Water Vapour and Methane Coupling in the Stratosphere observed with SCIAMACHY Solar Occultation Measurements

by S. Noël et al.

MS No.: acp-2017-893

Authors' Response

Reply to referee 1

We thank the reviewer for the detailed comments which will help us to improve the paper. In the following, the original reviewer's comments are given in *italics*, our answer in normal font and the proposed updated text for the new version of the manuscript in **bold** font.

Note: It seems that line numbers in the comments refer to the manuscript before technical corrections, not the published discussion version.

General Comments

- *The paper is generally well written, but some of the grammar and phrasing could be significantly improved by allowing a native English speaker to edit it.*

  We will try to improve the English in the revised version and let our English co-author check it again. Therefore, the updated text might change slightly in the final revised version.

- *The oxidation of hydrogen (H2) in the stratosphere is also a source of water vapor. How is it that the equation for total hydrogen ("potential water") does not include a term for H2 oxidation?*

  We use the definition of Nassar et al. (2005) for potential water which does not include H2 (assuming that variations of H2 are small). This is mentioned in the introduction.

- *The paper would benefit from an early paragraph dedicated to describing the influences of the QBO on stratospheric entry mixing ratios of H2O and on the conversion of CH4 to H2O during transport from the tropics to higher latitudes. Currently there is a lot of attribution of inter-annual variations in H2O and CH4 to the QBO, but the actual QBO mechanisms that drive these variations are not really mentioned until late in the paper. Similarly, an earlier introduction of concepts like the lower and upper branches of the Brewer-Dobson circulation, along with a description of mean age and its utility in discerning stratospheric transport pathways, would be very helpful when discussing the observed couplings between CH4 and H2O. Currently, these concepts are discussed too late in the paper. The reasons why total hydrogen is a conserved quantity above the lowermost stratosphere may escape some readers. A simple explanation should be given, perhaps illustrating how mixing between air masses during transport does not change total hydrogen.*

  Will will add a corresponding paragraph in the introduction, which will be largely re-written in the revised version.

- *I don't see the need for Figure 11 as I am not quite sure what it explains. There is no caption to describe what is meant by the different shadings of green and purple (and white) arrows. I don't see anything in this Figure that isn't already described in detail in the text.*

  Indeed, this figure does not contain additional information about the results, but we think it is helpful to visualise the different transport pathways and related processes. We therefore prefer to keep the figure in the manuscript, but move it to the introduction. Different shadings are mainly for artistic purpose and should illustrate dynamics.

- *All trend values in the text should be presented with their uncertainties (95% confidence intervals) so the reader can gauge their significance. At many altitudes (if not all), the 9-year trends of CH4, H2O and total hydrogen are not statistically significant. Labeling trends as "negative", "positive", or "near-zero" is not justified if they are not statistically different from zero.*

  We will add trend uncertainties (2σ values) and also adapt the text accordingly (see answers to specific comments below).

Specific Comments

- *Page 1, Line 4: "theses" should be "these"*

  Will be corrected.

- *P1, L6-8: Are these trends "significant" as stated? Please include their uncertainties to show that they are statistically different from zero.*

  The mentioned trends are significant. Uncertainties (about 0.008 ppm/year, see also Fig. 10) will be added.

- *P1, L10: "are strongly correlated" should be "are strongly anti-correlated"*

  Will be corrected.

- *Pages 1 and 8 have the QBO erroneously defined as the "Quasi-Biannual Oscillation" instead of "Quasi-Biennial Oscillation". You also use the term "bi-annual structure" on pages 8 and 11, where I assume you mean "biennial", since "bi-annual" means every 6 months.*

  The referee is absolutely right – it should be "biennial" in all cases, sorry for this mistake. We will correct this.

- *P1, L11: Why does it only "seem" that most of the water vapor is produced by methane? What else might produce water vapor above 20 km?*

  There are in fact other sources of stratospheric water vapour under discussion, e.g. from aviation or volcanoes. However, this is mainly relevant for the lowest parts of the stratosphere, therefore we will change this sentence to:

  Above about 20 km most of the water vapour is attributed to the oxidation of methane.

- *P1, L13-15: Why should there be a "balance between water vapor and methane" at lower altitudes, unless of course the air masses came from higher in the stratosphere where there is a photochemical balance between CH4 and H2O? But here you mention only "the lower branch of the Brewer-Dobson circulation" where this photochemical balance does not exist. I don't understand the intention of this sentence and, to me, it is confusing.*

  We agree that this may be confusing and will reformulate the sentence:

  The SCIAMACHY data confirm, that at lower altitudes the amount of water vapour and methane are transported from the tropics to higher latitudes via the shallow branch of the Brewer-Dobson circulation.

- *P1, L17-18: It is too strong to say that these three greenhouse gases "determine the climate on our planet" when there are many, many contributors to Earth's climate.*

  Agreed. We will reformulate this to:

  Water vapour (H2O), methane (CH4) and carbon dioxide (CO2) are all greenhouse gases.

- *P1, L22: If "methane is mainly produced in the troposphere", where else is it produced?*

  There are indeed no known stratospheric sources of methane. We will therefore remove "mainly".

- *P1, L23: For decades, there have been attempts to produce spatially-resolved estimates of CH4 sources using globally-distributed surface measurements and inverse models. This is not something novel. How are satellite measurements used to identify methane sinks?*

  Several satellite instruments (including SCIAMACHY, but also GOSAT and soon TROPOMI on Sentinel 5p) provide CH4 data, usually total columns determined from nadir measurements. These can be used in combination with inversion models to derive sources and sinks. The referee might have a look at the GHG-CCI web site (`http://www.esa-ghg-cci.org`) for more information about available data sets.

- *P2, L1: What is the "long" lifetime of "tropospheric methane"? Be more quantitative.*

  The lifetime of tropospheric methane is about 10 years, we will mention that.

- *P2, L5: There were papers published long before 2001 that describe the "cold trap". In fact, there was some pioneering work performed back in the 1940s by Brewer and Dobson.*

  It is true that the "cold trap" has been discussed before 2001. We only wanted to give some example references here. We will add as additional (early) example the work by Brewer(1949), see reference in Holton and Gettelman (2001).

- *P2, L8: What is the connection between "tropical upwelling" and the "freeze-drying process"?*

  Tropical upwelling transports air masses from the troposphere into the stratosphere. As mentioned before, the tropopause acts as a cold trap such that water vapour partly freezes out before reaching the stratosphere, which is therefore dry compared to the troposphere. We will explain this in the revised version.

- *P2, L10: Why only "in the middle stratosphere and above" is water vapor "produced from (the) oxidation of stratospheric methane"? Both le Texier et al. (1988) and Rohs et al. (JGR, 2006) clearly show that some methane is oxidized in the lower stratosphere.*

  In the lower stratosphere oxidation of methane is not the only source of water vapour, there is e.g. also a tropospheric source (as we discuss in the present manuscript). However, as this sentence may be misleading, we will replace "in the middle stratosphere and above" by "in the stratosphere".

- *P2, L17: The concept of potential water, historically referred to as "total hydrogen", being conserved in stratospheric air masses as they mix and photochemically age, has been known for a long time. It pre-dates Rinsland et al. (GRL, 1996), so citing a 2005 paper here ignores the pioneering work on this topic that was performed well before the 21st century.*

  The concept of potential water is indeed older than the mentioned publication from Nassar et al. (2005). However, Nassar et al. (2005) define the term "potential water" in contrast to "total hydrogen" (which includes H2) as we use it in our manuscript, therefore we cite this paper here, but we will also add the Rinsland reference.

- *P2, L19-21: It is not "the combination", but rather "simultaneous measurements of" H2O and CH4 profiles, that are useful in understanding the connection between the two gases. Why is it best that they be measured by the same instrument? Does this improve the accuracy of H2O and CH4 retrievals, and therefore total hydrogen values?*

  If measurements from the same instrument (and similar retrievals) are used, possible systematic effects caused by the instrument or the retrieval method may cancel. This should improve the accuracy of the resulting potential water / total hydrogen.

  We will reformulate this:

  Ideally, both water vapour and methane should be retrieved from measurements by the same instrument. In this case, the collocation of the two data sets is very close. Furthermore, possible systematic errors caused e.g. by instrument calibration or by the retrieval method may to some extent cancel.

- *P5, L9-11: A "criterium" is a bicycle race. Instead use "criterion" (singular form of criteria). I'm not sure what "a maximum time distance of 9 hours" means. And does "the closest match" refer to time or distance?*

  We will replace "criterium" by "criterion". "a maximum time distance of 9 hours" refers to the difference between the measurement times of the two instruments; "the closest match" refers to spatial distance. For clarification, we will reformulate the corresponding sentence:

  For MLS we use a maximum time distance of 9 hours between MLS and SCIAMACHY measurements and always take the spatially closest match.

- *P5, L15-17: What version of MLS retrievals are you using? Hopefully the latest and greatest, v4.2. The phrases "slightly higher" and "typically smaller" convey very little information. Please be more quantitative.*

  We indeed use MLS V4.2 and will mention this in the text and the related figure caption. We will also give quantitative numbers in the related sentence:

  The SCIAMACHY water vapour VMRs are usually about 2–3% higher than those of ACE-FTS, but (except for the lowest altitudes) typically 2–3% smaller than MLS VMRs.

- *P6, Figure 3: I would be careful when using the term "absolute differences" because "absolute" may infer absolute values. Given the x-axis units (ppmv or %) I think it is safe to remove "absolute" and "relative" from the Figure headings.*

  "absolute" might indeed be misleading as we show positive and negative values and can be removed. We will modify Figs. 3 & 4 and their captions accordingly. We see however no problem with "relative" and would prefer to keep this in order to better distinguish panels a) and b).

- *P6, Figure 3d: Why does this vertical profile of correlation coefficients for SCIA vs ACE have such an altitude-dependent shape? The scatter in SCIA-ACE differences (ppmv and %) does increase somewhat near the lower and upper altitude boundaries, but is this enough to decrease the correlation coefficients near 17 and 45 km by more than a factor of two from those in the 25-40 km range? Do the correlation coefficients decline because of diminishing data populations as the altitude boundaries are approached? Figure 4d has a similar shape, but the r values don't fall so severely as the boundaries are approached. What makes these panel (d) curves similar in shape but so different in r values near the altitude boundaries?*

  The possible reason for the decreasing r in Fig. 3 at lower altitudes is that the variability of the ACE-FTS data is higher than for SCIAMACHY. This can be seen from the standard deviations shown in panel c). High correlation is achieved when variability (standard deviation) is similar for both data sets, i.e. in this case both instruments see the same atmospheric changes. MLS standard deviation is at lower altitudes closer to that of SCIAMACHY, therefore the correlation is higher.

  We suggest to add the following text to explain this:

  The correlation between SCIAMACHY and both ACE-FTS and MLS data is generally high (reaching about 0.85 at 30km), but is poorer at lower and higher altitudes. The reduction at higher altitudes may be a consequence of the larger relative errors of the SCIAMACHY data, but as yet there is no clear explanation. At lower altitudes, differences in the variability of the data play a role, as can be inferred from the standard deviations shown in panels c) of Fig. 3 and 4. High correlation is achieved when variability and variance are similar for both data sets, i.e. in this case both instruments see the same atmospheric changes.

- *P8, L3-5: What is meant by "bi-annual structure" in Figure 6? I don't see any cycles in the H2O or CH4 anomalies that clearly repeat with a 6-month (biannual) or 2-year (biennial) period. I do see lots of inter-annual variability. Is that what you want to say? Also, why does one expect inter-annual variability in CH4 and H2O because of the QBO? What are the mechanisms that drive changes in both?*

We mean "biennial structure", i.e. a variation with a 2-year period. This is seen especially at altitudes around 25–30 km where red and blue patterns repeat about every two years. This is seen more clearly in the following figures; related mechanisms are discussed in the "Discussions" section later.

- *P8, L6-8: "show an inverted behavior". Do you instead mean "opposite behavior" since "opposite" implies negative vs positive? The water vapor anomalies are "about twice as high negative" is awkwardly worded. How about "The methane anomalies correspond to water vapor anomalies that are opposite in sign and twice the magnitude." Also, the statement "that most of the water vapor is produced from methane" is not correct since mixing ratios of H2O are ∼4 ppmv at stratospheric entry and ∼7 ppmv at 45 km.*

  Yes, we mean "opposite" and will change the text. "most of the water vapor is produced from methane" actually refers to anomalies, i.e. changes in water vapour and methane, we will clarify that.

  New text:

  The methane anomalies correspond to water vapour anomalies that are opposite in sign and twice the magnitude. This complies with the assumption, that most of the changes in water vapour are produced from methane via the net reaction (R2).

- *P9, L2-3: Don't the water vapor anomalies at 17 km also show year-to-year differences in the amount of water passing through the tropical cold trap, i.e., variability not related to the QBO? By how many months is the QBO signal at 17 km "shifted in phase" from that at 25 km? Is the reason for this phase shift that the QBO propagates downward?*

  Water vapour entering the stratosphere in the tropics varies also due to a combination of QBO and BDC effects. However, our measurements indicate that QBO effects dominate in this case. We try to explain this in the "Discussions" section later in the manuscript. According to our explanation, the air at 17 km is several years younger than the air above about 25 km (because of the different pathways of the Brewer-Dobson-Circulation). The phase shift between 17 and 25 km is therefore not only a few months but probably more than one 2-year period, and it is not possible to determine the exact value from our data. Above about 25 km there are indeed some indications for downward transport, as can be seen in the slanted structures of the anomalies shown in Fig. 6.

  We will add the following text for clarification:

  Note that the age of air at these altitudes may be up to about 8 years according to e.g. Haenel et al. (2015). Consequently, the actual phase shift is expected to be larger than one 2-year period of the QBO. It therefore cannot be determined well from our 9-year time series.

- *P9, L4: "downward peak" is contradictory. How about "dip"? I presume here you are still discussing the 17-km data?*

  We will reformulate the sentence to clarify this:

  The dip in the water vapour anomalies at 17 km in the middle of 2009 is related to the eruption of the Sarychev volcano...

- *P9, L10: I would call the Singapore zonal wind average a QBO "index" rather than a "proxy".*

  OK, will be changed.

- *Figure 8 caption: Not only is the y-axis for CH4 inverted, it is also scaled differently than the y-axis for H2O.*

  The caption will be changed accordingly:

  Note that the vertical axis of the methane data is inverted and scaled differently than for water vapour.

- *P10, L6-8: What is the average transport time from the tropics to the northern 50-70° latitude at 30 km? You could determine this by independently regressing the H2O and CH4 anomalies against U10*

and progressively delaying the U10 index one month at a time, finding the delay that produces the highest correlation coefficients. On Line 8 you say "positive anomaly in the wind data", but Figure 8 doesn't show wind anomalies. It is strange that the positive anomalies in H2O and CH4 at the beginning of 2010 were not preceded by positive zonal mean winds.

Age of air at these altitudes is about 8 years (see manuscript and above). Therefore the delay between tropospheric winds and stratospheric H2O or CH4 is more than one QBO period. We think the time series is too short and does not contain enough distinct features to determine these large delay times.

