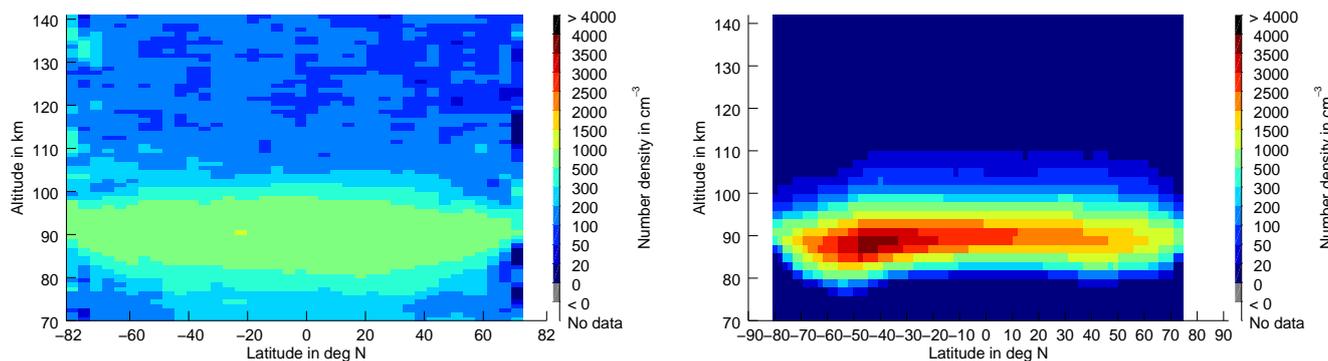


Figure 17. Annual means of Mg for SCIAMACHY (left) and WACCM (right). SCIAMACHY measures smaller peak density having a wider vertical profile than WACCM. The averaging for WACCM simulations is restricted to match the time periods, where SCIAMACHY measurements are available.

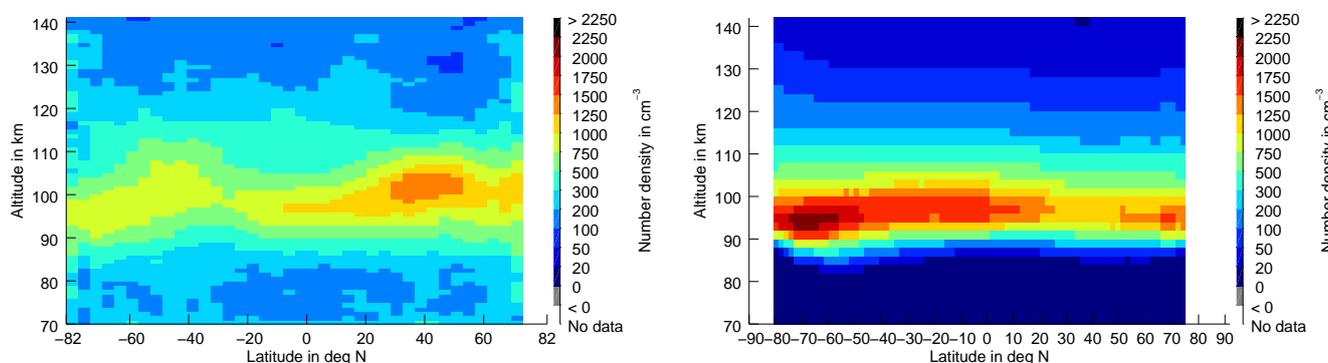


Figure 18. Annual means of Mg^+ for SCIAMACHY (left, 280.4 nm) and WACCM (right). SCIAMACHY shows a wider vertical profile, and a stronger latitudinal dependence of the peak altitude. The peak density of both is in very good agreement. The averaging for WACCM simulations is restricted to match the time periods, where SCIAMACHY measurements are available.

ever, the peak width of the SCIAMACHY profile is larger than for WACCM. Therefore, the VCD of SCIAMACHY and WACCM is globally similar, which shows that determining the Mg input rate so that the Mg^+ VCD is in agreement also leads to an agreement in the neutral Mg VCD. The altitude of the maximum number density of Mg at the equator is at 90 km for both SCIAMACHY and WACCM. In the high-latitude region, which is only covered by SCIAMACHY in summer, however, the maximum number density altitude of WACCM is about 2–4 km lower than for SCIAMACHY. Considering the 3.3 km vertical sampling in the SCIAMACHY measurements the ≈ 3.5 km vertical resolution of WACCM in the MLT and the altitude grid step size of 2 km for WACCM and 1 km for SCIAMACHY, this difference is small, but nevertheless significant.

A possible retrieval issue, which might explain the wider SCIAMACHY peak, is a strong Ring effect influence (Grainger and Ring, 1962) for the Mg spectral line. At the lower and upper peak edge, the SCIAMACHY number density is not zero. This may be related to the requirement in the retrievals that the density must be positive, which is needed for stability in the retrieval. However, the density is smaller

than the single day error there (error estimation for the Mg and Mg^+ data set has been done by (Langowski et al., 2013), e.g. Figs. 21–23). When averaging the data, it must be kept in mind that the error for the close to zero density region does not become smaller, as this is a systematic error induced by initial statistical errors, rather than simply a statistical error.

The agreement of WACCM and SCIAMACHY is better for Mg^+ . The WACCM Mg^+ peak and column densities are of similar magnitude as the SCIAMACHY results and also show the same seasonal variability with a summer maximum. There are also small differences: the global density maximum, which is found in the summer hemisphere and which moves over time to the other hemisphere, is not reduced in the WACCM data when passing the equatorial region during equinox and also has a stronger extension to the higher latitudes in summer. In addition, a second maximum appears in the winter hemisphere at high latitudes in the WACCM data set. SCIAMACHY makes no measurements during polar night and so this second maximum is not observed. The WACCM results do not show the strong seasonality and latitude dependence of the peak altitude, that can be found in the SCIAMACHY results. The peak altitude of 95 km in

