

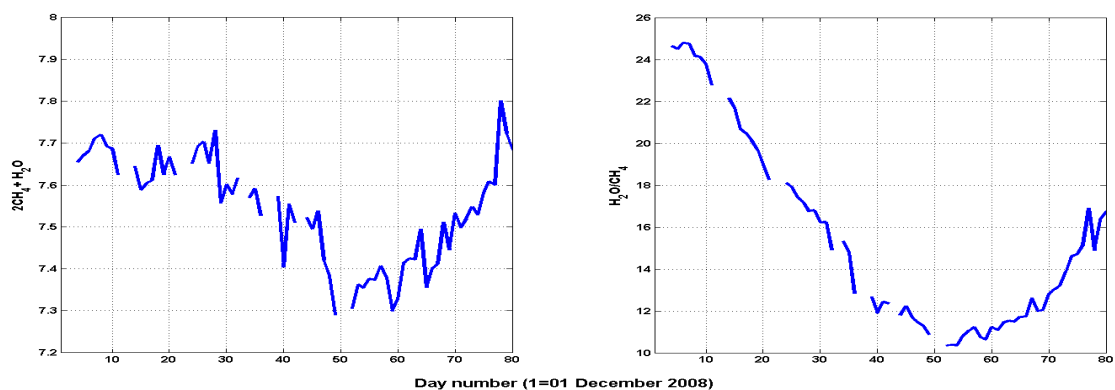
Response to Reviewer-2's comments

We thank the Reviewer for his/her comments, which greatly helped us to improve the manuscript. Our point-by-point response to his/her comments is given below in blue colour font.

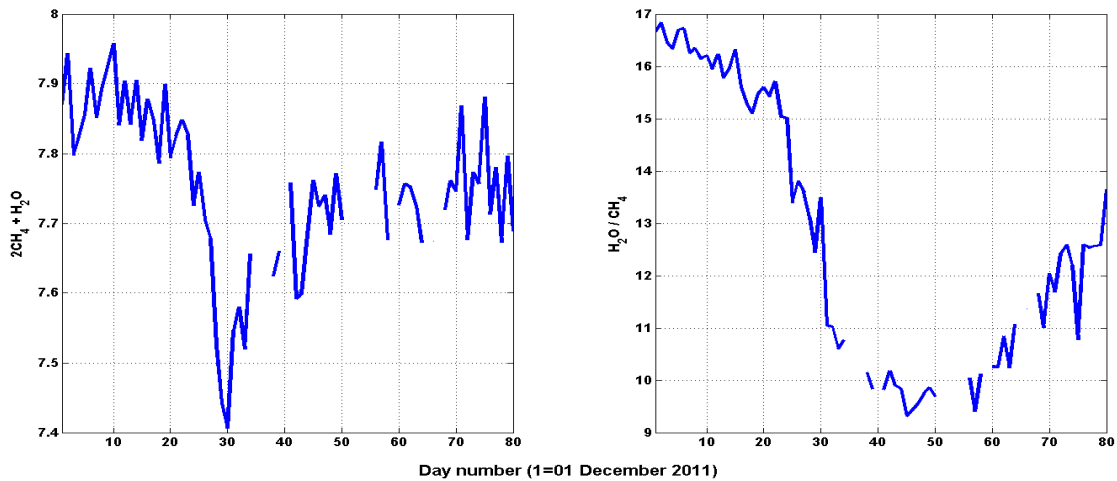
This paper discusses the response of trace constituents to three major SSWs in the past 12 years. They show changes in ozone, H₂O, CH₄ and OH. They attempt to relate CH₄ and H₂O changes to chemical changes related to OH. Unfortunately their arguments are superficial and most likely are simply wrong. Without more substantive analysis to back up their arguments, I regretfully cannot recommend this paper for publication. The most likely explanation for the observed change in the CH₄/H₂O ratio in the tropical upper stratosphere is variations in transport. As discussed by Wrotny et al (JGR, February, 2010), the sum of H₂O + 2*CH₄ is conserved to within several percent.

The authors want to thank the Reviewer for his/her nice comment. We agree that in general the sum H₂O+2*CH₄ is conserved, as methane raises in the atmosphere, it is oxidized resulting in the production of up to 2 H₂O molecules per CH₄ molecule. Any temporal increase in methane should produce a temporal increase in middle atmospheric in water vapour. However, during the SSW, there is an increase in CH₄. The increase in CH₄ should lead to increase in water vapour. But, there is a decrease in H₂O during the SSW. In the revised manuscript, the increase in CH₄ is shown to be due to tropical upwelling as suggested by the Reviewer and the decrease of H₂O is shown to be due to the dominance of loss reaction of H₂O over the production.