We will change "positive anomaly" to "positive values" as these are indeed no anomalies:

The positive values in the wind data around 2010/2011 are hardly detected in the methane and water vapour data.

The behaviour after 2010 is indeed strange and needs further investigations, as we mention in the text.

- *P11, L1: Water vapor is also produced by the oxidation of hydrogen (H2) in the stratosphere. How does this factor into H2O + 2*CH4 = constant?*

  Indeed, H2 needs to be considered in the sum as only total hydrogen is conserved. However, as mentioned in the introduction, for potential water we assume that H2 variations can be neglected.

- *P11, L4-5: Why is the QBO signal visible only below 20 km in Figure 9? What mechanism alters H2O + 2*CH4 below 20 km but not above this altitude? Only Figure 7d shows greater variations in H2O anomalies than in CH4 anomalies.*

  We discuss this in the "Discussions" section. The basic idea is that H2O at higher altitudes is produced from CH4 such that the combination does not show a QBO signal. At lower altitudes, H2O shows a QBO signal caused by variations due to QBO effects on tropopause temperature. CH4 transport into the stratosphere is not affected by tropopause temperature changes and therefore does not show a QBO signal.

- *P11, L11-13: What could possibly drive changes in H2O + 2*CH4 with a periodicity of 5-6 years? I don't think this statement is supported by Figure 9 that spans only 9 years.*

  There is no explanation for this 5–6 years periodicity yet. Possible reasons are variations in the Brewer-Dobson circulation or changes in water vapour trends; we will mention this in the discussion. We also agree that it is difficult to tell if this periodicity is real from our data.

  To clarify this we will reformulate this sentence to:

  This implies a periodicity of about 5 to 6 years, but due to the limited length of the time series, this can only be confirmed in the future.

- *P11, L15: I don't see the that scatter (std dev) in SCIAMACHY retrievals increases significantly above 40 km (Figures 3c and 4c), so what do you mean here by "large uncertainties of the ONPD data at higher altitudes"?*

  This refers to the (mean) error on the data which increases with altitude, see Figs. 3 & 4 panels a) and b).

- *P11, L17-18: Please expand your description of the linear trend fitting here, at least in a general way. At what altitudes did you determine trends? Did you perform any vertical averaging (other than averaging kernels) of the profiles before determining trends? There is not enough information presented here to simply reference an earlier paper.*

  We will modify the text to describe the fitting procedure further:

  To derive these changes, a linear regression has been fitted to the water vapour anomalies at each altitude similar to that used in the earlier methane study, see Noël et al. (2016). For this, we take the anomaly times series at a selected altitude (see e.g. Fig. 7) and fit a straight line to it. The slope of this line is the estimated trend for this altitude, the error of the trend is the error of the slope given by the fit. This procedure is undertaken at all altitudes from 17 to 45 km, in 1 km steps. The resulting trend profiles are displayed in Fig. 10.

- *P11, L20: Here and throughout, all trends need to be presented with their 95% confidence intervals. Otherwise, the reader has no idea if the trends are statistically significant or not unless they check Figure 10. Many of the trends between 25 and 40 km are NOT negative, they are indistinguishable from zero. Only the H2O trends between 31 and 37 km can be labeled as negative.*

  The derived values of the H2O trends between about 25 and 40 km are negative, but it is true that some of these trends are not significant. We explain in the text which regions are significant and which are not. For further clarification, we will add the uncertainties to the trends mentioned explicitly in the text.

- *Figure 10: Please scale the x-axis for CH4 accordingly for d[H2O]/dt + 2*(d[CH4]/dt) = 0. Wouldn't one expect a positive trend in CH4 accompanying the negative trend in H2O between 31 and 37 km?*

  We will scale the x-axis of the CH4 plot in Fig. 10 by a factor of 2. One would indeed expect a positive trend for CH4 between 31 and 37 km, but the resulting errors on the trends are high, so the CH4 trends and also the combined PW trends are not significant.

- *P12, L7-8: Please remove one of the repeated "an estimate"*

  OK.

- *P12, L12: "not disproved" is a very weak way to say this. How about "Given that the trends in potential water between 21 and 45 km lack statistical significance, there is no evidence that water vapor is produced in the stratosphere by any mechanism other than methane oxidation."*

  OK, will be changed.

- *P12, L13: "where the trend itself is close to zero" is not supported by the 95% confidence intervals of -0.015 to +0.014 ppmv/year in the 25-30 km altitude range.*

  Agreed. Although the value is close to zero the trend is not significant, we will remove this sentence.

- *P12, L19-20: Why is this? You haven't explained why the QBO might influence H2O but not CH4 in the lower stratosphere. You also haven't explained why there should be a lag between QBO water vapor signals in the upper and lower stratosphere. Is it a difference in the mean ages of the air masses? It would be a good idea to introduce the concept of mean age early in this paper if you are going to discuss differences in the "phasing" of QBO-induced water vapor signals at different altitudes.*

  An explanation for the observed features in this list is given in the subsequent paragraphs in the manuscript. We will reformulate this section and add some additional information about age of air in the introduction (see answer to general comments).

- *P13, L5-9: I think this explanation should appear earlier in the paper. This is not a conclusion of the paper, it is information pertinent to the understanding of why QBO "signals" in H2O at different altitudes are present at different times.*

  We will add some information about the different branches in the introduction:

  There are in principle two pathways for this transport (see e.g. Butchart, 2014, and references therein): At lower altitudes, air masses are transported via the shallow (or lower) branch of the Brewer-Dobson circulation. At higher altitudes the water vapour is transported by the deep (or upper) branch of the Brewer-Dobson circulation.

- *P13, L11: "water vapor is mainly produced from methane oxidation". What else produces water vapor at these altitudes? Also, I think you need to have a definitive statement earlier in the paper that the oxidation of methane to water occurs predominantly in the tropical stratosphere and the fraction of methane converted to water increases with altitude.*

  We will remove "mainly" and add some more information in the introduction.

- *P13, L15-17: Don't forget the main driver of variability in stratospheric H2O entry mixing ratios is the seasonal cycle of tropical tropopause temperatures. Also, ENSO can significantly influence water vapor input to the tropical lower stratosphere by affecting tropical tropopause temperatures and through convective activity. A lack of strong seasonal, QBO and ENSO influences on UTLS methane DOES explain the lack of CH4 variability at 17 km.*

  Since we are looking at anomalies here, seasonal cycle effects should be removed. During the period of SCIAMACHY measurements there were no strong ENSO events, so this impact should be limited. Therefore we think that the missing QBO influence is a valid (and in this specific case sufficient) explanation for the lack of CH4 variability at 17 km.

- *P14, L5-7: As per my previous comment about introducing the concept of mean age, here at the end of the paper is just such an introduction. I think the paper would benefit from this appearing much earlier.*

  We will add some sentences on age of air in the introduction (see answer to general comments).

- *P14, L10: This sentence makes it sound like CH4 was emitted at 17 km. And is mean age really the elapsed time from emission, including transport time from extra-tropical sources to the tropics?*

  The formulation is indeed misleading. We will change this to:

  about 2–3 years between injection into the stratosphere at the tropics and measurement at 17 km at higher latitudes

- *P14, L17: The concept of "QBO signal has to be carried by methane" is an awkward way of explaining QBO influences on the oxidation of CH4 to H2O. If the QBO can alter the strength of the Brewer-Dobson circulation then it can also change the amount of CH4 oxidized to H2O during poleward transport. Transport times depend on the strength of the B-D circulation because this can also alter the path (i.e., stronger = higher path) and therefore the amount of CH4 oxidized to H2O. I think a paragraph early in the paper should be dedicated to HOW the QBO affects stratospheric transport and therefore the amount of CH4 converted to H2O during transport from the tropical lower stratosphere to the higher latitudes of your data set.*

  We will add a corresponding part in the introduction, see answer to general comments.

- *P14, L29-30: Please include trend uncertainties with the trends.*

  Will be done.

- *P15, L1: "At altitudes above about 20 km, variations in water vapor . . ."*

  Will be added.

- *P15, L6: Why is potential water not constant over time? Were there changes in the stratospheric entry mixing ratios of H2O? Of CH4? Of both?*

  Actually, we do not know the reasons why potential water varies on a timescale of 5–6 years, but we will mention possible reasons (low-frequency variations in the Brewer-Dobson circulation or in water vapour trends) in the discussion. Our data set does not extend to the tropics, therefore we cannot infer changes of the entry mixing ratios.

Reply to referee 2

We thank the reviewer for the comments and will consider them in the revised paper as described below. In the following, the original reviewer's comments are given in *italics*, our answer in normal font and the proposed updated text for the new version of the manuscript in **bold** font.

General comments

- *This paper describes a water vapor data set derived from SCIAMACHY solar occultation measurements. It covers the altitude region from 17-45 km and the latitude region from 50-70N over the time period Aug 2002 to Apr 2012. The authors describe the method, the data set and then attempt trend analysis and describe the co-relationship between their CH4 and H2O data. I think a new data set is a valuable contribution, and the validation comparing to ACE and MLS is also valuable. The analysis of variations related to the QBO and discussion of the BDC is repeating work that has already been done, much going back to studies from measurements taken by UARS or LIMS/SAM. I think the paper could be significantly shortened into a data description/validation paper and much of the QBO and total hydrogen (or potential water) discussion eliminated.*

  The aim of the paper is not only to present and validate the new SCIAMACHY H2O data set. We also want to show the usefulness of the H2O SCIAMACHY data in combination with other data, e.g. in the context of dynamical studies. The results obtained related to BDC or QBO are indeed not new, but we can confirm them with the new SCIAMACHY data. Therefore we prefer to keep the discussion on dynamical effects in the paper, but will clarify this in the revised version (see also answers to comments of other referees).

- *General comment: Please have the native English speaking co-author edit the text when revised.*

  Will be done. Therefore, the updated text might change slightly in the final revised version.

Specific comments:

- *Abstract, line 13-15, I would think that at lower altitude, water vapor is largely impacted by the stratospheric input value (so tropical tropopause temperatures). The "balance" hasn't had time to be established with young lower stratospheric air.*

  Agreed, "balance" is misleading. We will reformulate this as follows:

  The SCIAMACHY data confirm, that at lower altitudes the amount of water vapour and methane are transported from the tropics to higher latitudes via the shallow branch of the Brewer-Dobson circulation. Further, the increasing methane input into the stratosphere due to the rise of tropospheric methane after 2007 may contribute to the increased water vapour.

- *Page 1, Introduction, L17-18, the climate of the planet is determined by many factors, not just greenhouse gases. Please rewrite this sentence.*

  Agreed. New text:

  Water vapour (H2O), methane (CH4) and carbon dioxide (CO2) are all greenhouse gases.

- *Page 2, line 3, the sentence "Most of the water vapour is of natural origin and located in the troposphere."and then change "It enters" to "Water vapor enters"*

  This part will be rewritten:

  The amount of water vapour in the troposphere is very large compared with that in the rest of the atmosphere. Water vapour enters the stratosphere mainly through the tropical tropopause layer ...

- *Page 2, line 8, I don't think this is an entirely accurate statement, in particular that the BDC controls the freeze drying process. The BDC is a zonally averaged construct, and freeze drying (and the associated microphysics) is a local process.*

The term "controls" indeed might not be accurate here w.r.t. to freeze drying. We will reformulate the text as follows:

The Brewer-Dobson circulation controls the tropical upwelling, i.e. the transport of air masses from the troposphere into the stratosphere (both water vapor and methane) and influences the freeze-drying, i.e. the process through which the tropopause acts as a cold trap such that water vapour partly freezes out before reaching the stratosphere.

- *Page 5, figure 2; (and related text). Some descriptions as to what the improvements made in the algorithm between the 2010 product 2.0.2 and the current one is warranted (rather than simply referring to the 2016 methane paper).*

  We will add the following information:

  This is due to the improved retrieval method as described in Noël et al. (2016). The most relevant changes are:

  - **Use of a weighting function DOAS based fit at each altitude.**
  - **Better consideration of altitudes below the actual tangent height.**
  - **Improved selection of measurements.**
  - **Use of improved input spectral data (better pointing information and calibration).**
  - **Use of an updated radiative transfer model (SCIATRAN V3).**
  - **Updated error calculation.**

- *Page 8, line 3&4..i think you mean biennial not bi-annual*

  Indeed. Will be changed.

- *Page 8, discussion of the "inverted behavior" (or anti-correlation) between water and methane. This is well known behavior and probably doesn't need the extensive following discussion regarding the QBO.*

  As mentioned above, we would like to keep this discussion on QBO in order to show the capabilities of the SCIAMACHY data.

- *Page 11: line 14. You don't have a long enough time series to talk about 5-6 year oscillations, just delete that comment.*

  We agree that it is difficult to tell if this 5-6 year periodicity is real from our data, as we state in the text. To clarify this we will reformulate this sentence to:

  This implies a periodicity of about 5 to 6 years, but due to the limited length of the time series, this can only be confirmed in the future.

- *Page 12: trend discussion: the data set under consideration is just 10 years. That is not long enough to talk about trends. The so called trend noted on line 8 (Urban et al 2014) is really a step function like feature, not a trend. With 10 years, you can look at interannual variability, and perhaps should stick to just that. Show a time series, not a linear trend.*

  Indeed 10 years is too short for a trend in the climatological sense. Therefore, what we present here are essentially estimated changes over this time interval. Knowing their limitations, these changes can nevertheless provide interesting information. We therefore would like to keep the "trend" results in the paper, but we will add a clarification at the begin of the trends section:

  The time series of SCIAMACHY data covers only ten (nine complete) years. Consequently it is not possible to derive from these data long-term trends. In this sense, the trends shown in the following have to be interpreted as changes over the corresponding time interval 2003 to 2011. To derive these changes, a linear regression has been fitted to the water vapour anomalies ...

- *Page 12, line 13 "an estimate" is duplicated*

  Will be removed.

- *Page 12, line 14. It is not true to say that if potential water is conserved, the trend should be zero. You could have a trend in water vapor entry value, thereby allowing a potential water trend. You could also have a trend in the input of methane, again allowing a potential water trend.*

  We are referring here to the trend in potential water, not then individual CH4 and H2O trends. A trend in the H2O or CH4 input would indeed result in a corresponding potential water trend, but then potential water would not be conserved (unless both trends balance, which is not expected for tropospheric trends). On the other hand, if potential water is conserved, there should be no trend in potential water.

  For clarification, we will reformulate this sentence:

  If potential water is conserved, the potential water trend should be zero.

- *Page 12: I really don't understand the point of this sentence "Considering this error, the combined trend above about 20 km is in a statistical sense not significant, meaning that the assumption that all water vapour is produced from methane via the net reaction (R2) is not disproved by the measurements." One should keep in mind that all water vapor is not produced from methane (ie, the average entry value is on the order of 3.5 ppmv, current methane is ∼1.8 ppmv, so if all were oxidized you could get a contributions of 3.6 ppmv, so at most you could get half of water vapor from methane. It may be that here the authors are trying to assess contribution to the trend. Rohs et al, 2006, JGR, determined for the 78-03 trend in stratospheric water vapor, only 25% can be due to a trend in methane. A similar analysis could be done here, for the SCIAMACHY period.*

  Indeed, since we are looking at anomalies, we refer here to the changes of water vapour and methane, i.e. stratospheric production/loss. As suggested by referee #1, this sentence will be changed to:

  Given that the trends in potential water between 21 and 45 km lack statistical significance, there is no evidence that water vapour is produced in the stratosphere by any mechanism other than methane oxidation.