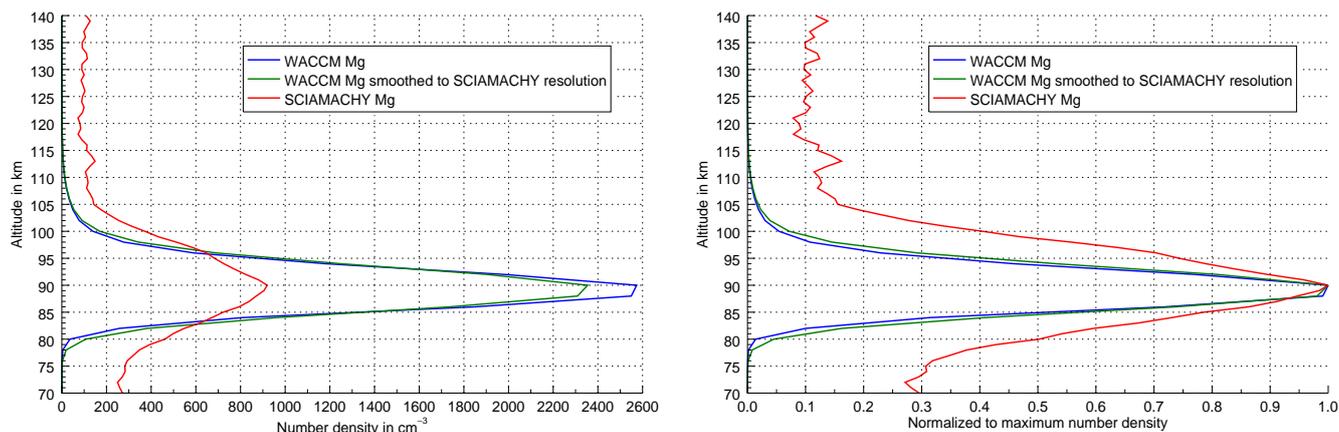


Figure 19. Equatorial annual mean vertical profile of Mg for SCIAMACHY and WACCM. The right plot shows the profiles normalized to the maximum of each profile, to better compare the shape of the profiles. The smoothed profile is smoothed with a triangular function with a base width of 4 km. The VCD between 70 and 140 km is $2.3 \times 10^9 \text{ cm}^{-2}$ for SCIAMACHY and $2.5 \times 10^9 \text{ cm}^{-2}$ for WACCM. Note that the statistical error for SCIAMACHY estimated by Langowski et al. (2013) (Fig. 21) is $\approx \pm 200 \text{ cm}^{-3}$ for the low-density region above 100 km and below 80 km and $\approx \pm 400 \text{ cm}^{-3}$ at 90 km.

Table 4. Ion–molecule chemistry of magnesium added into WACCM.

No.	Reaction	Rate/ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Reference
R16	$\text{Mg}^+ + \text{O}_3 \rightarrow \text{MgO}^+ + \text{O}_2$	$k_{16} = 1.2 \times 10^{-9}$	Whalley et al. (2011)
R17	$\text{MgO}^+ + \text{O} \rightarrow \text{Mg}^+ + \text{O}_2$	$k_{17} = 5.9 \times 10^{-10}$	Whalley and Plane (2010)
R18	$\text{MgO}^+ + \text{O}_3 \rightarrow \text{Mg}^+ + 2\text{O}_2$	$k_{18} = 1.8 \times 10^{-10}$	Whalley et al. (2011)
R19	$\text{MgO}^+ + \text{O}_3 \rightarrow \text{MgO}_2^+ + \text{O}_2$	$k_{19} = 3.3 \times 10^{-10}$	Whalley et al. (2011)
R20	$\text{Mg}^+ + \text{N}_2 + \text{M} \rightarrow \text{MgN}_2^+ + \text{M}$	$k_{20} = 1.8 \times 10^{-30} (T/200)^{-1.72}$	Whalley et al. (2011)
R21	$\text{Mg}^+ + \text{O}_2 + \text{M} \rightarrow \text{MgN}_2^+ + \text{M}$	$k_{21} = 2.4 \times 10^{-30} (T/200)^{-1.65}$	Whalley et al. (2011)
R22	$\text{MgN}_2^+ + \text{e}^- \rightarrow \text{Mg} + \text{N}_2$	$k_{22} = 3.0 \times 10^{-7} (T/200)^{-0.5}$	Plane and Whalley (2012)
R23	$\text{MgCO}_2^+ + \text{e}^- \rightarrow \text{Mg} + \text{CO}_2$	$k_{23} = 3.0 \times 10^{-7} (T/200)^{-0.5}$	Plane and Whalley (2012)
R24	$\text{MgH}_2\text{O}^+ + \text{e}^- \rightarrow \text{Mg} + \text{H}_2\text{O}$	$k_{24} = 3.0 \times 10^{-7} (T/200)^{-0.5}$	Plane and Whalley (2012)
R25	$\text{MgO}^+ + \text{e}^- \rightarrow \text{Mg} + \text{O}$	$k_{25} = 3.0 \times 10^{-7} (T/200)^{-0.5}$	Plane and Whalley (2012)
R26	$\text{MgO}_2^+ + \text{e}^- \rightarrow \text{Mg} + \text{O}_2$	$k_{26} = 3.0 \times 10^{-7} (T/200)^{-0.5}$	Plane and Whalley (2012)
R27	$\text{Mg}^+ + \text{e}^- \rightarrow \text{Mg} + h\nu$	$k_{27} = 1.0 \times 10^{-12}$	Plane and Helmer (1995)
R28	$\text{Mg} + \text{O}_2^+ \rightarrow \text{Mg}^+ + \text{O}_2$	$k_{28} = 1.2 \times 10^{-9}$	Rutherford et al. (1971)
R29	$\text{Mg} + \text{NO}^+ \rightarrow \text{Mg}^+ + \text{NO}$	$k_{29} = 8.2 \times 10^{-10}$	Rutherford et al. (1971)
R30	$\text{MgN}_2^+ + \text{O}_2 \rightarrow \text{MgO}_2^+ + \text{N}_2$	$k_{30} = 3.5 \times 10^{-12}$	Whalley et al. (2011)
R31	$\text{MgO}_2^+ + \text{O} \rightarrow \text{MgO}^+ + \text{O}_2$	$k_{31} = 6.5 \times 10^{-10}$	Whalley and Plane (2010)
R32	$\text{Mg}^+ + \text{H}_2\text{O} + \text{M} \rightarrow \text{MgH}_2\text{O}^+ + \text{M}$	$k_{32} = 2.3 \times 10^{-28} (T/200)^{-2.53}$	Martínez-Núñez et al. (2010)
R33	$\text{Mg}^+ + \text{CO}_2 + \text{M} \rightarrow \text{MgCO}_2^+ + \text{M}$	$k_{33} = 4.6 \times 10^{-29} (T/200)^{-1.42}$	Whalley and Plane (2010)

WACCM is in slightly better agreement with the rocket data than with SCIAMACHY. The differences of the vertical profile of WACCM and SCIAMACHY are small especially at the equator (see Fig. 20).

The lower peak edge of Mg^+ is in better agreement than for Mg. The impact of the filling-in of the Fraunhofer lines in the atmosphere by rotational Raman scattering by air molecules is much weaker for Mg^+ than for Mg. The agreement of the peak edge becomes worse with larger distance from the peak altitude. Nevertheless, the FWHM of the peak is in good agreement.