As mentioned by the Reviewer, Wrotny et al., 2010 have discussed about the total hydrogen budget of equatorial upper stratosphere. The paper deals with a long-term data set (1991-2008) and calculated that any changes of the 2*CH₄+H₂O mixing to be within the 3% of the magnitude for the equatorial upper stratosphere. In the current study, we have tried to focus on the eventual variation of water vapour which is observed during the sudden stratospheric warming events of 2004, 2009 and 2012. When we calculated the 2*CH₄+H₂O as well as the ratio of absolute values of H₂O/CH₄ for the two warming events of 2009 and 2012, we observed a profound decrease in the absolute values of these two factors (R2figs.1-2):



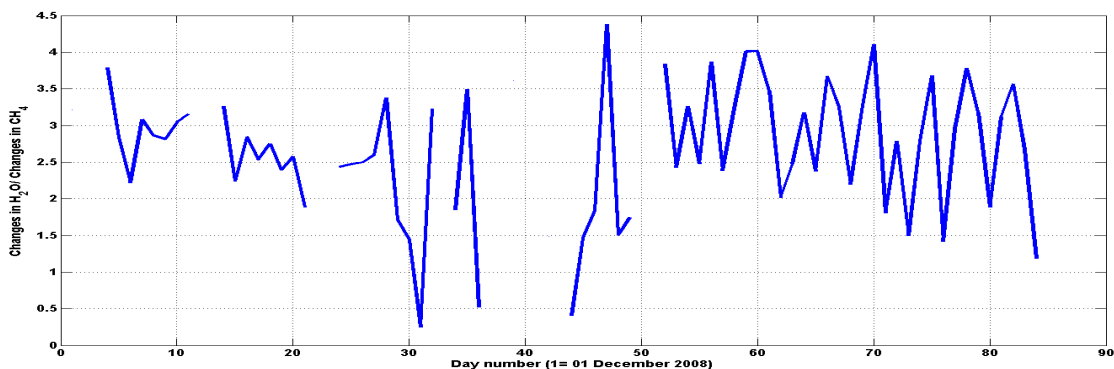
R2fig1. Daily variation of 2*CH₄+H₂O (left panel) and the ratio H₂O/CH₄ (right panel) for the 1-90 days starting from 1 December 2008.

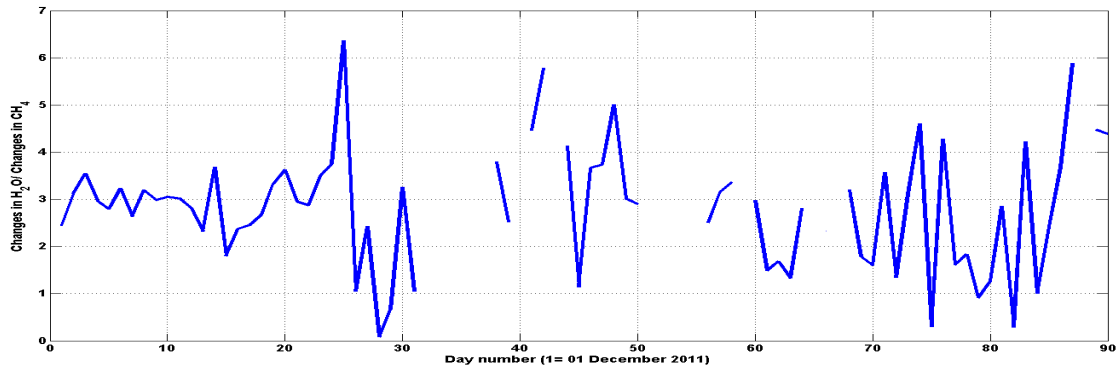


R2fig2. Daily variation of $2\text{CH}_4 + \text{H}_2\text{O}$ (left panel) and the ratio $\text{H}_2\text{O}/\text{CH}_4$ (right panel) for the 1-90 days starting from 1 December 2011.

The duration of 2009 SSW was during day number 52 -57 whereas for 2012 SSW it was during day number 43-64. In the above two figures we have shown the $2\text{CH}_4 + \text{H}_2\text{O}$ (in ppmv) as well as the ratio of H_2O and CH_4 for the two warming events of 2009 (top panel) and 2012 (bottom panel) of R2Fig.1-2. In case of both the factors we can see a clear decrease in the values during the warming time. For 2009 SSW, the sum of $2\text{CH}_4 + \text{H}_2\text{O}$ decreases from 7.6 ppmv on day number 30 to 7.3 on day number 52; the $\text{H}_2\text{O}/\text{CH}_4$ ratio reduces from around 16.1 on day number 30 to around 10.2 on day number 52. Similarly for the 2012 SSW, the total of $2\text{CH}_4 + \text{H}_2\text{O}$ decreases sharply from 7.8 on day number 20 to 7.4 on day number 30, then it increases little up to 7.6 on day number 42 although the overall decrease can be visible quite clearly. The $\text{H}_2\text{O}/\text{CH}_4$ ratio decreases from 11 on day number 30 to around 10.1 on day number 42. From both the observations during the two warming events, it can be concluded that changes occur to the methane and water vapour budget during the warming events.