  The analysis of Rohs et al. requires as input in addition to stratospheric CH4 and H2O trends also the tropospheric CH4 trends and information about age of air. It is not possible to derive tropospheric trends and age of air from our data, and the stratospheric trends we derive are very small and often not significant (as are the tropospheric trends during this time period). Therefore we think it is not reasonable to include results from such an assessment in the manuscript.

- *Page 14, line 26-30: this description of the processes going on is in error. In the upper altitudes, water vapor changes are anti correlated with methane, and simply reflect age of air variations; the QBO signal is not "carried by methane".*

  This paragraph has been reformulated for clarification (see also comments of other referees):

  The QBO signal is observed in both methane and water vapour at higher stratospheric altitudes. In contrast, the tropospheric methane entering the stratosphere via the lower branch of the Brewer-Dobson circulation is not impacted by the QBO at lower altitudes. The QBO signature in the upper altitude data can be explained by a QBO-dependent modulation of the transport to higher latitudes via the deep branch of the Brewer-Dobson circulation, similar to the variation in tropical aerosol extinction coefficients as seen by Brinkhoff et al. (2015) at 30 km.

Reply to referee 3

We thank the reviewer for the comments and will consider them in the revised paper as described below. In the following, the original reviewer's comments are given in *italics*, our answer in normal font and the proposed updated text for the new version of the manuscript in **bold** font.

- *This study nicely presents the SCIAMACHY H2O and CH4 measurements and their relationship. The SCIAMACHY measurements are a very valuable addition to the available H2O and CH4 measurements in the middle atmosphere over the period 2003-2012, and the results shown here are scientifically valuable. However, in much of the text the authors seem to be trying very hard to create a mystery where there is none. There is (1) a QBO signature in H2O crossing the tropical tropopause and (2) a QBO signal due to changes in transport (age-of-air) which causes a variation in the amount of CH4 that has been oxidized to produce H2O. The authors repeatedly overemphasize the importance of small tropospheric CH4 variations on the observed variations in stratospheric H2O. While gradually increasing anthropogenic CH4 is a very important driver of long-term change in H2O, variations in CH4 entering the stratosphere are only marginally relevant to the variations observed in these measurements, which span a decade. Small changes in tropopause temperature are a far more important driver of interannual changes in H2O entering the stratosphere as has been shown by many authors (e.g. Dessler et al., JGR 2014).*

  We agree that some of the statements/formulations in the manuscript may be misleading. We do not aim to propose new dynamical processes or explanations. Our intention is to present the new SCIAMACHY H2O data set and show via the combination with CH4 that information about atmospheric dynamics can be derived. This is not necessarily new information, but it shows the usefulness of the SCIAMACHY data.

  We will clarify this in the revised version of the manuscript (see answers to the following comments and also our answers to the comments of referee #1).

- *Figure 11 is appropriate for a review paper on atmospheric dynamics, and might be appropriate if the authors were running a dynamical model to compare with their measurements, but it seems inappropriate here.*

  We agree that Figure 11 does not present any new results. However, it summarises the different dynamical processes discussed in the manuscript and is therefore considered as helpful especially for the non-expert reader. We therefore prefer to keep this figure in the manuscript but will move it to the (modified) introduction.

- *On page 14 line 7 they state: "This is not the case for methane, which could explain the missing QBO signature in the methane time series at 17km." There is no need for a "could" here. The H2O entering is governed by tropopause temperatures, and the CH4 is not.*

  Agreed. We will remove "could".

- *In paragraph following this (and in the last sentence of the conclusion) they again try to overemphasize the importance of CH4. There is nothing inherently wrong with pointing out that changes in CH4 may play a small part in the observed changes of H2O, but an increase of 8 ppbv/yr in CH4 over 4 years would yield only at most ∼0.064 ppmv of H2O over 4 years. This looks small when compared to the observed variations in potential water, and if CH4 were the major driver of these variations potential water would not show decreases. Only finally, at the end of this paragraph, do the authors mention that: "However, from the current data set an additional influence of varying tropospheric water vapour input on the observed increase of potential water cannot be ruled out." This is certainly the primary driver of the variations in potential water, as is well understood. In the last sentence of the manuscript the authors again seem to only reluctantly accept that "possibly in combination with changes of water vapour" are important. Presumably this refers to changes in water vapour entering the stratosphere, but even that is not clear.*

  Actually, the referee is right here. An increase in CH4 due to tropospheric trends alone cannot quantitatively explain the observed increase in potential water.

We will therefore reformulate this part:

Schneising et al. (2011) estimated for the time interval 2007 to 2009 a tropospheric increase of methane of about 8 ppbv year^{-1} following a period of no significant change from 2003 to 2007. Taking into account the delay between the tropospheric and a possible stratospheric trend related to the age of air (about 2–3 years between injection into the stratosphere at the tropics and measurement at 17 km at higher latitudes according to Haenel et al., 2015) explains part but not all of the increase of potential water at lower altitudes after 2009/2010 shown in Fig. 9. An additional influence of varying tropical tropospheric water vapour on the observed increase of potential water is therefore likely. Prior to the end of 2011 the positive potential water anomaly extends to higher altitudes. This is in agreement with the increasing age of air at higher altitudes.

The conclusions will also be adapted:

The increase of tropospheric methane after 2007 reaches these lower stratospheric altitudes with a delay of about 2 years. This contributes in part to the observed increase of potential water after 2009, but additional processes such as changes of tropospheric water vapour input are required for a quantitative explanation.

- *Then, in the final paragraph of the discussion they say: "A remaining open issue is the QBO signal observed in both methane and water vapour at higher stratospheric altitudes ... Therefore the QBO signal has to be carried by methane, but as can be seen at lower altitudes the methane entering the stratosphere is not varied by QBO." This is all well understood, as the authors finally admit in the second half of this paragraph.*

  As requested by reviewer #1, the introduction of the revised paper will contain more information about known dynamical processes.

  For clarification, we will also reformulate this part as follows:

  Above 20 km, in the region of the deep branch of the Brewer-Dobson circulation, air is older. This enables oxidation of methane to water vapour to be completed rapidly. As a result variations of both gases are in phase and potential water is essentially conserved (Fig. 7). Consequently at these altitudes water vapour changes can be concluded to be determined by the oxidation of methane. The QBO signal is observed in both methane and water vapour at higher stratospheric altitudes. In contrast, the tropospheric methane entering the stratosphere via the lower branch of the Brewer-Dobson circulation is not impacted by the QBO at lower altitudes.

- *The abstract is similarly unnecessarily confusing. First, the phrase "SCIAMACHY methane and water vapour time series reveals that stratospheric methane and water vapour are strongly correlated". The implication seems to be that this is a new result. Please rephrase this as "reveals [or, better yet, "shows"] the expected anticorrelation between methane and water vapour".*

  We will rephrase this sentence as suggested:

  The combined analysis of the SCIAMACHY methane and water vapour time series shows the expected anti-correlation between stratospheric methane and water vapour and a clear temporal variation related to the Quasi-Biennial-Oscillation (QBO).

- *The next sentence reads: "Above about 20km most of the water vapour seems to be produced by methane, but short-term fluctuations and a temporal variation on a scale of 5âĂŞ6 years are observed." First, there is no reason for a "seems" here. The authors should be able to calculate how much of the observed water vapour is produced by methane. Secondly, I do not understand how the second part of this sentence follows from the first following a "but".*

  This part of the abstract will be reformulated accordingly:

  Above about 20 km most of the water vapour is produced by methane. In addition, short-term fluctuations and a temporal variation on a scale of 5–6 years are observed.

- *I finally have to admit that I do not understand what new point the authors are trying to make in the last sentence of the abstract.*

  There is indeed no new finding here. We only want to state here, that the described effects can be seen in the SCIAMACHY data.

  We will clarify this:

  The SCIAMACHY data confirm, that at lower altitudes the amount of water vapour and methane are transported from the tropics to higher latitudes via the shallow branch of the Brewer-Dobson circulation. Further, the increasing methane input into the stratosphere due to the rise of tropospheric methane after 2007 may have contributed to the increased water vapour in the extratropical lower stratosphere as observed by SCIAMACHY.

- *A few minor additional points in the text: I don't understand the statement on page 2 line 19: "roughly conserved in the stratosphere if no changes in mixing of air masses occur". What does "changes in mixing of air masses" mean?*

  This refers to additional production / loss processes others than via the net reaction (R2), like production of H2O by oxidation of other hydrocarbons, but these are indeed rather negligible (as e.g. stated by Nassar et al., 2005). We therefore will remove "if no changes in mixing of air masses occur".

- *On page 9 line 6: "the remaining sensitivity of the retrieval method to aerosol" is rather a roundabout way of saying "errors in the water vapour retrieval due to aerosols". This is essentially what the authors say in the next line.*

  To clarify this, we will reformulate this sentence as follows:

  Note that this observed reduction of water vapour after the Sarychev eruption may be introduced by errors in the water vapour retrieval due to the remaining sensitivity of the retrieval method to aerosol.

List of changes

Changes according to the comments mentioned above have been made in the revised manuscript. Especially, the introduction and discussions sections have been largely modified. Please note that figure numbering has changed. The changes are marked in the attached version of the revised manuscript.

Water Vapour and Methane Coupling in the Stratosphere observed with SCIAMACHY Solar Occultation Measurements

Stefan Noël, Katja Weigel, Klaus Bramstedt, Alexei Rozanov, Mark Weber, Heinrich Bovensmann, and John P. Burrows

Institute of Environmental Physics, University of Bremen, FB 1, P.O. Box 330440, 28334 Bremen, Germany

Correspondence to: S. Noël (stefan.noel@iup.physik.uni-bremen.de)

Abstract.

An improved stratospheric water vapour data set has been ~~derived~~ retrieved from SCIAMACHY/ENVISAT solar occultation measurements. It is ~~based on the same algorithm which has already been~~ similar to that successfully applied to methane and carbon dioxide~~retrievals, thus resulting in a consistent data set for theses~~ . There is now a consistent set of data products for the three constituents covering the altitudes 17–45 km, the latitude range between about 50 and 70°N, and the ~~time interval~~ period August 2002 to April 2012.

The new water vapour ~~data~~ concentration profiles agree with collocated results from ACE-FTS and MLS/Aura ~~within about~~ to within ~5%. A significant positive water vapour trend for the time 2003–2011 is observed at lower stratospheric altitudes with a value of about 0.015 ± 0.008 ppmv year^{-1} around 17 km. Between 30 and 37 km the trends become significantly negative (about -0.01 ~~±~~ 0.008 ppmv year^{-1}); all errors are 2σ values.

The combined analysis of the SCIAMACHY methane and water vapour time series ~~reveals that~~ shows the expected anti-correlation between stratospheric methane and water vapour ~~are strongly correlated and show~~ and a clear temporal variation related to the ~~Quasi-Biannual-Oscillation~~ Quasi-Biennial-Oscillation (QBO). Above about 20 km most of the water vapour ~~seems to be produced by methane, but~~ is attributed to the oxidation of methane. In addition short-term fluctuations and a ~~temporal variation on a scale of 5–6~~ periodic oscillation having a period of 5-6 years are observed.

~~At~~ The SCIAMACHY data confirm, that at lower altitudes the ~~balance between water vapour and methane is affected by stratospheric transport~~ amount of water vapour and methane are transported from the tropics to higher latitudes via the shallow branch of the Brewer-Dobson circulation~~and by~~ . Further, the increasing methane input into the stratosphere due to the rise of tropospheric methane after ~~2007.~~ 2007 may have contributed to the increased water vapour in the extratropical lower stratosphere as observed by SCIAMACHY.

1 Introduction

Water vapour (H_2O)~~and~~ , methane (CH_4) ~~are beside~~ and carbon dioxide (CO_2) ~~the most important greenhouse gasesand therefore determine the climate on our planet. In the stratosphere they also~~ are all greenhouse gases. The stratosphere is much drier than the troposphere. Carbon dioxide absorption of the upwelling radiation from the Earth's surface in the troposphere is

so strong that CO_2 cools the stratosphere. Water vapour and methane play an important role in ~~chemistry, e. g. in ozone loss due to~~ the chemistry of the stratosphere. For example the oxidation of methane generates the HO_x ~~gas phase chemistry and heterogeneous reactionson~~ radicals which catalytically destroy ozone (O_3) and are involved in many important stratospheric reactions. Water vapour is a key constituent of polar stratospheric clouds (PSCs) which play a unique role in the chemistry of the polar vortex, see e.g. Seinfeld and Pandis (2006). However, ~~since~~ both water vapour and methane ~~(and also carbon dioxide) are very stable, they~~ can also be used as dynamical tracers.

Methane is ~~mainly~~ produced in the troposphere by various natural and anthropogenic emission processes. The identification of methane sources and sinks ~~by the use of satellite measurements is currently a major topic of scientific investigations~~ from the measurements of remote sensing instrumentation on satellites is currently an important research area (see e.g. Buchwitz et al., 2017, and references therein). ~~Due to its long lifetime, tropospheric methane is then~~ The tropospheric lifetime of methane is about 10 years (Prinn et al., 2005). Consequently it is transported into the stratosphere.

~~Most of the water vapour is of natural origin and located~~ The vast majority of liquid water and ice on Earth is found in the oceans and the cryosphere. The amount of water vapour in the troposphere ~~. It~~ is very large compared with that in the rest of the atmosphere. Water vapour enters the stratosphere mainly through the tropical tropopause layer (TTL; see e.g. Randel et al., 2004, Randel and Jensen, 2013, and references therein). There, the cold temperatures of the tropical tropopause ~~yield~~ result in a 'cold trap' (see e.g. Brewer, 1949, Holton and Gettelman, 2001~~) causing lower concentrations of water vapourin the stratosphere than in the troposphere~~, Read et al., 2004). A minimum in water vapour, which is around 2 km above the tropopause, is called the hygropause. The water vapour, which enters the stratosphere through the TTL, is then transported via the Brewer-Dobson circulation from the tropics to higher latitudes. ~~The~~ There are in principle two pathways for this transport (see e.g. Butchart, 2014, and references therein): At lower altitudes, air masses are transported via the shallow (or lower) branch of the Brewer-Dobson circulation. At higher altitudes the water vapour is transported by the deep (or upper) branch of the Brewer-Dobson circulation. This is illustrated in Fig. 1.