A part of the differences between the WACCM results and the SCIAMACHY measurements may be attributed to transport processes of charged particles in electromagnetic fields in the lower thermosphere. The equatorial electron distribution with transport from the equator to higher latitudes has been observed in ionospheric soundings. It is known as the equatorial anomaly or Appleton anomaly (Kendall and Windle, 1965). Typically there are fewer electrons at the equator than at 20° on either side of the equator due to this transport.

Similar transport processes have also been observed for the ions and in situ satellite measurements of the metals

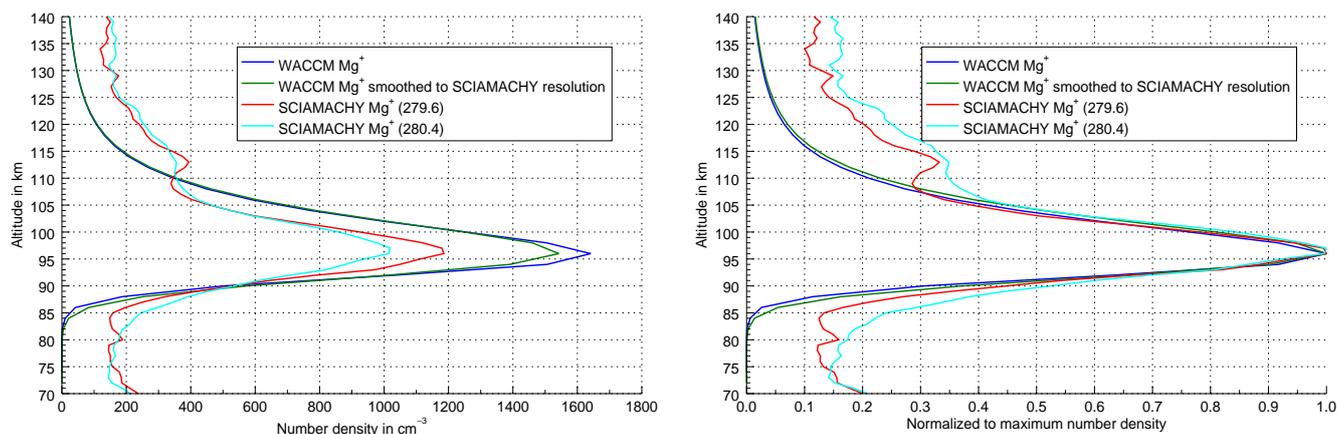


Figure 20. Vertical profiles of Mg^+ for SCIAMACHY and WACCM at the equator. The right plot shows the profiles normalized to the maximum of each profile, to better compare the shape of the profiles. The VCD between 70 and 140 km at the equator is $2.7 \times 10^9 \text{ cm}^{-2}$ for SCIAMACHY (both 279.6 nm and 280.4 nm) and $2.4 \times 10^9 \text{ cm}^{-2}$ for WACCM. Note that the statistical error for SCIAMACHY estimated by (Langowski et al., 2013) (Figs. 22 and 23) is $\approx \pm 150 \text{ cm}^{-3}$ for the 279.6 nm line and $\approx \pm 250 \text{ cm}^{-3}$ for the 280.4 nm line.

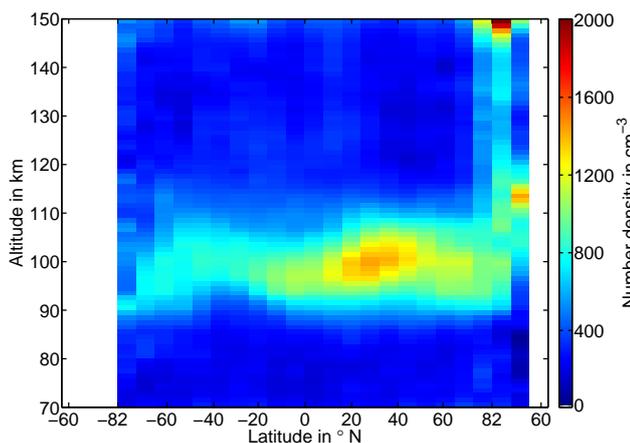


Figure 21. Mg^+ profiles averaged over all available data for 2008–2012 for the Mg^+ line at 280.4 nm. The stray-light contaminated measurements at the start of the sunlit part of each orbit are also used here extending the coverage to higher northern latitudes and even the ascending node side. High Mg^+ density is observed at the north pole. See Fig. 1 and Sect. 4 (second paragraph) for an explanation of the x -axis labels. Note that this is an older plot, which shows data with a wrong polarization correction, which is, however, unimportant for the effect shown here.

above 120 km, e.g. have been carried out using the Atmospheric Explorer satellite. A discussion of this data set can be found in Grebowsky and Aikin (2002).

The vertical upward transport of Mg^+ near the equator has been discussed, e.g. in Hanson and Sterling (1972), which is followed here. The sun is passing the equatorial region from east to west. The ionization in the thermosphere is strong for low solar zenith angles which leads to denser plasmas there. This leads to a strong electric field from east to west, which results in a strong eastwards current, the so-called equatorial

electrojet (see, e.g. (Forbes, 1981)) within $\pm 3^\circ$ around the geomagnetic equator.

The motion of a single charged particle with charge q can be separated into the gyration in the magnetic field \mathbf{B} , and the motion of the guiding centre. For a force \mathbf{F} , which is perpendicular to the magnetic field, the guiding centre moves perpendicular to \mathbf{B} and \mathbf{F} with the drift velocity $\mathbf{v} = \frac{1}{q} \frac{\mathbf{F} \times \mathbf{B}}{B^2}$. Using the Lorentz force $\mathbf{F} = q\mathbf{E}$ results in the drift velocity $\mathbf{v} = \frac{\mathbf{E} \times \mathbf{B}}{B^2}$. This drift is called $\mathbf{E} \times \mathbf{B}$ -Drift (see, e.g. the textbook of Chen, 1984).

The magnetic field along the meridians and the electric field along the equator lead to an $\mathbf{E} \times \mathbf{B}$ -Drift perpendicular to both fields into the radial direction, which lifts both electrons and ions into higher-altitude regions and even above the F-layer. However, because of the limited extent of the equatorial electrojet, this effect can only explain an upward transport of Mg^+ within $\pm 3^\circ$ N geomagnetic latitude. Fesen et al. (1983) showed that additionally neutral meridional winds have to be taken into account in order to explain vertical transport also at higher latitudes up to 30° and this was experimentally shown, e.g. in Fesen and Hays (1982a, b) and Gérard and Monfils (1978).