The combination of water vapour and methane entering the stratosphere in the tropics depends on the changing strength of the sources (e.g. possible tropospheric trends) as well as on dynamical effects, i.e. variations in the Brewer-Dobson circulation ~~also~~ (on seasonal and inter-annual time scales) and the Quasi-Biennial-Oscillation (QBO), see e.g. Baldwin et al. (2001); Butchart (2014), and references therein. The Brewer-Dobson circulation controls the tropical upwelling~~and~~ , i.e. the transport of air masses from the troposphere into the stratosphere (both water vapor and methane) and influences the freeze-drying~~process that in turn~~ , i.e. the process through which the tropopause acts as a cold trap such that water vapour partly freezes out before reaching the stratosphere (e.g. Fueglistaler and Haynes, 2005). The Brewer-Dobson circulation is driven by middle latitude planetary waves entering the stratosphere and as a consequence leads to adiabatic cooling in the tropical UTLS (upper troposphere / lower stratosphere region) related to the increased upwelling which strongly determines the stratospheric entry of water vapour in the tropics (Randel et al., 2006; Dhomse et al., 2008). Both QBO and Brewer-Dobson circulation are related as the planetary wave propagation is modulated by the QBO (e.g. Baldwin et al., 2001). An additional complexity is the existence of a fine scale vertical feature, which is known as the tropopause inversion layer, TIL, see e.g. Birner et al. (2006), through which water vapour must pass.

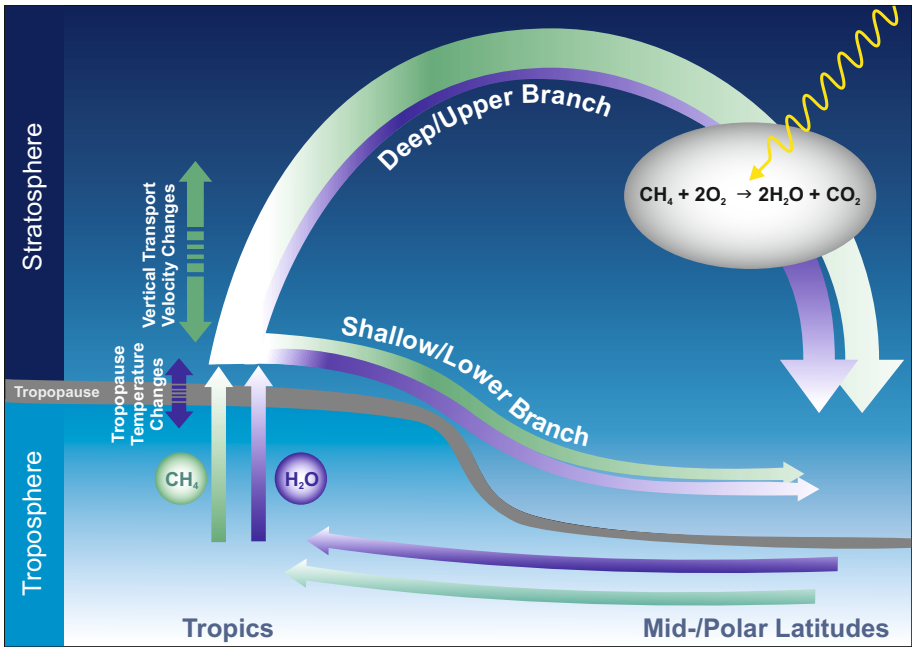

Figure 1. Simplified schematic view of transport pathways within the Brewer-Dobson circulation.

~~In the middle stratosphereand above~~

In the stratosphere, water vapour is ~~in fact~~ mainly produced from oxidation of stratospheric methane via the reaction

$$CH_4 + OH \rightarrow H_2O + CH_3 \quad \text{(R1)}$$

~~Via various~~ Rapid photochemical processes (see e.g. le Texier et al., 1988) result in the CH_3 ~~is~~ being converted first to HCHO and then to H_2O resulting in the net reaction:

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \quad \text{(R2)}$$

~~According to this~~ For this overall reaction one methane molecule finally produces two water vapour molecules, which means that the sum of volume mixing ratios $[H_2O] + 2[CH_4]$, referred to as potential water (PW), see e.g. Rinsland et al. (1996); Nassar et al. (2005) and references therein, is expected to be roughly conserved in the stratosphere~~if no changes in mixing of air masses occur and if~~ . Since the actually conserved quantity is total hydrogen, this assumes that variations in H_2 can be neglected. The latter is in fact not always the case, as investigations by e.g. Juckes (2007) and Wrotny et al. (2010) indicate.

The ~~combination of water vapour and~~ rate determining step for the reaction (R2) is probably the photolysis of the different speciation in the reaction mechanism and thus depends on the availability of UV radiation. The reaction is therefore more effective higher in the stratosphere.

Another aspect to be considered is the transport time. The longer an air mass resides in the stratosphere, the more methane can be oxidised to water vapour. Measurements of age of air (see e.g. Haenel et al., 2015) indicate an increase of age of air with

altitude at higher mid-latitudes from about 2 years at 15 km to about 8 years at 30 km. Therefore, the methane–water vapour conversion process is expected to be more rapid and thus effective along the deep branch of the Brewer-Dobson circulation. However, the mixing of air masses during transport does not affect the total hydrogen balance such that potential water should still be conserved.

Simultaneous measurements of water vapour and methane data can therefore give information about sources and sinks of water vapour and dynamical effects in the stratosphere. This requires long-term data sets, which can be provided by satellite measurements~~; in the best case~~. Ideally, both water vapour and methane should be ~~measured~~ retrieved from measurements by the same instrument. In this case, the collocation of the two data sets is very close. Furthermore, possible systematic errors caused e.g. by instrument calibration or by the retrieval method may to some extent cancel.

~~So far~~Up to the present, data sets which fulfil these criteria are available only from a few instruments. This includes the Halogen Occultation Experiment (HALOE; Russell et al., 1993) on the Upper Atmospheric Research Satellite (UARS) measuring in solar occultation geometry from 1991 until 2005, see Rosenlof (2002)~~. Furthermore,~~ , and the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) on SCISAT (Bernath et al., 2005) ~~is~~ operating also in solar occultation geometry and ~~provides~~ providing scientific data since 2004. ~~Among~~ Methane and water vapour are two of the numerous ACE-FTS data products ~~are also methane and water vapour,~~ see e.g. Nassar et al. (2005). Stratospheric methane and water vapour profiles were also measured by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS; Fischer et al., 2008) on ENVISAT from 2002 to 2012 in limb geometry, see e.g. Payan et al. (2009); Laeng et al. (2015); Plieninger et al. (2016). Some early results from a combination of stratospheric methane and water vapour from MIPAS are given in Payne et al. (2005). Although primarily dedicated to measurements of polar mesospheric clouds (PMCs), the Aeronomy of Ice in the Mesosphere (AIM) Solar Occultation for Ice Experiment (SOFIE; Gordley et al., 2009) instrument also provides profiles of water vapour and methane. ~~In the context of~~ As part of the validation of the SOFIE V1.3 methane product, Rong et al. (2016) presented results from a combination of SOFIE and MIPAS methane with water vapour profiles from the Aura Microwave Limb Sounder (MLS; Waters et al., 2006)~~on Aura~~.

The SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY; Bovensmann et al., 1999; Gottwald and Bovensmann, 2011) on ENVISAT performed measurements in various viewing geometries over a large spectral range from the UV to the SWIR. Among these are solar occultation measurements, which cover – depending on season – the spatial region between about 50°N and 70°N. Noël et al. (2016) presented an updated data set for stratospheric methane derived from SCIAMACHY solar occultation using the onion-peeling DOAS (ONPD) method. Already some years ago, Noël et al. (2010) showed first retrieval results for stratospheric water vapour profiles from SCIAMACHY which were based on a similar algorithm. Recently, the improved method used by Noël et al. (2016) has also been applied to water vapour, resulting in a consistent set of SCIAMACHY stratospheric water vapour and methane data.

In this manuscript, we shortly describe the updated water vapour algorithm in section 2. We then present the new water vapour results in section 3, which also includes a first validation by comparison with independent data sets and a combination of the new water vapour data with the methane data from Noël et al. (2016). The results are discussed in section 4. The conclusions are then presented in section 5.

2 H_2O Retrieval

The retrieval method used in this study is essentially the same as described in Noël et al. (2016), therefore only the principle idea is explained here.

We use transmission spectra as function of viewing (tangent) altitude derived from SCIAMACHY solar occultation measurements. For the water vapour retrieval, we take data in the spectral range 928 nm to 968 nm. The ONPD retrieval is then based on a combination of a weighting function DOAS fit (see e.g. Perner and Platt, 1979; Burrows et al., 1999; Coldewey-Egbers et al., 2005) with a classical onion peeling method (see e.g. Russell and Drayson, 1972). The retrieval altitude grid is 0 to 50 km in 1 km steps. The measured spectra are interpolated to this grid. The analysis starts at the top level and then proceeds downwards, taking into account the results from the upper levels. At each level, we determine the water vapour density from the difference between the measured transmission and a modelled one. This is done by fitting to the data a set of factors describing the change of an atmospheric parameter in combination with corresponding weighting functions. Such a weighting function describes the change of the spectrum ~~when changing a certain~~ for a given change in a selected parameter, e.g. the water vapour concentration at this altitude. In the present case we consider in addition to water vapour also changes in ozone (which also absorbs in the spectral window used). ~~Actual~~ The pressure and temperature profiles used in the study have been taken from ECMWF ERA Interim data (Dee et al., 2011). The related weighting functions have been determined from radiative transfer calculations using the SCIATRAN model (Rozanov et al., 2014).

To account for spectrally broadband effects resulting from e.g. aerosols we also fit a polynomial to the spectra. A possible misalignment of the wavelength axis of the measured data is ~~considered by fitting corresponding~~ accounted for by fitting shift and squeeze parameters.

An example for the results of the fitting procedure is shown in Fig. 2. As can be seen, the measured transmissions ~~can be~~ is reproduced within an error of about 0.1%.

After the retrieval several additional corrections are performed as described in Noël et al. (2016):

- The retrieved profiles are smoothed with a 4.3 km boxcar to account for the vertical resolution of the measurements and to reduce oscillations in the retrieved number densities.
- Additional correction factors are applied for non-linearity and saturation effects (due to the limited spectral resolution of the measurements).
- The resulting errors are multiplied by a factor of 0.66 to correct for correlations between different layers not considered in the fit (see Noël et al., 2016, for details).

The resulting number density profiles are converted to volume mixing ratios (VMRs) using ECMWF pressure and temperature. The useful vertical range of the SCIAMACHY ONPD data is currently considered to be 17 to 45 km, mainly limited by noise and numerical effects at the upper altitudes and by tropospheric effects (e.g. clouds and increased refraction)) at the lower altitudes.

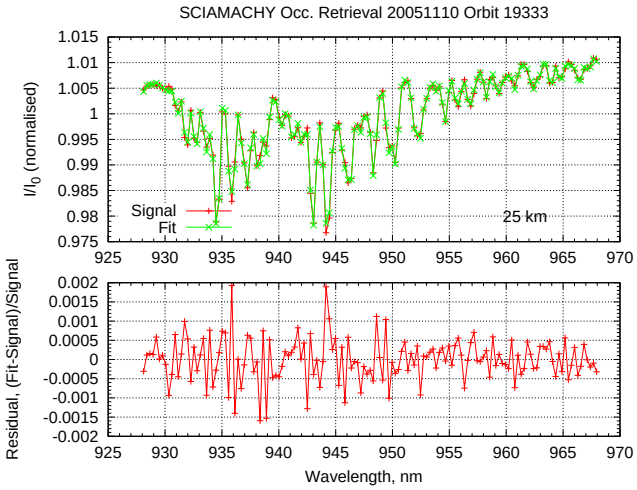

Figure 2. Example of a spectral fit. Top: normalised measured spectrum (red line) and fitted spectrum (green line) at 25 km tangent altitude. Bottom: resulting residual, i.e. relative difference between measurement and fit.

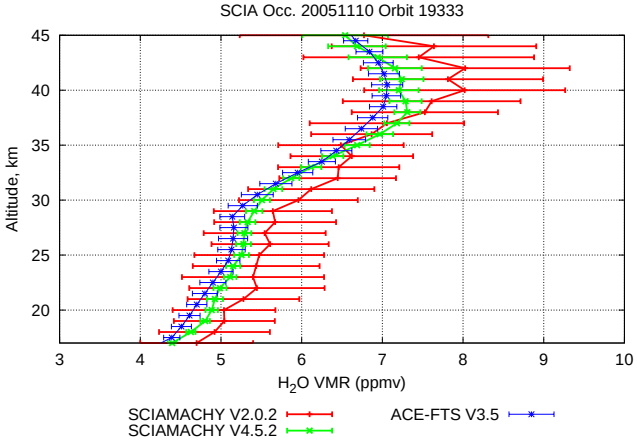

Figure 3. Example for H_2O VMR profiles. Red: previous product (V2.0.2) from Noël et al. (2010). Green: current product (V4.5.2). Blue: collocated profile from ACE-FTS V3.5.

3 Results

3.1 H_2O example data

Fig. 3 shows as an example the resulting water vapour VMR profile from a SCIAMACHY occultation measurement in November 2005. In green the result of the updated retrieval (V4.5.2) is shown. For comparison, the corresponding profile derived with the Noël et al. (2010) algorithm (V2.0.2) is plotted in red, and a collocated ACE-FTS profile (V3.5) in blue. The error bars denote the errors given in the products. Obviously, the new SCIAMACHY product is closer to the ACE-FTS results and the

reported error is ~~largely~~ reduced compared to the older version. This is due to the improved retrieval method ~~and to the updated calculation of errors~~ as described in Noël et al. (2016). The most relevant changes are:

- Use of a weighting function DOAS based fit at each altitude.
- Better consideration of altitudes below the actual tangent height.
- Improved selection of measurements.
- Use of improved input spectral data (better pointing information and calibration).
- Use of an updated radiative transfer model (SCIATRAN V3).
- Updated error calculation.

3.2 H_2O validation

A large number of water vapour data products have ~~contributed~~ been used in the analyses contributing to the second SPARC (Stratosphere-troposphere Processes And their Role in Climate) water vapour assessment (WAVAS-II; see e.g. Lossow et al., 2017, further publications in preparation). One activity of WAVAS-II was the inter-comparison of the different data sets, including a preliminary earlier version (V4.2.1) of the SCIAMACHY ONPD product. The performance of the V4.2.1 product is very similar to the V4.5.2 product described in this manuscript. ~~We therefore show~~ Consequently, in this section ~~only two~~ comparisons with collocated ACE-FTS (see e.g. Nassar et al., 2005) and MLS (see e.g. Carr et al., 1995; Lambert et al., 2007) data ~~as an example~~have been the focus of the additional validation. In both cases the spatial collocation ~~criterium~~ criterion is 800 km. For the ACE-FTS dataset we use only sunset data, ~~meaning that~~ as a result the local time difference to the SCIAMACHY data is usually less than one hour. For MLS we use a maximum time ~~distance~~ difference of 9 hours ~~to the~~ between the MLS and the SCIAMACHY measurements and always take the spatially closest match. ~~This~~ Overall, this results in 1330 collocations with ACE-FTS data products and almost 35000 collocations with MLS data products between 2004 and 2012.

Fig. 4 shows the results of the comparison between the SCIAMACHY ONPD V4.5.2 water vapour profiles and ACE-FTS V3.5 data. The MLS results are displayed in Fig. 5. The SCIAMACHY water vapour profiles agree with both data sets within less than 5%. The SCIAMACHY water vapour VMRs are usually ~~slightly~~ about 2–3% higher than those of ACE-FTS, but (except for the lowest altitudes) typically 2–3% smaller than MLS VMRs. A small vertical oscillation of 1–2% amplitude is ~~visible~~ observed in the differences~~; this is caused by~~ . This is attributed to the SCIAMACHY data and is probably a retrieval artifact which was also seen in the SCIAMACHY ONPD methane and CO_2 data (Noël et al., 2016). The observed deviations are ~~within~~ significantly smaller than the typical error ~~of the~~ on the data products.

The correlation between SCIAMACHY and both ACE-FTS and MLS data is generally high (reaching about 0.85 at 30 km), but is poorer at lower and higher altitudes. The reduction at higher altitudes may be a consequence of the larger relative errors of the SCIAMACHY data, but as yet there is no clear explanation. At lower altitudes, differences in the variability of the data play a role, as can be inferred from the standard deviations shown in panels c) of Fig. 4 and 5. High correlation is achieved

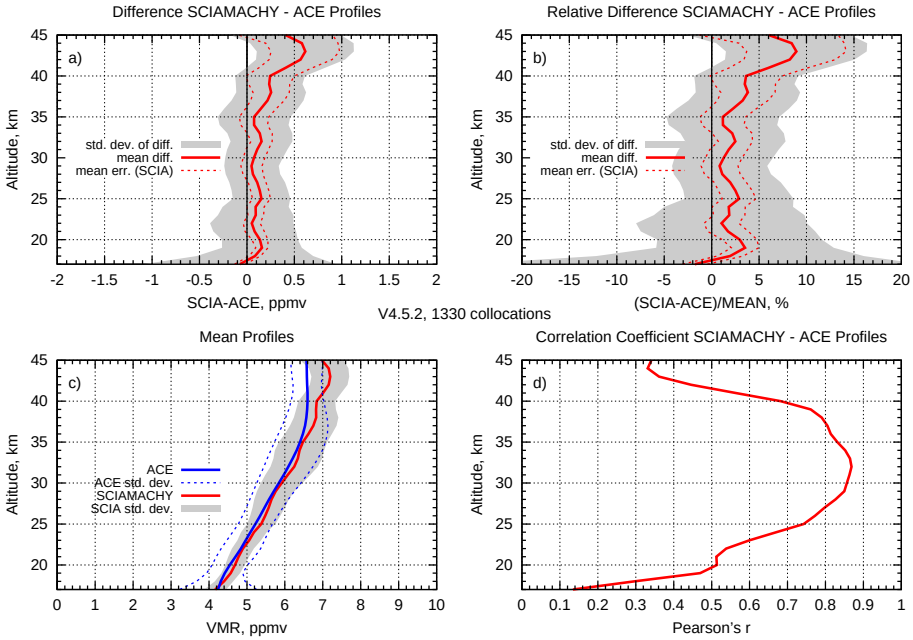

Figure 4. Comparison of retrieved SCIAMACHY H_2O profiles with ACE-FTS data 2004–2012. **(a)** Mean ~~absolute~~ difference plus/minus one standard deviation (shaded area) and mean ~~absolute~~ error of SCIAMACHY data (dotted line). **(b)** Mean relative difference plus/minus one standard deviation (shaded area) and mean relative error of SCIAMACHY data (dotted line). **(c)** Mean profiles and standard deviations (red: SCIAMACHY, blue: ACE-FTS). **(d)** Correlation between SCIAMACHY and ACE-FTS data.

when variability and variance are similar for both data sets, i.e. in this case both instruments see the same atmospheric changes.

3.3 Time series

The ONPD algorithm for water vapour has been applied to the ~~whole~~ entire set of SCIAMACHY measurements from August 2002 to April 2012. From the individual VMR profiles daily averages have been computed which are shown in Fig. 6 as function of time and altitude. As can be seen from the top curve in this figure, ~~there is a direct relation between~~ the latitude of the observation and the time in the year are coupled. Observations in summer are typically at lower latitudes than in winter. This pattern is ~~caused by the sun-fixed~~ a result of the sun synchronous orbit of ENVISAT and ~~thus repeats every year~~the changing location of the solar occultation as a function of season. The average tropopause height, derived from collocated ECMWF data and shown by the black line near the bottom, varies in a similar way. The SCIAMACHY solar occultation data have therefore a specific temporal and spatial sampling.

The SCIAMACHY water vapour profiles ~~perform~~ behave in general as expected: Highest VMRs (up to about 8 ppmv) occur at ~~upper~~ high altitudes, lowest VMRs at lower altitudes. The variation with time follows roughly the tropopause / latitude pattern.

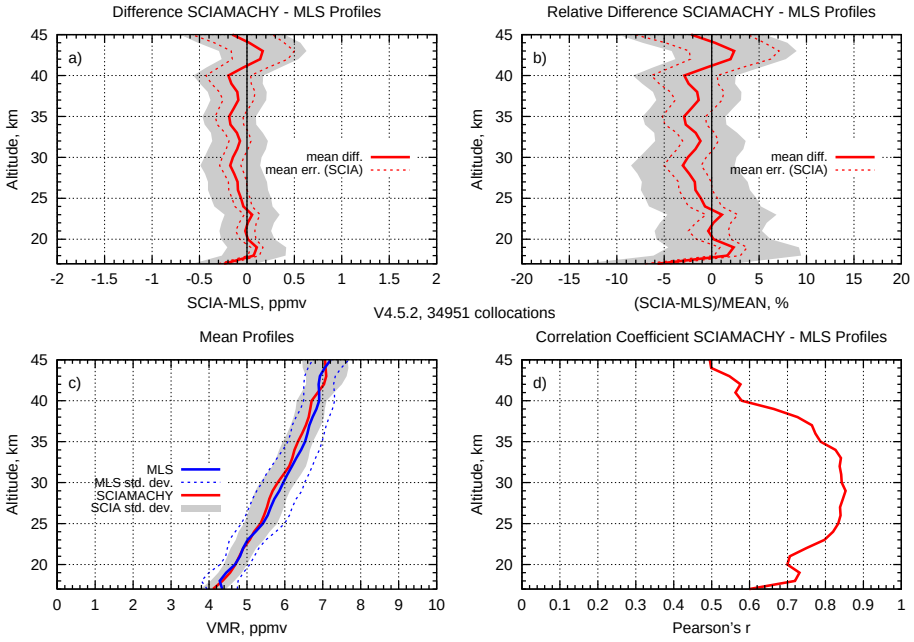

Figure 5. Same as Fig. 4, but for comparison of retrieved SCIAMACHY H_2O profiles with MLS V4.2 data 2004–2012.

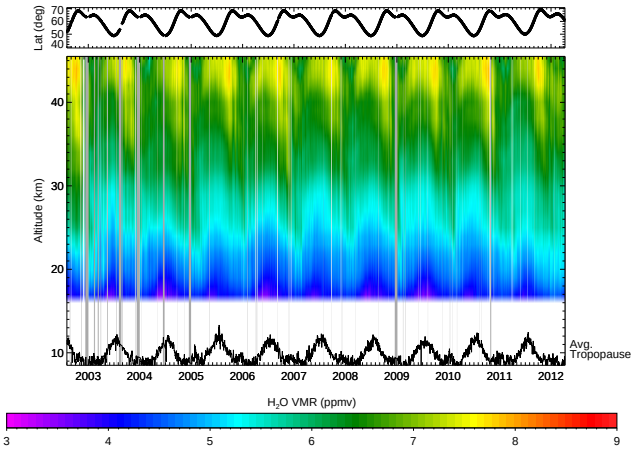

Figure 6. Time series of daily averaged SCIAMACHY H_2O VMR profiles from August 2002 to April 2012. In the top graph the latitudes of observations as function of time are shown. Grey vertical bars mask out times of reduced SCIAMACHY performance or missing data. The black curve at lower altitudes shows the average tropopause height.

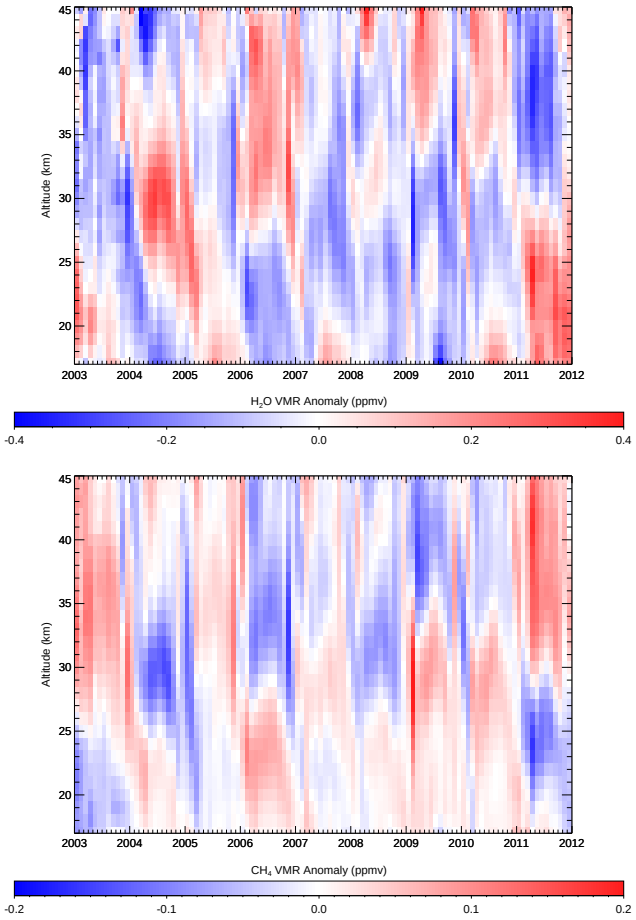

Figure 7. Time series of SCIAMACHY H_2O (top) and CH_4 (bottom) monthly VMR anomaly profiles from January 2003 to December 2011. The CH_4 plot is taken from Noël et al. (2016).

For a more detailed ~~analysis including the combination of~~ investigation of the observed behaviour of the water vapour and methane ~~results~~data products, we computed monthly anomalies from the SCIAMACHY H_2O data in the same way as described Noël et al. (2016) and ~~put them in relation to~~ compared them with the CH_4 data from this study. This is ~~done~~ achieved by first averaging the daily data over the months and then subtracting the long-term average for each month. To avoid different weighting of different months we limit this analysis to the time interval 2003 to 2011, i.e. we use only years for which data for all months are available.

In Fig. 7 the time series of the H_2O and CH_4 anomalies are shown. There is a clear ~~bi-annual~~ biennial structure visible in both ~~data sets with~~ of the data sets but of an opposite sign. As already mentioned in Noël et al. (2016), this structure is ~~related to the Quasi-Biannual-Oscillation~~ attributed to the Quasi-Biennial-Oscillation (QBO), see e.g. Baldwin et al. (2001).

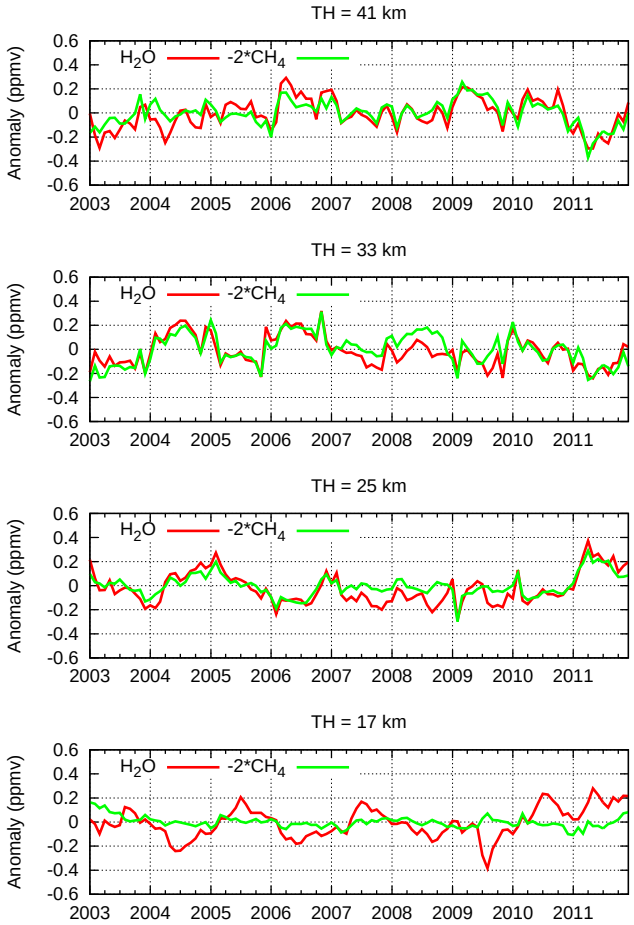

Figure 8. Time series of SCIAMACHY water vapour and methane anomalies at different altitudes. Methane data have been scaled by a factor -2.

~~However, although the structures are quite similar, water vapour and methane variations show an inverted behaviour: Positive methane~~ The methane anomalies correspond to ~~about twice as high negative~~ water vapour anomalies ~~and vice versa. This is in line~~ that are opposite in sign and twice the magnitude. This complies with the assumption, that most of the ~~water vapour is~~ changes in water vapour are produced from methane via the net reaction (R2).

To investigate this further, Fig. 8 shows for some selected altitudes the water vapour anomalies as a function of time together with the methane anomalies multiplied by -2. If water vapour ~~would be~~ were produced solely via reaction (R2), both curves would be identical. This is ~~in fact nearly~~ to a good approximation the case for altitudes above about 25 km, where the water vapour variations follow quite well the methane variation. At 17 km, however, the methane anomaly does not vary much whereas the water vapour anomaly still shows a clear QBO signature, which is shifted in phase with respect to 25 km.