The annual mean of SCIAMACHY Mg^+ density (see Fig. 7) shows a higher density above 110 km at the northernmost and southernmost latitudes due to less coverage and, therefore, higher statistical errors. However, at high northern latitudes and at the ascending node side, which is cut off in the shown results, high density is retrieved when also using the stray-light contaminated measurements. This is shown in Fig. 21. The results as well as the input raw data show low density below 90 km and at different altitudes in between the high signal region, which makes a differentiation between a stray-light effect and a true metal emission complicated. Should this feature be real it could be explained by the cleft

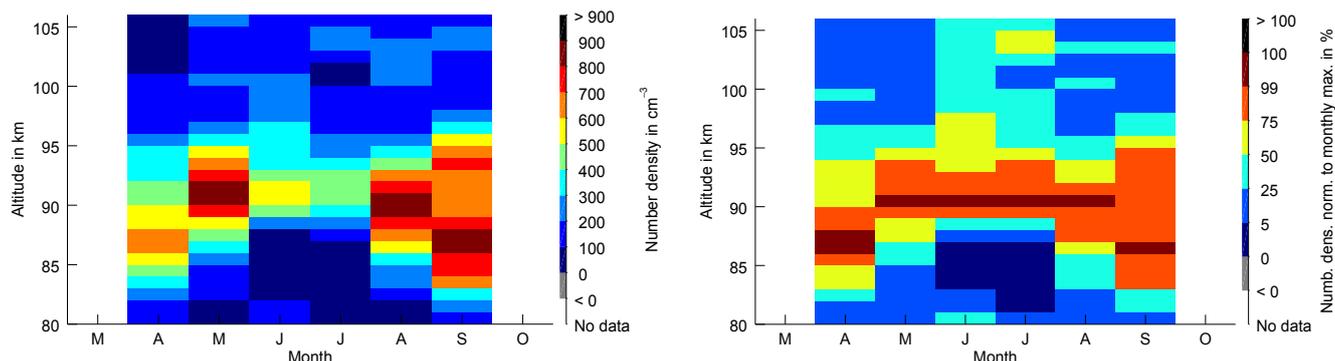


Figure 22. Vertical profile of Mg density (left) and Mg density normalized to the monthly maximum (right) at 70° N, a latitude observed with SCIAMACHY before, during and after the period when NLCs occur. NLCs occur at this latitude between about the end of May and mid-August.

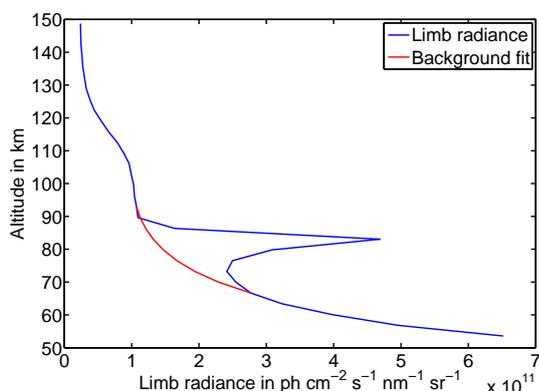


Figure 23. Averaged SCIAMACHY limb MLT signal between 458 and 552 nm showing a NLC signature at 84 km and a background fit. The NLC radiance is quantified as the summed up differences between the signal and the background fit in the vicinity of the NLCs signal.

ion fountain found by Lockwood et al. (1985), which describes the transport of charged particles along the magnetic field lines, which strongly converge at the pole. This transport may lift charged particles up to several Earth radii until they become neutralized and sink down if they are heavy enough and are not quickly ionized again.

8 Mg, Mg^+ and noctilucent clouds

Metal chemistry plays a role in the generation of nucleation nuclei required for the formation of NLCs. Consequently it is interesting to investigate the change of the Mg and Mg^+ layers in the vicinity of NLCs. The vertical profile shape of Mg at around 70° N shown in Fig. 22 changes during the summer and shows a weak uplift and thinning of the layer (especially in June and July), which, however, is hard to qualify as significant, as Mg shows strong variations and in addition the latitudinal edge region of the retrieval bears potential for

systematic errors, since, e.g. the latitudinal smoothing constraint used does not work well at the edge. An uplift of the layer, may also be attributed to transport due to the upper mesospheric meridional circulation (Note that in Figs. 22 and 24 fewer data are cut out at the high latitudes, so that more months are covered, with the tradeoff of more edge artifacts, especially in the south).

The VCD, however, is significantly reduced at polar latitudes during the summer and the reduction is stronger in the NH than in the SH. In contrast to the WACCM-Mg model results Mg^+ does not show the highest density in summer at high latitudes, but at mid latitudes. NLCs, which are not considered in WACCM-Mg, occur at polar latitudes during a 3 month period in the summer hemisphere.

NLCs can be detected in many different ways. For example they show an increased amplitude of backscattered radiation at the altitude of their appearance. This is used here to quantify the amount of NLCs. A two-step algorithm is used (for details see Langowski, 2015). First it is determined whether NLCs are detected at all. Afterwards the amount of NLCs is determined only for the cases where NLCs are identified, as otherwise this quantification produces wrong results. The quantification is illustrated in Fig. 23. At a certain wavelength window (here we use 458 to 552 nm), where the signal is dominated mainly by Rayleigh scattering, the average signal is formed for each tangent altitude of the MLT measurements. NLCs are typically observed as peaks at around 84 km. The background spectra, which results only from Rayleigh-scattering without NLCs, is fitted and subtracted from the limb radiance. The remaining signal is summed up and the resulting quantity is called NLC radiance here.

The VCD of Mg and Mg^+ and the NLC radiance are shown in Fig. 24. The NLC radiance is well anticorrelated with both the Mg and Mg^+ density at high latitudes. However, this does not unambiguously imply that the lower VCD of Mg and Mg^+ is dominated by Mg being taken up by NLC particles, as other effects may play a more dominant role. For

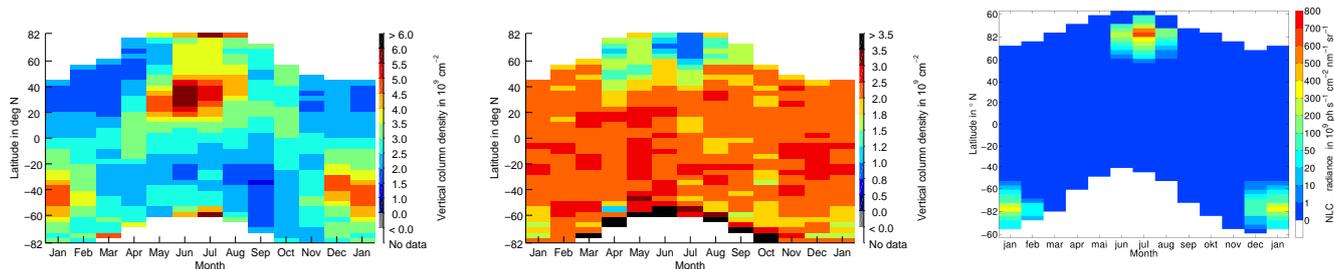


Figure 24. Vertical column density of Mg^+ (left), Mg (mid) and NLC radiance (right) retrieved from SCIAMACHY. A clear reduction of Mg^+ and Mg VCD is observed in the vicinity of NLCs. However, this is also observed in neighbouring regions without NLCs and can also be explained by other processes. (Note that the NLCs retrieval includes more latitudes from the ascending node side).

example, the seasonal variation with a summer minimum for Mg is even more pronounced in the WACCM-Mg (also for Na and Fe) model, which does not consider NLCs, than in the SCIAMACHY results, and in the SCIAMACHY results the Mg density is also reduced at regions, e.g. 50°N in April, where no NLCs occur. The Mg^+ layer is formed at the top of the NLC particles region and only weakly overlaps with the region where NLCs are formed. Furthermore, Lorentz-force-induced upward transport may reduce the Mg^+ density at the poles.