The ~~downward peak~~ dip in the water vapour anomalies at 17 km in the middle of 2009 is related to the eruption of the Sarychev volcano on 12 June 2009, which reached these altitudes (Jégou et al., 2013). Note that this observed reduction of

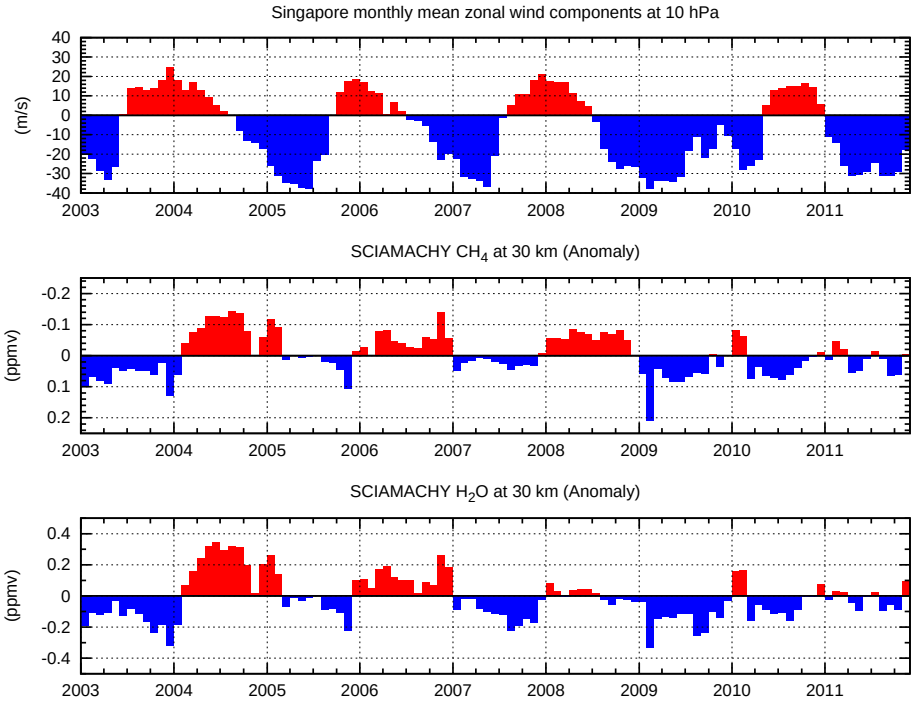

Figure 9. Time series of methane and water vapour anomalies at 30 km (middle and lower plots) and Singapore zonal wind at 10 hPa, corresponding to about 30 km (top). Note that the vertical axis of the methane data is inverted and scaled differently than for water vapour.

water vapour after the Sarychev eruption may be introduced by ~~the~~ errors in the water vapour retrieval due to the remaining sensitivity of the retrieval method to aerosol. In the retrieval only spectrally broadband contributions of aerosols are considered, but there are also (second order) effects e.g. caused by the vertical integration of the signal over the field of view, which may play a role in case of large aerosol concentrations. This issue is still under investigation.

The ~~relation to~~ impact of the QBO is illustrated in Fig. 9 which shows SCIAMACHY methane and water vapour anomalies at 30 km altitude as a function of time in comparison to the Singapore monthly mean stratospheric zonal wind at 10 hPa (corresponding to about the same altitude), which is commonly used as ~~proxy~~ index for the QBO (see e.g. Gebhardt et al., 2014). The Singapore wind data have been provided by Freie Universität Berlin (2014). Negative wind direction corresponds to Easterly winds (marked blue in Fig. 9), positive direction to Westerly winds (marked red). Water vapour negative and positive anomalies are also plotted in blue and red, respectively. For the methane plot, the vertical axis and colouring has been inverted ~~, because~~ in order to take account of the production of water vapour from methane, where an increase in water vapour should correspond to a reduction of methane according to (R2).

Fig. 9 shows that water vapour and (inverted) methane anomalies follow the variation of the Singapore winds / QBO quite well, supporting the proposal that the changes are mainly affected by transport processes. The phase shift between stratospheric wind and SCIAMACHY data is related to the time delay caused by the transport of air from the tropics (where Singapore winds

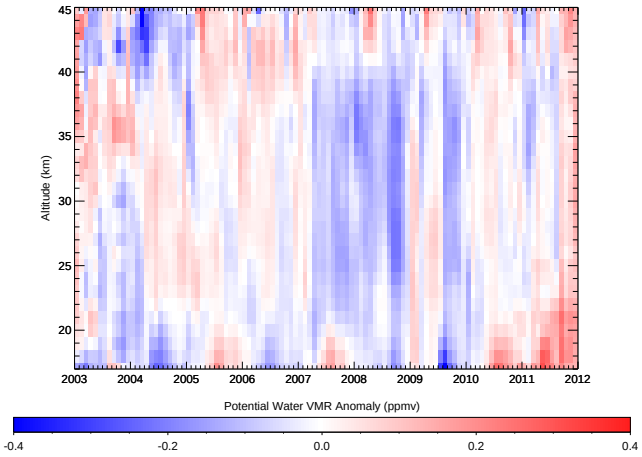

Figure 10. Potential water anomalies derived from combination of SCIAMACHY H_2O and CH_4 anomalies (Fig. 7).

are measured) and the mid/high latitudes of the SCIAMACHY data. Note that the age of air at these altitudes may be up to about 8 years according to e.g. Haenel et al. (2015). Consequently, the actual phase shift is expected to be larger than one 2-year period of the QBO. It therefore cannot be determined well from our 9-year time series. After about 2010 there are some differences between the wind data and the SCIAMACHY results. ~~Especially, the positive anomaly~~ The positive values in the wind data around 2010/2011 ~~is only hardly visible~~ are hardly detected in the methane and water vapour data. On the other hand, positive anomalies of water vapour and (inverted) methane are quite strong at the begin of the time series. Possible reasons for ~~this~~ these differences are currently unclear; maybe this is related to trends in the SCIAMACHY data (see below)~~, but this requires further investigations~~.

3.4 Potential water

To further investigate the ~~temporal variabilities~~ production of water vapour from methane in the stratosphere a time series has been derived by adding ~~to~~ the water vapour VMR anomalies to two times the methane VMR anomalies. As mentioned above this combination, referred to as potential water (Nassar et al., 2005), is assumed to be conserved if water vapour is solely produced from methane oxidation, and temporal variations of this quantity ~~can be related to~~ indicate changes in transport or additional sources and sinks. The result is displayed in Fig. 10.

Below about 20 km the ~~bi-annual~~ biennial structure of the QBO is visible. After about 2010 there seems to be an additional increase of potential water, which is transported upwards. From the methane and water vapour time series shown in Fig. 8 it is evident that most of these changes are due to changing water vapour VMRs. The negative values in the second half of 2009 are ~~related to~~ associated with the Sarychev eruption, as explained before.

Between 20 and 40 km the vertical profile of the potential water anomaly is ~~especially~~ in summer (i.e. at lower latitudes) rather constant. In winter (corresponding to higher latitudes) sometimes larger variability is observed, possibly due to influences

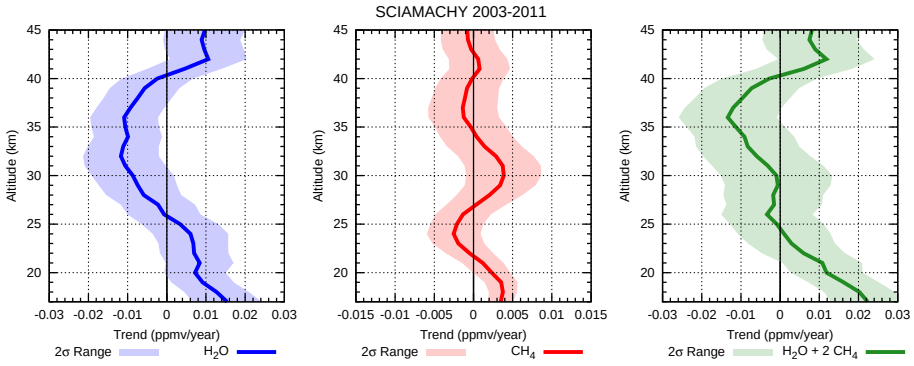

Figure 11. Calculated VMR trends of H_2O (blue; left) and CH_4 (red; middle) from 2003 to 2011 as function of altitude. Methane data are from Noël et al. (2016). Right plot: Potential water trend derived from the combination of H_2O and CH_4 trends.

of the polar vortex. In 2003 and the first months of 2004, patterns are more patchy due to the different vertical sampling of the measurements at this time (see also Noël et al., 2016). In this time interval, positive anomalies occur around 35 km, negative anomalies above and below. Between about 2004 and 2007 potential water anomalies are typically positive whereas from 2007 to 2009 or 2010 they are mainly negative, ~~later on~~ and then later on in the time series they tend to be positive again. This ~~suggests~~ implies a periodicity of about 5 to 6 years, but due to the ~~shortness~~ limited length of the time series~~it is not possible to confirm this~~ , this can only be confirmed in the future.

Above 40 km the variability of the potential water anomaly is quite high. This may be ~~related~~ connected to the larger ~~uncertainties~~ error and variance of the ONPD data at higher altitudes.

3.5 Trends

~~A linear trend model~~ The time series of SCIAMACHY data covers only ten (nine complete) years. Consequently it is not possible to derive from these data long-term trends. In this sense, the trends shown in the following have to be interpreted as changes over the corresponding time interval 2003 to 2011.

To derive these changes, a linear regression has been fitted to the water vapour anomalies at each altitude similar to ~~what has been applied~~ that used in the earlier methane study, see Noël et al. (2016). ~~The trend~~ For this, we take the anomaly times series at a selected altitude (see e.g. Fig. 8) and fit a straight line to it. The slope of this line is the estimated trend for this altitude, the error of the trend is the error of the slope given by the fit. This procedure is undertaken at each of the altitudes from 17 to 45 km, in 1 km steps. The resulting trend profiles are displayed in Fig. 11.

The derived water vapour trends (left plot) are positive at altitudes below about 25 km, reaching a maximum value of about 0.015 ± 0.008 ppmv year^{-1} at 17 km. Between about 25 and 40 km the water vapour trends are negative and up to about -0.01 ± 0.008 ppmv year^{-1} ~~.~~ (all errors are two standard deviations i.e. 2σ values). The 2σ error or uncertainty ranges also plotted indicate that the water vapour trends are not ~~significant in a statistical sense~~ statistically significant at altitudes above 37 km and between 20 and 30 km where the trend switches sign. A positive trend in lower stratospheric water vapour during

the time interval considered in this study has been observed by Urban et al. (2014) and Weigel et al. (2016) mainly in the tropics. As already discussed in Noël et al. (2016) methane trends are also not significant except for the lowest altitudes, where they are in general agreement with tropospheric trends. However, it should be noted that errors of the data and autocorrelation of noise have not been considered in the trend fits, which might affect the trend errors.

The potential water vapour trend is the sum of the water vapour trend and two times the methane trend. This is an estimate ~~an estimate~~ for water vapour changes or methane changes not related to the stratospheric production of water vapour by methane. If potential water is conserved, ~~this~~ the potential water trend should be zero. The potential water trend profile is shown in the right plot of Fig. 11. The error of the potential water trend has been derived via propagation of the errors of the methane and water vapour trends. ~~Considering this error, the combined trend above about 20~~Given that the trends in potential water between 21 and 45 km ~~is in a statistical sense not significant, meaning that the assumption that all~~ lack statistical significance, there is no evidence that water vapour is produced ~~from methane via the net reaction (R2) is not disproved by the measurements. This is especially the case between 25 and 30 where the trend itself is close to zero.~~ in the stratosphere by any mechanism other than methane oxidation. At the lower altitudes, a significant deviation of the potential water trend from zero is observed (up to about 0.02 ± 0.018 ppmv year^{-1}).

4 Discussion

The findings of ~~the previous section can be~~ this study are summarised as follows:

- Water vapour and methane time series and trends ~~look~~ are different above and below about 20 km.
- ~~In the upper~~ At higher altitudes both water vapour and methane time series show a pronounced QBO signature.
- In the lower stratosphere, QBO signature is only visible in the water vapour data.
- There is a phase shift in the water vapour QBO signal between upper and lower altitudes.
- Potential water, the combination of methane and water vapour VMRs, is essentially conserved at ~~upper altitudesexcept for~~ higher stratospheric altitudes; the exceptions being some short-term events and a longer-term variation ~~with a period~~ having patterns of about 5–6 years duration.
- The QBO signal is also visible in the potential water data at lower altitudes until about 2009/2010 ~~; after that~~ after which potential water increases slowly.

~~Simplified schematic view of transport pathways within the Brewer-Dobson circulation.~~

~~These observations can be explained by~~ These observations are consistent with a separation of the stratosphere into two vertical regimes. The lower ~~region~~ regime is mainly affected by the shallow (or lower) branch of the Brewer-Dobson circulation Butchart (2014), whereas in the upper part the deep (or upper) branch of the Brewer-Dobson circulation dominates, see also Fig. 1. According to the data of the present study, this separation occurs at about 20 km~~; however~~. However it has to be kept

in mind that this is an ~~approximated~~ approximate value and that the vertical resolution of the SCIAMACHY solar occultation data is about 4 km.

In the lower ~~region, variability is determined by water vapour~~ regime, water vapour variability is mainly determined by variations due to ~~QBO effects on tropopause temperature and /or stratospheric transport and due to tropospheric methane variations; above, water vapour is mainly produced from methane oxidation and potential water anomalies are more homogeneous with altitude and change on longer time scales.~~

~~Water vapour and methane below 20 are therefore dominated by the variations imprinted on them from their tropospheric sources especially during their vertical transport into the stratosphere at tropical regions. The amount of water vapour entering the tropical stratosphere is related to the tropopause temperaturewhich varies with QBO~~the impact of the QBO and the Brewer-Dobson circulation on the tropopause temperature, see e.g. Fueglistaler and Haynes (2005). ~~This is not the case for methane , which could explain the missing QBO signature in the methane time series at 17 (Fig. 8).~~ Methane entering the tropical stratosphere is mainly affected by tropospheric methane trends. In the lowermost extratropical stratosphere the water vapour and methane amounts follow the tropical amounts delayed by the transport time via the shallow branch of the Brewer-Dobson circulation.

The ~~missing balance between~~ lack of a balance between the oxidation of methane and water vapour at lower altitudes is in fact not surprising, because the photochemical processes involved in the conversion of methane to water vapour are less effective there~~since~~ . This is because less UV radiation reaches these altitudes (le Texier et al., 1988). Furthermore, since the transport via the shallow branch is comparably fast (~~less than about one year~~ depending on latitude, altitude and season a few years or less from the entry point in the tropics to mid-latitudes, see Birner and Bönisch, 2011) the ~~balance between~~ changes in water vapour and methane ~~is also not reached~~ are not coupled in the extratropical lowermost stratosphere. This ~~could explain the phase shift in the water vapour QBO signal between 25 and 17 (Fig. 8) and is in line with measurements of age of air by e. g. which show that the air at 17 is younger than the air above.~~ is the main reason why potential water is not conserved in this regime.

Schneising et al. (2011) estimated for the time interval 2007 to 2009 a tropospheric increase of methane of about 8 $\mathrm{ppbv\ year^{-1}}$ following a period of no significant change from 2003 to 2007. ~~Considering a~~ Taking into account the delay between the tropospheric and a possible stratospheric trend related to the age of air (about 2–3 years ~~since emission at~~ between injection into the stratosphere at the tropics and measurement at 17 km at higher latitudes according to Haenel et al., 2015) ~~, this could explain~~ explains part but not all of the increase of potential water at lower altitudes after 2009/2010 shown in Fig. 10. ~~Until~~ An additional influence of varying tropical tropospheric water vapour on the observed increase of potential water is therefore likely. Prior to the end of 2011 the positive potential water anomaly extends to higher altitudes. This is in agreement with the increasing age of air at higher altitudes. ~~However, from the current data set an additional influence of varying tropospheric water vapour input on the observed increase of potential water cannot be ruled out.~~

In the upper dynamical regime water vapour is produced from methane oxidation and potential water anomalies are to a good approximation homogeneous with altitude and change on longer time scales. Above 20 km, in the region of the deep branch of the Brewer-Dobson circulation, air is older~~such that the conversion process from~~ . This enables oxidation of methane

to water vapour ~~has reached an equilibrium,~~ to be completed rapidly. As a result variations of both gases are in phase and potential water is essentially conserved (Fig. 8). ~~A remaining open issue is the QBO signal observed in both methane and water vapour at higher stratospheric altitudes. The conservation of potential water indicates that at~~ Consequently at these altitudes water vapour changes ~~are mainly related to changes~~ can be concluded to be mainly determined by the oxidation of methane. ~~Therefore the QBO signal has to be carried by methane , but as can be seen at lower altitudesthe methane entering the stratosphere is not varied by QBO. The QBO signature in the upper altitude data~~

Another feature observed in the SCIAMACHY data is a change of potential water at higher altitudes on a timescale of 5–6 years. This could be attributed to low-frequency changes in the Brewer-Dobson circulation or long-term variations in water vapour trends currently under discussion (see e.g. Hegglin et al. (2014)).