In summary it is interesting to note that the VCD of both Mg and Mg^+ is lower in summer during NLCs episodes but further investigations are needed to understand the origin of the lower Mg and Mg^+ density to decide whether loss to NLCs or other processes are dominant.

9 Summary and conclusions

Monthly averaged global vertical and latitudinal density distributions of Mg and Mg^+ retrieved from the SCIAMACHY limb MLT measurements from 2008 to 2012 have been shown. The MLT measurements cover the vertical region between 70 km and 150 km and have a good vertical resolution in the peak region.

Mg shows highly variable results and variability is mostly affected by the measurement error and no clear seasonal cycle can be observed for Mg, apart from the northern high latitudes where a summer minimum is observed. The peak altitude of Mg is nearly constant at around 90 km for all latitudes and times.

Mg^+ shows a clear seasonal cycle with a summer maximum in the peak density, most pronounced at mid latitudes. Mg^+ shows a seasonal variation of the peak altitude with higher altitudes in the summer, as well as a latitudinal dependence of the peak altitudes with up to 5–10 km higher altitudes at mid latitudes compared to the equatorial peak altitude of 95 km.

The SCIAMACHY results are reasonably consistent with previously published rocket profiles and significantly extend the amount of data of Mg and Mg^+ . The peak density values

and the observed seasonality for Mg^+ are in good agreement. However, the rocket measurements do not show the latitudinal dependence of the peak altitude, but typically show peak altitudes at slightly below 95 km.

The SCIAMACHY results were compared with WACCM-Mg model results. For Mg WACCM shows a clearer seasonal cycle with a winter maximum at the poles than SCIAMACHY. The WACCM Mg peak density is roughly a factor 2–3 bigger than the SCIAMACHY peak density. The peak altitude and peak shape are in good agreement with SCIAMACHY, which shows a slightly wider profile. The combination of higher peak density for WACCM, but wider peak profile for SCIAMACHY, leads to very similar values for the VCD.

The agreement between WACCM and SCIAMACHY is generally better for Mg^+ than for Mg. Both SCIAMACHY and WACCM Mg^+ results show a clear seasonal cycle with a summer maximum and the peak density is in good agreement. However, similar to the limited number of the rocket measurements, WACCM does not show a latitudinal dependence of the peak altitude. The peak shape of Mg^+ agrees well for WACCM and SCIAMACHY in the high-density region, where the SCIAMACHY error is low.

During the arctic summer Mg and Mg^+ show a density minimum at high latitudes. This is in coincidence with the occurrence of NLCs, but our results do not allow the conclusion that the Mg and Mg^+ reduction at high latitudes during summer is related to the occurrence of NLCs. Further investigations involving model simulations are required to address this question.

Acknowledgements. We wish to thank AFOSR and EOARD for the financial support of the project (grant#FA8655-09-3012). SCIAMACHY is jointly funded by Germany, the Netherlands and Belgium. This work was in part supported by the University of Bremen and Ernst-Moritz-Arndt-University of Greifswald and by the ESA Mesosphero project. SCIAMACHY data were kindly provided by the European Space Agency (ESA). The WACCM-Mg modelling work was supported by the UK Natural Environment Research Council (NERC grant NE/G019487/1) and the European Research Council (project number 291332-CODITA). The National

Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under sponsorship of the National Science Foundation.