A QBO signal is observed in both methane and water vapour at higher stratospheric altitudes. This QBO signature can be explained by a ~~QBO-related~~ QBO-dependent modulation of the transport to higher altitudes and to higher latitudes via the deep branch of the Brewer-Dobson circulation, similar to the variation in tropical aerosol extinction coefficients as seen by Brinkhoff et al. (2015) at 30 km. ~~Also~~ Randel et al. (1998) also observed a QBO signal in tropical methane from HALOE measurements on UARS above about 35 km but not below, correlated with the residual mean wind circulation. This is also in ~~line~~ agreement with results from e.g. Niwano et al. (2003) and Minschwaner et al. (2016) who determined the vertical transport velocity in the tropics from HALOE and MLS measurements, respectively, and confirmed a variation with QBO. The phase shift in the observed QBO signal of water vapour between 17 and 25 km (Fig. 8) is in agreement with the measurements of age of air by Haenel et al. (2015), which indicate differences in transport time.

5 Conclusions

A new stratospheric water vapour data set based on SCIAMACHY solar occultation measurements is made available. It covers the latitude range between about 50 and 70°N and the altitude range from 17 to 45 km. It has been generated in a similar way ~~as the corresponding~~ to the methane product (Noël et al., 2016)~~resulting in a consistent data set~~. Comparisons with independent data indicate ~~an accuracy~~ the error of the water vapour profiles ~~of~~ to be about 5%. Between 2003 and 2011 a significant positive water vapour trend is observed at altitudes below 20 km (0.015$\pm$0.008 ppmv year^{-1} at 17 km). On the other hand, a significant negative water vapour trend of about -0.01$\pm$0.008 ppmv year^{-1} is derived for the altitude range 30–37 km; all errors are 2σ values.

The combination of the methane and water vapour time series data gives information about sources and transport of water vapour in the stratosphere.

~~Variations~~ At altitudes above about 20 km, variations in water vapour are clearly correlated with those of methane. A QBO signature is visible in both water vapour and methane anomaly time series, showing that transport from the tropics affects essentially the whole altitude range under investigation in this study.

The analysis of the combined water vapour and methane data sets reveals, that potential water, the sum of water vapour VMR and two time methane VMR, seems to be ~~overall~~ conserved between about 20 and 40–45 km. However, potential water

is not constant over time. In addition to short term fluctuations a variation on a timescale of 5–6 years is observed~~, which needs further investigation~~.

At altitudes below about 20 km the QBO signature is only visible in water vapour but not in methane data. As a consequence, potential water also shows a significant QBO variation~~, but also~~. In addition a continuous increase is observed after about 2009.

We explain this behaviour by a separation of the stratosphere into two regimes: ~~Altitudes~~ i) altitudes above about 20 km ~~are~~ being fed via the deep branch of the Brewer-Dobson circulation, and water vapour ~~is essentially~~ being produced from methane oxidation~~. At~~ ; ii) at altitudes below water vapour and methane have been transported from the tropics to higher latitudes via the shallow branch of the Brewer-Dobson circulation. The ~~rise~~ increase of tropospheric methane after 2007 reaches these lower stratospheric altitudes with a delay of about 2 years~~, resulting – possibly in combination with changes of water vapour – in~~ . This contributes in part to the observed increase of potential water after ~~2009.~~ 2009, but additional processes such as changes of tropospheric water vapour input are required for a quantitative explanation.

Data availability. SCIAMACHY Level 1b data are available from ESA (https://earth.esa.int) after registration. All SCIAMACHY ONPD data V4.5.2 are available on request from S. Noël. The methane product V4.5.2 is also provided via the GHG-CCI web site http://www.esa-ghg-cci.org/ and accessible after registration.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. The Atmospheric Chemistry Experiment (ACE), also known as SCISAT, is a Canadian-led mission mainly supported by the Canadian Space Agency and the Natural Sciences and Engineering Research Council of Canada. The MLS data used in this research were produced by the Jet Propulsion Laboratory, California Institute of Technology under contract with the National Aeronautics and Space Adminstration (https://urs.earthdata.nasa.gov/, https://mls.jpl.nasa.gov/). The European Centre for Medium Range Weather Forecasts (ECMWF) provided the ERA Interim meteorological data used in this study. FU Berlin provided Singapore winds data. Geoffrey Toon of the NASA Jet Propulsion Laboratory is acknowledged for providing the empirical solar line list used in the retrieval. Part of this work was supported by the DFG Forschergruppe SHARP Water Vapor (SHARP-WV). This work has been funded by DLR Space Agency (Germany), the ESA GHG-CCI and by the University and the state of Bremen.

References

Baldwin, M. P., Gray, L. J., Dunkerton, T. J., Hamilton, K., Haynes, P. H., Randel, W. J., Holton, J. R., Alexander, M. J., Hirota, I., Horinouchi, T., Jones, D. B. A., Kinnersley, J. S., Marquardt, C., Sato, K., and Takahashi, M.: The quasi-biennial oscillation, Reviews of Geophysics, 39, 179–229, https://doi.org/10.1029/1999RG000073, http://dx.doi.org/10.1029/1999RG000073, 2001.

Bernath, P. F., McElroy, C. T., Abrams, M. C., Boone, C. D., Butler, M., Camy-Peyret, C., Carleer, M., Clerbaux, C., Coheur, P.-F., Colin, R., DeCola, P., DeMazière, M., Drummond, J. R., Dufour, D., Evans, W. F. J., Fast, H., Fussen, D., Gilbert, K., Jennings, D. E., Llewellyn, E. J., Lowe, R. P., Mahieu, E., McConnell, J. C., McHugh, M., McLeod, S. D., Michaud, R., Midwinter, C., Nassar, R., Nichitiu, F., Nowlan, C., Rinsland, C. P., Rochon, Y. J., Rowlands, N., Semeniuk, K., Simon, P., Skelton, R., Sloan, J. J., Soucy, M.-A., Strong, K., Tremblay, P., Turnbull, D., Walker, K. A., Walkty, I., Wardle, D. A., Wehrle, V., Zander, R., and Zou, J.: Atmospheric Chemistry Experiment (ACE): Mission overview, Geophys. Res. Lett., 32, ~~L15S01,~~ https://doi.org/10.1029/2005GL022386, L15S01, 2005.

Birner, T. and Bönisch, H.: Residual circulation trajectories and transit times into the extratropical lowermost stratosphere, Atmos. Chem. Phys., 11, 817–827, https://doi.org/10.5194/acp-11-817-2011, https://www.atmos-chem-phys.net/11/817/2011/, 2011.

Birner, T., Sankey, D., and Shepherd, T. G.: The tropopause inversion layer in models and analyses, Geophys. Res. Lett., 33, https://doi.org/10.1029/2006GL026549, http://dx.doi.org/10.1029/2006GL026549, L14804, 2006.

Bovensmann, H., Burrows, J. P., Buchwitz, M., Frerick, J., Noël, S., Rozanov, V. V., Chance, K. V., and Goede, A. H. P.: SCIAMACHY — Mission Objectives and Measurement Modes, J. Atmos. Sci., 56, 127–150, 1999.

Brewer, A. W.: Evidence for a world circulation provided by the measurements of helium and water vapour distribution in the stratosphere, Quart. J. Royal Met. Soc., 75, 351–363, https://doi.org/10.1002/qj.49707532603, http://dx.doi.org/10.1002/qj.49707532603, 1949.

Brinkhoff, L. A., Rozanov, A., Hommel, R., von Savigny, C., Ernst, F., Bovensmann, H., and Burrows, J. P.: Ten-Year SCIAMACHY Stratospheric Aerosol Data Record: Signature of the Secondary Meridional Circulation Associated with the Quasi-Biennial Oscillation, in: Towards an Interdisciplinary Approach in Earth System Science: Advances of a Helmholtz Graduate Research School, edited by Lohmann, G., Meggers, H., Unnithan, V., Wolf-Gladrow, D., Notholt, J., and Bracher, A., pp. 49–58, Springer International Publishing, https://doi.org/10.1007/978-3-319-13865-7_6, https://doi.org/10.1007/978-3-319-13865-7_6, 2015.

Buchwitz, M., Schneising, O., Reuter, M., Heymann, J., Krautwurst, S., Bovensmann, H., Burrows, J. P., Boesch, H., Parker, R. J., Somkuti, P., Detmers, R. G., Hasekamp, O. P., Aben, I., Butz, A., Frankenberg, C., and Turner, A. J.: Satellite-derived methane hotspot emission estimates using a fast data-driven method, Atmos. Chem. Phys., 17, 5751–5774, https://doi.org/10.5194/acp-17-5751-2017, http://www.atmos-chem-phys.net/17/5751/2017/, 2017.

Burrows, J. P., Weber, M., Buchwitz, M., Rozanov, V., Ladstätter-Weißenmayer, A., Richter, A., de Beek, R., Hoogen, R., Bramstedt, K., Eichmann, K.-U., Eisinger, M., and Perner, D.: The Global Ozone Monitoring Experiment (GOME): Mission Concept and First Scientific Results, J. Atmos. Sci., 56, 151–175, 1999.

Butchart, N.: The Brewer-Dobson circulation, Rev. Geophys., 52, 157–184, https://doi.org/10.1002/2013RG000448, http://dx.doi.org/10.1002/2013RG000448, 2014.

Carr, E. S., Harwood, R. S., Mote, P. W., Peckham, G. E., Suttie, R. A., Lahoz, W. A., O'Neill, A., Froidevaux, L., Jarnot, R. F., Read, W. G., Waters, J. W., and Swinbank, R.: Tropical stratospheric water vapor measured by the Microwave Limb Sounder (MLS), Geophys. Res. Lett., 22, 691–694, https://doi.org/10.1029/95GL00626, http://dx.doi.org/10.1029/95GL00626, 1995.

Coldewey-Egbers, M., Weber, M., Lamsal, L. N., de Beek, R., Buchwitz, M., and Burrows, J. P.: Total ozone retrieval from GOME UV spectral data using the weighting function DOAS approach, Atmospheric Chemistry and Physics, 5, 1015–1025, https://doi.org/10.5194/acp-5-1015-2005, http://www.atmos-chem-phys.net/5/1015/2005/, 2005.

Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, L., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park, B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N., and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, Quart. J. Royal Met. Soc., 137, 553–597, https://doi.org/10.1002/qj.828, http://dx.doi.org/10.1002/qj.828, 2011.

Dhomse, S., Weber, M., and Burrows, J.: The relationship between tropospheric wave forcing and tropical lower stratospheric water vapor, Atmos. Chem. Phys., 8, 471–480, https://doi.org/10.5194/acp-8-471-2008, https://www.atmos-chem-phys.net/8/471/2008/, 2008.

Fischer, H., Birk, M., Blom, C., Carli, B., Carlotti, M., von Clarmann, T., Delbouille, L., Dudhia, A., Ehhalt, D., Endemann, M., Flaud, J. M., Gessner, R., Kleinert, A., Koopman, R., Langen, J., López-Puertas, M., Mosner, P., Nett, H., Oelhaf, H., Perron, G., Remedios, J., Ridolfi, M., Stiller, G., and Zander, R.: MIPAS: an instrument for atmospheric and climate research, Atmos. Chem. Phys., 8, 2151–2188, http://www.atmos-chem-phys.net/8/2151/2008/, 2008.

Freie Universität Berlin: Die Quasi-Biennial-Oszillation (QBO) Datenreihe, Fachbereich Geowissenschaften / Institut für Meteorologie, AG Atmosphärendynamik, http://www.geo.fu-berlin.de/met/ag/strat/produkte/qbo/index.html, downloaded 9 July, 2014.

Fueglistaler, S. and Haynes, P. H.: Control of interannual and longer-term variability of stratospheric water vapor, J. Geophys. Res. Atmos., 110, https://doi.org/10.1029/2005JD006019, http://dx.doi.org/10.1029/2005JD006019, ~~d24108~~D24108, 2005.

Gebhardt, C., Rozanov, A., Hommel, R., Weber, M., Bovensmann, H., Burrows, J. P., Degenstein, D., Froidevaux, L., and Thompson, A. M.: Stratospheric ozone trends and variability as seen by SCIAMACHY from 2002 to 2012, Atmos. Chem. Phys., 14, 831–846, https://doi.org/10.5194/acp-14-831-2014, https://www.atmos-chem-phys.net/14/831/2014/, 2014.

Gordley, L. L., Hervig, M. E., Fish, C., Russell, J. M., Bailey, S., Cook, J., Hansen, S., Shumway, A., Paxton, G., Deaver, L., Marshall, T., Burton, J., Magill, B., Brown, C., Thompson, E., and Kemp, J.: The solar occultation for ice experiment, J. Atmos. Sol.-Terr. Phys., 71, 300 – 315, https://doi.org/http://dx.doi.org/10.1016/j.jastp.2008.07.012, http://www.sciencedirect.com/science/article/pii/S136468260800206X, global Perspectives on the Aeronomy of the Summer Mesopause Region, 2009.

Gottwald, M. and Bovensmann, H., eds.: SCIAMACHY - Exploring the Changing Earth's Atmosphere, Springer Dordrecht Heidelberg London New York, https://doi.org/10.1007/978-90-481-9896-2, 2011.

Haenel, F. J., Stiller, G. P., von Clarmann, T., Funke, B., Eckert, E., Glatthor, N., Grabowski, U., Kellmann, S., Kiefer, M., Linden, A., and Reddmann, T.: Reassessment of MIPAS age of air trends and variability, Atmos. Chem. Phys., 15, 13 161–13 176, https://doi.org/10.5194/acp-15-13161-2015, https://www.atmos-chem-phys.net/15/13161/2015/, 2015.

Hegglin, M. I., Plummer, D. A., Shepherd, T. G., Scinocca, J. F., Anderson, J., Froidevaux, L., Funke, B., Hurst, D., Rozanov, A., Urban, J., von Clarmann, T., Walker, K. A., Wang, H. J., Tegtmeier, S., and Weigel, K.: Vertical structure of stratospheric water vapour trends derived from merged satellite data, Nature Geosci., 7, 768–776, https://doi.org/10.1038/ngeo2236, http://dx.doi.org/10.1038/ngeo2236, 2014.

Holton, J. R. and Gettelman, A.: Horizontal transport and the dehydration of the stratosphere, Geophys. Res. Lett., 28, 2799–2802, https://doi.org/10.1029/2001GL013148, http://dx.doi.org/10.1029/2001GL013148, 2001.