Edited by: E. Kyrölä

References

- Aikin, A. C. and Goldberg, R. A.: Metallic ions in the equatorial ionosphere, *J. Geophys. Res.*, 78, 734–745, 1973.
- Anderson, J. G. and Barth, C. A.: Rocket investigation of the Mg I and Mg II dayglow, *J. Geophys. Res.*, 76, 3723–3732, 1971.
- Bender, S., Sinnhuber, M., Burrows, J. P., Langowski, M., Funke, B., and López-Puertas, M.: Retrieval of nitric oxide in the mesosphere and lower thermosphere from SCIAMACHY limb spectra, *Atmos. Meas. Tech.*, 6, 2521–2531, doi:10.5194/amt-6-2521-2013, 2013.
- Boksenberg, A. and Gérard, J. C.: Ultraviolet observations of equatorial dayglow above the F_2 Peak, *J. Geophys. Res.*, 78, 4641–4650, 1973.
- Bovensmann, H., Burrows, J. P., Buchwitz, M., Frerick, J., Noël, S., Rozanov, V. V., Chance, K. V., and Goede, A. P. H.: SCIAMACHY: mission objectives and measurement modes, *J. Atmos. Sci.*, 56, 127–150, 1999.
- Brown, P. and Jones, J.: A determination of the strengths of the sporadic radio-meteor sources, *Earth Moon Planets*, 68, 223–245, 1995.
- Burrows, J. P., Hölzle, E., Goede, A. P. H., Visser, H., and Fricke, W.: SCIAMACHY–scanning imaging absorption spectrometer for atmospheric cartography, *Acta Astronaut.*, 35, 445–451, 1995.
- Cepelcha, Z., Borovička, J., Elford, W. G., Revelle, D. O., Hawkes, R. L., Porubčan, V., and Šimek, M.: Meteor phenomena and bodies, *Space Sci. Rev.*, 84, 327–471, 1998.
- Chandrasekhar, S.: *Radiative Transfer*, Dover Publ., New York, 1960.
- Chen, F. F.: *Introduction to plasma physics and controlled fusion volume 1: plasma physics*, 2nd ed., Springer, New York, 1984.
- Correia, J.: *Temporal and Spatial Distribution of Metallic Species in the Upper Atmosphere*, Ph.D. thesis, The Catholic University of America, Washington D.C., 2009.
- Correia, J., Aikin, A. C., Grebowsky, J. M., Pesnell, W. D., and Burrows, J. P.: Seasonal variations of magnesium atoms in the mesosphere-thermosphere, *Geophys. Res. Lett.*, 35, 330–337, 2008.
- Correia, J., Aikin, A. C., Grebowsky, J. M., and Burrows, J. P.: Metal concentrations in the upper atmosphere during meteor showers, *Atmos. Chem. Phys.*, 10, 909–917, doi:10.5194/acp-10-909-2010, 2010.
- Curtius, J., Weigel, R., Vössing, H.-J., Wernli, H., Werner, A., Volk, C.-M., Konopka, P., Krebsbach, M., Schiller, C., Roiger, A., Schlager, H., Dreiling, V., and Borrmann, S.: Observations of meteoric material and implications for aerosol nucleation in the winter arctic lower stratosphere derived from in situ particle measurements, *Atmos. Chem. Phys.*, 5, 3053–3069, doi:10.5194/acp-5-3053-2005, 2005.
- Feng, W., Marsh, D. R., Chipperfield, M. P., Janches, D., Hoffner, J., Yi, F., and Plane, J. M. C.: A global atmospheric model of meteoric iron, *J. Geophys. Res.-Atmos.*, 118, 9456–9474, 2013.
- Fentzke, J. T. and Janches, D.: A semi-empirical model of the contribution from sporadic meteoroid sources on the meteor input function observed at arecibo, *J. Geophys. Res.*, 113, A03304, doi:10.1029/2007JA012531, 2008.
- Fesen, C. G., and Hays, P. B.: Mg^+ Morphology from visual airglow experiment observations, *J. Geophys. Res.*, 87, 9217–9223, 1982a.
- Fesen, C. G., and Hays, P. B.: Two-dimensional inversion technique for satellite airglow data, *Appl. Optics*, 21, 3784–3791, 1982b.
- Fesen, C. G., Hays, P. B., and Anderson, D. N.: Theoretical Modelling of Low-Latitude Mg^+ , *J. Geophys. Res.*, 88, 3211–3223, 1983.
- Flynn, G.: Chapter 4 in: *Meteors in the Earth’s Atmosphere*, edited by: Murad, E. and Williams, I. P., Cambridge University Press, Cambridge, 2002.
- Forbes, J. M.: The equatorial electrojet, *Rev. of Geophys.*, 19, 469–504, 1981.
- Frisch, M., Trucks, G., Schlegel, H., Scuseria, G., Robb, M., Cheeseman, J., Scalmani, G., Barone, V., Mennucci, B., Petersson, G., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H., Izmaylov, A., Bloino, J., Zheng, G., Sonnenberg, J., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., J. A. Montgomery, J., Peralta, J., Ogliaro, F., Bearpark, M., Heyd, J., Brothers, E., Kudin, K., Staroverov, V., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J., Iyengar, S., Tomasi, J., Cossi, M., Rega, N., Millam, J., Klene, M., Knox, J., Cross, J., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R., Yazyev, O., Austin, A., Cammi, R., Pomelli, C., Ochterski, J., Martin, R., Morokuma, K., Zakrzewski, V., Voth, G., Salvador, P., Dannenberg, J., Dapprich, S., Daniels, A., Farkas, O., Foresman, J., Ortiz, J., Cioslowski, J., and Fox, D.: *Gaussian 09, Revision A.1*, Gaussian Inc., available at: www.gaussian.com (14 November 2011), 2009.
- García, R. R., Marsh, D. R., Kinnison, D. E., Boville, B. A., and Sassi, F.: Simulation of secular trends in the middle atmosphere, 1950–2003, *J. Geophys. Res.*, 112, D09301, doi:10.1029/2006JD007485, 2007.
- Gardner, J. A., Viereck, R. A., Murad, E., Knecht, J., Pike, C. P., Broadfoot, A. L., and Anderson, E. R.: Simultaneous observations of neutral and ionic magnesium in the thermosphere, *Geophys. Res. Lett.*, 22, 2119–2122, 1995.
- Gardner, J. A., Broadfoot, A. L., McNeil, W. J., Lai, S. T., and Murad, E.: Analysis and modeling of the GLO-I observations of meteoric metals in the thermosphere, *J. Atmos. Sol.-Terr. Phys.*, 61, 542–562, 1999.
- Gardner, C. S., Liu, A. Z., Marsh, D. R., Feng, W., and Plane, J. M. C.: Inferring the Global Cosmic Dust Influx to the Earth’s Atmosphere from Lidar Observations of the Vertical Flux of Mesospheric Na, *J. Geophys. Res. – Space Physics*, doi:10.1002/2014JA020383, 2014.
- Gérard, J. C. and Monfils, A.: Satellite Observations of the Equatorial Mg II Dayglow Intensity Distribution, *J. Geophys. Res.*, 79, 2544–2550, 1974.