Jégou, F., Berthet, G., Brogniez, C., Renard, J.-B., François, P., Haywood, J. M., Jones, A., Bourgeois, Q., Lurton, T., Auriol, F., Godin-Beekmann, S., Guimbaud, C., Krysztofiak, G., Gaubicher, B., Chartier, M., Clarisse, L., Clerbaux, C., Balois, J. Y., Verwaerde, C., and

Daugeron, D.: Stratospheric aerosols from the Sarychev volcano eruption in the 2009 Arctic summer, Atmos. Chem. Phys., 13, 6533–6552, https://doi.org/10.5194/acp-13-6533-2013, http://www.atmos-chem-phys.net/13/6533/2013/, 2013.

Juckes, M. N.: An annual cycle of long lived stratospheric gases from MIPAS, Atmos. Chem. Phys., 7, 1879–1897, https://doi.org/10.5194/acp-7-1879-2007, https://www.atmos-chem-phys.net/7/1879/2007/, 2007.

Laeng, A., Plieninger, J., von Clarmann, T., Grabowski, U., Stiller, G., Eckert, E., Glatthor, N., Haenel, F., Kellmann, S., Kiefer, M., Linden, A., Lossow, S., Deaver, L., Engel, A., Hervig, M., Levin, I., McHugh, M., Noël, S., Toon, G., and Walker, K.: Validation of MIPAS IMK/IAA methane profiles, Atmos. Meas. Tech., 8, 5251–5261, https://doi.org/10.5194/amt-8-5251-2015, http://www.atmos-meas-tech.net/8/5251/2015/, 2015.

Lambert, A., Read, W. G., Livesey, N. J., Santee, M. L., Manney, G. L., Froidevaux, L., Wu, D. L., Schwartz, M. J., Pumphrey, H. C., Jimenez, C., Nedoluha, G. E., Cofield, R. E., Cuddy, D. T., Daffer, W. H., Drouin, B. J., Fuller, R. A., Jarnot, R. F., Knosp, B. W., Pickett, H. M., Perun, V. S., Snyder, W. V., Stek, P. C., Thurstans, R. P., Wagner, P. A., Waters, J. W., Jucks, K. W., Toon, G. C., Stachnik, R. A., Bernath, P. F., Boone, C. D., Walker, K. A., Urban, J., Murtagh, D., Elkins, J. W., and Atlas, E.: Validation of the Aura Microwave Limb Sounder middle atmosphere water vapor and nitrous oxide measurements, J. Geophys. Res. Atmos., 112, n/a–n/a, https://doi.org/10.1029/2007JD008724, http://dx.doi.org/10.1029/2007JD008724, ~~d24S36~~D24S36, 2007.

le Texier, H., Solomon, S., and Garcia, R. R.: The role of molecular hydrogen and methane oxidation in the water vapour budget of the stratosphere, Quart. J. Royal Met. Soc., 114, 281–295, https://doi.org/10.1002/qj.49711448002, http://dx.doi.org/10.1002/qj.49711448002, 1988.

Lossow, S., Khosrawi, F., Nedoluha, G. E., Azam, F., Bramstedt, K., Burrows, Dinelli, B. M., Eriksson, P., Espy, P. J., García-Comas, M., Gille, J. C., Kiefer, M., Noël, S., Raspollini, P., Read, W. G., Rosenlof, K. H., Rozanov, A., Sioris, C. E., Stiller, G. P., Walker, K. A., and Weigel, K.: The SPARC water vapour assessment II: comparison of annual, semi-annual and quasi-biennial variations in stratospheric and lower mesospheric water vapour observed from satellites, Atmos. Meas. Tech., 10, 1111–1137, https://doi.org/10.5194/amt-10-1111-2017, http://www.atmos-meas-tech.net/10/1111/2017/, 2017.

Minschwaner, K., Su, H., and Jiang, J. H.: The upward branch of the Brewer-Dobson circulation quantified by tropical stratospheric water vapor and carbon monoxide measurements from the Aura Microwave Limb Sounder, J. Geophys. Res. Atmos., 121, 2790–2804, https://doi.org/10.1002/2015JD023961, http://dx.doi.org/10.1002/2015JD023961, 2015JD023961, 2016.

Nassar, R., Bernath, P. F., Boone, C. D., Manney, G. L., McLeod, S. D., Rinsland, C. P., Skelton, R., and Walker, K. A.: Stratospheric abundances of water and methane based on ACE-FTS measurements, Geophys. Res. Lett., 32, https://doi.org/10.1029/2005GL022383, http://dx.doi.org/10.1029/2005GL022383, ~~I15S04~~L15S04, 2005.

Niwano, M., Yamazaki, K., and Shiotani, M.: Seasonal and QBO variations of ascent rate in the tropical lower stratosphere as inferred from UARS HALOE trace gas data, J. Geophys. Res. Atmos., 108, n/a–n/a, https://doi.org/10.1029/2003JD003871, http://dx.doi.org/10.1029/2003JD003871, 4794, 2003.

Noël, S., Bramstedt, K., Rozanov, A., Bovensmann, H., and Burrows, J. P.: Water vapour profiles from SCIAMACHY solar occultation measurements derived with an onion peeling approach, Atmos. Meas. Tech., 3, 523–535, http://www.atmos-meas-tech.net/3/523/2010/, 2010.

Noël, S., Bramstedt, K., Hilker, M., Liebing, P., Plieninger, J., Reuter, M., Rozanov, A., Sioris, C. E., Bovensmann, H., and Burrows, J. P.: Stratospheric CH_4 and CO_2 profiles derived from SCIAMACHY solar occultation measurements, Atmos. Meas. Tech., 9, 1485–1503, https://doi.org/10.5194/amt-9-1485-2016, http://www.atmos-meas-tech.net/9/1485/2016/, 2016.

Payan, S., Camy-Peyret, C., Oelhaf, H., Wetzel, G., Maucher, G., Keim, C., Pirre, M., Huret, N., Engel, A., Volk, M. C., Kuellmann, H., Kuttippurath, J., Cortesi, U., Bianchini, G., Mencaraglia, F., Raspollini, P., Redaelli, G., Vigouroux, C., De Maziére, M., Mikuteit, S., Blumenstock, T., Velazco, V., Notholt, J., Mahieu, E., Duchatelet, P., Smale, D., Wood, S., Jones, N., Piccolo, C., Payne, V., Bracher, A., Glatthor, N., Stiller, G., Grunow, K., Jeseck, P., Te, Y., and Butz, A.: Validation of version-4.61 methane and nitrous oxide observed by MIPAS, Atmos. Chem. Phys., 9, 413–442, https://doi.org/10.5194/acp-9-413-2009, http://www.atmos-chem-phys.net/9/413/2009/, 2009.

Payne, V., Dudhia, A., and Piccolo, C.: Analysis of Water Vapour and Methane from the MIPAS Satellite Instrument, in: Proceedings of the 2004 Envisat & ERS Symposium 6–10 September 2004, Salzburg, Austria, edited by Lacoste, H. and Ouwehand, L., vol. 572 of *ESA Special Publication*, 2005.

Perner, D. and Platt, U.: Detection of Nitrous Acid in the Atmosphere by Differential Optical Absorption, Geophys. Res. Lett., 6, 917–920, 1979.

Plieninger, J., Laeng, A., Lossow, S., von Clarmann, T., Stiller, G. P., Kellmann, S., Linden, A., Kiefer, M., Walker, K. A., Noël, S., Hervig, M. E., McHugh, M., Lambert, A., Urban, J., Elkins, J. W., and Murtagh, D.: Validation of revised methane and nitrous oxide profiles from MIPAS–ENVISAT, Atmos. Meas. Tech., 9, 765–779, https://doi.org/10.5194/amt-9-765-2016, http://www.atmos-meas-tech.net/9/765/2016/, 2016.

Prinn, R. G., Huang, J., Weiss, R. F., Cunnold, D. M., Fraser, P. J., Simmonds, P. G., McCulloch, A., Harth, C., Reimann, S., Salameh, P., O'Doherty, S., Wang, R. H. J., Porter, L. W., Miller, B. R., and Krummel, P. B.: Evidence for variability of atmospheric hydroxyl radicals over the past quarter century, Geophys. Res. Lett., 32, https://doi.org/10.1029/2004GL022228, http://dx.doi.org/10.1029/2004GL022228, L07809, 2005.

Randel, W. J. and Jensen, E. J.: Physical processes in the tropical tropopause layer and their roles in a changing climate, Nature Geosci., 6, 169–176, https://doi.org/10.1038/ngeo1733, 2013.

Randel, W. J., Wu, F., Russell, III, J. M., Roche, A., and Waters, J. W.: Seasonal Cycles and QBO Variations in Stratospheric CH_4 and H_2O Observed in UARS HALOE Data., J. Atmos. Sci., 55, 163–185, https://doi.org/10.1175/1520-0469(1998)055<0163:SCAQVI>2.0.CO;2, 1998.

Randel, W. J., Wu, F., Oltmans, S. J., Rosenlof, K., and Nedoluha, G. E.: Interannual Changes of Stratospheric Water Vapor and Correlations with Tropical Tropopause Temperatures, J. Atmos. Sci., 61, 2133–2148, https://doi.org/10.1175/1520-0469(2004)061<2133:ICOSWV>2.0.CO;2, https://doi.org/10.1175/1520-0469(2004)061<2133:ICOSWV>2.0.CO;2, 2004.

Randel, W. J., Wu, F., Vömel, H., Nedoluha, G. E., and Forster, P.: Decreases in stratospheric water vapor after 2001: Links to changes in the tropical tropopause and the Brewer-Dobson circulation, J. Geophys. Res. Atmos., 111, https://doi.org/10.1029/2005JD006744, http://dx.doi.org/10.1029/2005JD006744, ~~d12312~~D12312, 2006.

Read, W. G., Wu, D. L., Waters, J. W., and Pumphrey, H. C.: Dehydration in the tropical tropopause layer: Implications from the UARS Microwave Limb Sounder, J. Geophys. Res. Atmos., 109, https://doi.org/10.1029/2003JD004056, http://dx.doi.org/10.1029/2003JD004056, ~~d06110~~D06110, 2004.

Rinsland, C. P., Gunson, M. R., Salawitch, R. J., Newchurch, M. J., Zander, R., Abbas, M. M., Abrams, M. C., Manney, G. L., Michelsen, H. A., Chang, A. Y., and Goldman, A.: ATMOS measurements of H2O+2CH4 and total reactive nitrogen in the November 1994 Antarctic stratosphere: Dehydration and denitrification in the vortex, Geophys. Res. Lett., 23, 2397–2400, https://doi.org/10.1029/96GL00048, http://dx.doi.org/10.1029/96GL00048, 1996.

Rong, P. P., Russell, J. M., Marshall, B. T., Siskind, D. E., Hervig, M. E., Gordley, L. L., Bernath, P. F., and Walker, K. A.: Version 1.3 AIM SOFIE measured methane (CH_4): Validation and seasonal climatology, J. Geophys. Res. Atmos., 121, 13,158–13,179, https://doi.org/10.1002/2016JD025415, http://dx.doi.org/10.1002/2016JD025415, 2016JD025415, 2016.

Rosenlof, K. H.: Transport Changes Inferred from HALOE Water and Methane Measurements, J. Met. Soc. Japan, 80, 831–848, https://doi.org/10.2151/jmsj.80.831, 2002.

Rozanov, V. V., Rozanov, A. V., Kokhanovsky, A. A., and Burrows, J. P.: Radiative transfer through terrestrial atmosphere and ocean: Software package SCIATRAN, J. Quant. Spectr. Rad. Transf., 133, 13–71, https://doi.org/10.1016/j.jqsrt.2013.07.004, http://www.sciencedirect.com/science/article/pii/S0022407313002872, 2014.

Russell, III, J. M. and Drayson, S. R.: The Inference of Atmospheric Ozone Using Satellite Horizon Measurements in the 1042 cm^{-1} Band, J. Atmos. Sci., 29, 376–390, 1972.

Russell, III, J. M., Gordley, L. L., Park, J. H., Drayson, S. R., Hesketh, W. D., Cicerone, R. J., Tuck, A. F., Frederick, J. E., Harries, J. E., and Crutzen, P. J.: The Halogen Occultation Experiment, J. Geophys. Res., 98, 10 777–10 797, 1993.

Schneising, O., Buchwitz, M., Reuter, M., Heymann, J., Bovensmann, H., and Burrows, J. P.: Long-term analysis of carbon dioxide and methane column-averaged mole fractions retrieved from SCIAMACHY, Atmos. Chem. Phys., 11, 2863–2880, https://doi.org/10.5194/acp-11-2863-2011, http://www.atmos-chem-phys.net/11/2863/2011/, 2011.

Seinfeld, J. and Pandis, S.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, Wiley, 2 edn., 2006.

Urban, J., Lossow, S., Stiller, G., and Read, W.: Another Drop in Water Vapor, Eos, 95, 245–246, https://doi.org/10.1002/2014EO270001, http://dx.doi.org/10.1002/2014EO270001, 2014.

Waters, J. W., Froidevaux, L., Harwood, R. S., Jarnot, R. F., Pickett, H. M., Read, W. G., Siegel, P. H., Cofield, R. E., Filipiak, M. J., Flower, D. A., Holden, J. R., Lau, G. K., Livesey, N. J., Manney, G. L., Pumphrey, H. C., Santee, M. L., Wu, D. L., Cuddy, D. T., Lay, R. R., Loo, M. S., Perun, V. S., Schwartz, M. J., Stek, P. C., Thurstans, R. P., Boyles, M. A., Chandra, K. M., Chavez, M. C., Chen, G.-S., Chudasama, B. V., Dodge, R., Fuller, R. A., Girard, M. A., Jiang, J. H., Jiang, Y., Knosp, B. W., LaBelle, R. C., Lam, J. C., Lee, K. A., Miller, D., Oswald, J. E., Patel, N. C., Pukala, D. M., Quintero, O., Scaff, D. M., Snyder, W. V., Tope, M. C., Wagner, P. A., and Walch, M. J.: The Earth observing system microwave limb sounder (EOS MLS) on the aura Satellite, Trans. Geosci. Remote Sens., 44, 1075–1092, https://doi.org/10.1109/TGRS.2006.873771, 2006.

Weigel, K., Rozanov, A., Azam, F., Bramstedt, K., Damadeo, R., Eichmann, K.-U., Gebhardt, C., Hurst, D., Kraemer, M., Lossow, S., Read, W., Spelten, N., Stiller, G. P., Walker, K. A., Weber, M., Bovensmann, H., and Burrows, J. P.: UTLS water vapour from SCIAMACHY limb measurements V3.01 (2002–2012), Atmos. Meas. Tech., 9, 133–158, https://doi.org/10.5194/amt-9-133-2016, https://www.atmos-meas-tech.net/9/133/2016/, 2016.

Wrotny, J. E., Nedoluha, G. E., Boone, C., Stiller, G. P., and McCormack, J. P.: Total hydrogen budget of the equatorial upper stratosphere, J. Geophys. Res. Atmos., 115, https://doi.org/10.1029/2009JD012135, http://dx.doi.org/10.1029/2009JD012135, ~~d04302~~D04302, 2010.