- Gérard, J. C. and Monfils, A.: The MgII Equatorial Airglow Altitude Distribution, *J. Geophys. Res.*, 83, 4389–4391, 1978.
- Grainger, J. and Ring, J.: Anomalous Fraunhofer Line Profiles, *Nature*, 193, 762, 1962.
- Grebowsky, J. M. and Aikin, A. C.: Chapter 8 in: *Meteors in the Earth's Atmosphere*, edited by: Murad, E. and Williams, I. P., Cambridge University Press, Cambridge, 2002.
- Grebowsky, J. M., Goldberg, R. A., and Pesnell, W. D.: Do meteor showers significantly perturb the ionosphere?, *J. Atmos. Sol-Terr. Phys.*, 60, 607–615, 1998.
- Hamilton, D. R.: The resonance radiation induced by elliptically polarized light, *Astrophys. J.*, 106, 457–465, 1947.
- Hanson, W. B. and Sterling, D. L.: Source and Identification of Heavy Ions in the Equatorial F Layer, *J. Geophys. Res.*, 77, 5530–5541, 1972.
- Herrmann, U., Eberhardt, P., Hidalgo, M. A., and Kopp, E.: Metal ions and isotopes in sporadic E-layer during Perseid meteor shower, *Space Res.*, 18, 249–252, 1978.
- Hunten, D. M., Turco, R. P., and Toon, O. B.: Smoke and dust particles of meteoric origin in the mesosphere and stratosphere, *J. Atmos. Sci.*, 37, 1342–1357, 1980.
- Istomin, V.: Ions of extra-terrestrial origin in the earth's ionosphere, *Planet. Space Sci.*, 11, 173–181, 1963.
- Janches, D., Heinselman, C., Chau, J., Chandran, A., and Woodman, R.: Modeling the global micrometeor input function in the upper atmosphere observed by high power and large aperture radars, *J. Geophys. Res.*, 111, A07317, doi:10.1029/2006JA011628, 2006.
- Janches, D., Dyrud, L. P., Broadley, S. L., and Plane, J. M. C.: First observations of micrometeoroid differential ablation in the atmosphere, *Geophys. Res. Lett.*, 36, L06101, doi:10.1029/2009GL037389, 2009.
- Jenniskens, P.: *Meteor Showers and Their Parent Comets*, Cambridge University Press, Cambridge, 2006.
- Johnson, C. Y. and Meadows, E. B.: First Investigation of Ambient Positive-Ion Composition to 219 km by Rocket-Borne Spectrometer, *J. Geophys. Res.*, 60, 193–203, 1955.
- Joiner, J. and Aikin, A. C.: Temporal and spatial variations in upper atmospheric Mg⁺, *J. Geophys. Res.*, 101, 5239–5250, 1996.
- Kalashnikova, O., Horanyi, M., Thomas, G. E., and Toon, O. B.: Meteoric smoke production in the atmosphere, *Geophys. Res. Lett.*, 27, 3293–3296, 2000.
- Kendall, P. C. and Windle, D. W.: The Appleton anomaly, *Nature*, 207, 964–965, 1965.
- Kopp, E.: On the abundance of metal ions in the lower ionosphere, *J. Geophys. Res.*, 102, 9667–9674, 1997.
- Kopp, E. and Herrmann, U.: Ion composition in the lower ionosphere, *Ann. Geophys.*, 2, 83–94, 1984, <http://www.ann-geophys.net/2/83/1984/>.
- Kopp, E., Eberhardt, U., Herrmann, U., and Björn, L.: Positive ion composition of the high latitude summer D-region with noctilucent clouds, *J. Geophys. Res.*, 90, 13041–13053, 1985a.
- Kopp, E., Ramseyer, H., and Björn, L.: Positive ion composition and electron density in a combined auroral and NLC event, *Adv. Space Res.*, 4, 157–161, 1985b.
- Kramida, A., Ralchenko, Y., Reader, J., and NIST ASD Team: NIST Atomic Spectra Database (version 5.0), National Institute of Standards and Technology, Gaithersburg, MD, 2012.
- Krijger, J. M., Snell, R., van Harten, G., Rietjens, J. H. H., and Aben, I.: Mirror contamination in space I: approach, *Atmos. Meas. Tech. Discuss.*, 7, 1213–1246, 2014, <http://www.atmos-meas-tech-discuss.net/7/1213/2014/>.
- Langowski, M., Sinnhuber, M., Aikin, A. C., von Savigny, C., and Burrows, J. P.: Retrieval algorithm for densities of mesospheric and lower thermospheric metal atom and ion species from satellite borne limb emission signals, *Atmos. Meas. Tech.*, 7, 29–48, doi:10.5194/amt-7-29-2014, 2014.
- Langowski, M.: Investigation of metal atoms and ions in the mesosphere and lower thermosphere by satellite remote sensing with SCIAMACHY/Envisat, Ph. D. thesis, 2015.
- Liebing, P., Bramstedt, K., Noël, S., Rozanov, V., Bovensmann, H., and Burrows, J. P.: Polarization data from SCIAMACHY limb backscatter observations compared to vector radiative transfer model simulations, *Atmos. Meas. Tech.*, 6, 1503–1520, 2013, <http://www.atmos-meas-tech.net/6/1503/2013/>.
- Lockwood, M., Horwitz, J. R., Chandler, M. O., Waite, J. H., Moore, T. E., and Chappel, C. R.: The cleft ion fountain, *J. Geophys. Res.*, 90, 9736–9748, 1985.
- Marsh, D. R., Garcia, R. R., Kinnison, D. E., Boville, B. A., Sassi, F., Solomon, S. C., and Matthes, K.: Modeling the whole atmosphere response to solar cycle changes in radiative and geomagnetic forcing, *J. Geophys. Res.*, 112, D23306, doi:10.1029/2006JD008306, 2007.
- Marsh, D. R., Janches, D., Feng, W., and Plane, J. M. C.: A global model of meteoric sodium, *J. Geophys. Res.-Atmos.*, 118, 11442–11452, doi:10.1002/jgrd.50870, 2013a.
- Marsh, D. R., Mills, M. J., Kinnison, D. E., Lamarque, J. F., Calvo, N., and Polvani, L. M.: Climate Change from 1850 to 2005 Simulated in CESM1(WACCM), *J. Climate*, 26, 7372–7391, doi:10.1175/JCLI-D-12-00558.1, 2013b.
- Martínez-Núñez, E., Whalley, C. L., Shalashilin, D., and Plane, J. M. C.: Dynamics of Mg⁺+H₂O+He: Capture, collisional stabilization and collision-induced dissociation, *J. Phys. Chem. A*, 114, 6472–6479, doi:10.1021/jp102454j, 2010.
- Mathews, J. D., Janches, D., Meisel, D. D., and Zhou, Q.-H.: The micrometeoroid mass flux into the upper atmosphere: Arecibo results and a comparison with prior estimates, *Geophys. Res. Lett.*, 28, 1929–1932, 2001.
- McNeil, W. J., Lai, S. T., and Murad, E.: Differential ablation of cosmic dust and implications for the relative abundances of atmospheric metals, *J. Geophys. Res.*, 103, 10899–10911, 1998.
- Mende, S. B., Swenson, G. R., and Miller, K. L.: Observations of E and F Region Mg⁺ from Spacelab 1, *J. Geophys. Res.*, 90, 6667–6673, 1985.
- Minschwaner, K., Herceg, D., Budzien, S. A., Dymond, K. F., Fortna, C., and P., M. R.: Observations of middle ultraviolet emissions in the middle and lower thermosphere: NO, O₂, O and Mg⁺, *J. Geophys. Res.*, 112, A10311, 2007.
- Murad, E. and Williams, I. P.: *Meteors in the Earth's atmosphere*, Cambridge University Press, Cambridge, 2002.
- Narcisi, R. S.: Composition studies of the lower ionosphere, in: *Physics of the Upper Atmosphere*, edited by: Verniani, F., Editrice Compositori, Bologna, p. 12, 1971.
- Narcisi, R. S. and Bailey, A. D.: Mass spectrometric measurements of positive ions at altitudes from 64 to 112 kilometers, *J. Geophys. Res.*, 70, 3687–3700, 1965.

- Nesvorný, D., Jenniskens, P., Levison, H. F., Bottke, W., Vokrouhlický, D., and Gounelle, M.: Cometary origin of the Zodiacal Cloud and carbonaceous micrometeorites, implications for hot debris disks, *Astrophys. J.*, 713, 816–836, 2010.
- Nesvorný, D., Janches, D., Vokrouhlický, P., Pokorný, P., Bottke, W. F., and Jenniskens, P.: Dynamical model for the zodiacal cloud and sporadic meteors, *Astrophys. J.*, 743, 129, 2011a.
- Nesvorný, D., Vokrouhlický, P., Pokorný, P., and Janches, D.: Dynamics of dust particles released from oort cloud comets and their contribution to radar meteors, *Astrophys. J.*, 743, 37, 2011b.
- Philbrick, C. R., Narcisi, R. S., Good, R., Hoffmann, H. S., Keneshea, T. J., MacLeod, M. A., Zimmermann, S. P., and Reinisch, B. W.: The Aladdin Experiment – Part II, Composition, *Space Res.*, VII, 441–449, 1973.
- Plane, J. M. C.: Atmospheric chemistry of meteoric metals, *Chem. Rev.*, 103, 4963–4984, 2003.
- Plane, J. M. C.: Cosmic dust in the earth's atmosphere, *J. Atmos. Sol.-Terr. Phys.*, 41, 6507–6518, 2012.
- Plane, J. M. C., Feng, W., Dawkins, E., Chipperfield, M. P. C., Höffner, J., Janches, D. and Marsh, D. R.: Resolving the strange behaviour of extra-terrestrial potassium in the upper atmosphere, *Geophys. Res. Lett.*, doi:10.1002/2014GL060334, 2014.
- Plane, J. M. C. and Helmer, M.: Laboratory Study of Reactions $Mg + O_3$ and $MgO + O_3$, implications for the chemistry of magnesium in the upper atmosphere, *Faraday Discuss.*, 100, 411–430, 1995.
- Plane, J. M. C. and Whalley, C. L.: A new model for magnesium chemistry in the upper atmosphere, *J. Phys. Chem. A*, 116, 6240–6252, 2012.
- Rapp, M and Thomas, G. E.: Modelling the microphysics of mesospheric ice particles: Assessment of current capabilities and basic sensitivities, *J. Atm. Sol. Terr. Phys.*, 68, 715-744, 2006.
- Roddy, P. A., Earle, G. D., Swenson, C., Carlson, C. G., and Bullett, T. W.: Relative concentrations of molecular and metallic ions in the midlatitude intermediate and sporadic-E layers, *Geophys. Res. Lett.*, 31, L19807, 2004.
- Rollason, R. J. and Plane, J. M. C.: A kinetic study of the reactions of MgO with H_2O , CO_2 and O_2 : implications for magnesium chemistry in the mesosphere, *Phys. Chem. Chem. Phys.*, 3, 4733–4740, 2001.
- Rožanov, V. V., Rožanov, A. V., Kokhanovsky, A. A., and Burrows, J. P.: Radiative transfer through terrestrial atmosphere and ocean: Software package SCIATRAN, *J. Quant. Spect. Rad. Trans.* 133, 13–71, doi:10.5194/acp-8-1963-2008, 2014.
- Rutherford, J. A., Mathis, R. F., Turner, B. R. and Vroom, D. A.: Formation of Magnesium ions by charge transfer, *J. Chem. Phys.*, 55, 3785–3793, 1971.
- Saunders, R. W. and Plane, J. M. C.: A laboratory study of meteor smoke analogues: composition, optical properties and growth kinetics, *J. Atmos. Sol.-Terr. Phys.*, 68, 550–553, 2006.
- Scharringhausen, M.: Investigation of Mesospheric and Thermospheric Magnesium Species from Space, Ph.D. thesis, Universität Bremen, Bremen, Germany, 2007.
- Scharringhausen, M., Aikin, A. C., Burrows, J. P., and Sinnhuber, M.: Space-borne measurements of mesospheric magnesium species – a retrieval algorithm and preliminary profiles, *Atmos. Chem. Phys.*, 8, 1963–1983, doi:10.5194/acp-8-1963-2008, 2008a.
- Scharringhausen, M., Aikin, A. C., Burrows, J. P., and Sinnhuber, M.: Global column density retrieval of mesospheric and thermospheric MgI and MgII from SCIAMACHY limb and nadir radiance data, *J. Geophys. Res.*, 113, D13303, doi:10.1029/2007JD009043, 2008b.
- Suarez, M. J., Rienecker, M. M., Todling, R., Bacmeister, J., Takacs, L., Liu, H. C., Gu, W., Sinkiewicz, M., Kostar, R. D., Gelero, R., Stajner, I., and Nielsen, J. E.: The GEOS-5 Data Assimilation System-Documentation of Versions 5.0.1, 5.1.0, and 5.2.0, NASA/TM-2008-104606-VOL-27, 2008.
- Swider, W.: Ionic and neutral concentrations of Mg and Fe near 92 km, *Planet. Space Sci.*, 32, 307–312, 1984.
- Voigt, C., Schlager, H., Luo, B. P., Dörnbrack, A., Roiger, A., Stock, P., Curtius, J., Vössing, H., Borrmann, S., Davies, S., Konopka, P., Schiller, C., Shur, G., and Peter, T.: Nitric Acid Trihydrate (NAT) formation at low NAT supersaturation in Polar Stratospheric Clouds (PSC), *Atmos. Chem. Phys.*, 5, 1371–1381, doi:10.5194/acp-5-1371-2005, 2005.
- von Savigny, C., Kaiser, J. W., Bovensmann, H., Burrows, J. P., McDermid, I. S., and Leblanc, T.: Spatial and temporal characterization of SCIAMACHY limb pointing errors during the first three years of the mission, *Atmos. Chem. Phys.*, 5, 2593–2602, doi:10.5194/acp-5-2593-2005, 2005.
- von Savigny, C., Bovensmann, H., Bramstedt, K., Dikty, S., Ebojje, F., Jones, A., Noël, S., Rožanov, A., and Sinnhuber, B.-M.: Indications for long-term trends and seasonal variations in the SCIAMACHY Level 1 version 6.03 tangent height information, *Techn. Note-IUP-scia-pointing-2009-01*, University of Bremen, Bremen, Germany, Issue 2, 2009.
- Vondrak, T., Plane, J. M. C., Broadley, S., and Janches, D.: A chemical model of meteoric ablation, *Atmos. Chem. Phys.*, 8, 7015–7031, doi:10.5194/acp-8-7015-2008, 2008.
- Whalley, C. L. and Plane, J. M. C.: Meteoric ion layers in the Martian atmosphere, *Faraday Discuss.*, 147, 349–368, 2010.
- Whalley, C. L., Gómez Martín, J. C., Wright, T. G. and Plane, J. M. C.: A kinetic study of Mg^+ and Mg-containing ions reacting with O_3 , O_2 , N_2 , CO_2 , N_2O and H_2O , implications for magnesium ion chemistry in the upper atmosphere, *Phys. Chem. Chem. Phys.*, 13, 6352–6364, doi:10.1039/c0cp02637a, 2011.
- Zbinden, P. A., Hidalgo, M. A., Eberhardt, P., and Geiss, J.: Mass spectrometer measurements of the positive ion composition in the D- and E-Regions of the ionosphere, *Planet. Space Sci.*, 23, 1621–1642, 1975.