Ratio of changes in water vapour to changes in methane ($\Delta\text{H}_2\text{O}/\Delta\text{CH}_4$) are also shown (R2Fig.-3) for the winters 2011-12 and 2008-09, when SSW events occurred during day numbers 43-64 and 52-57 respectively. The values are > 2 most of the times. Earlier, Remsberg et al. (1984) observed significant variations in $\Delta\text{H}_2\text{O}/\Delta\text{CH}_4$ from 2.0 in the equatorial middle atmosphere.

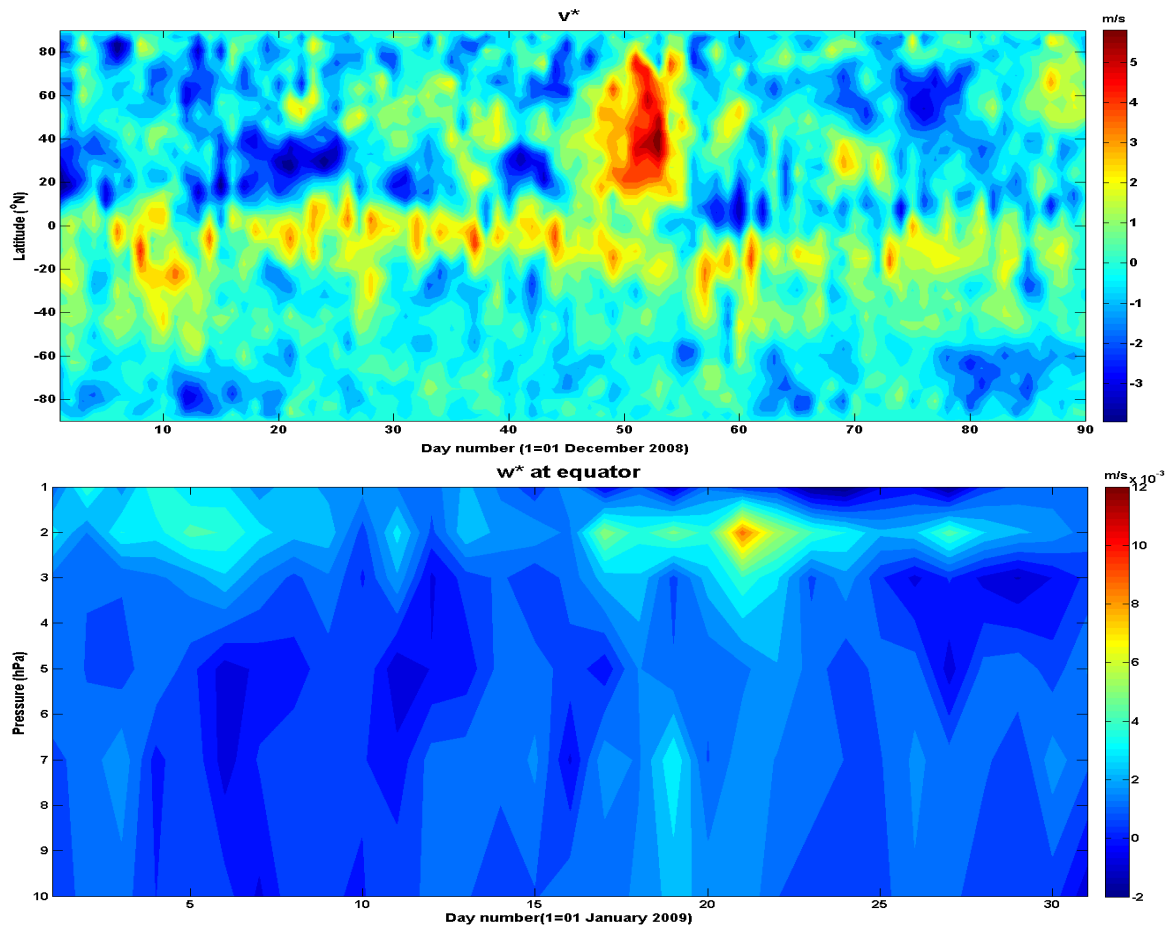




R2fig3. Daily variations of the ratio $\Delta\text{H}_2\text{O}/\Delta\text{CH}_4$ for the 1-90 days starting from 1 December 2008 (top panel) and 1 December 2011 (bottom panel).

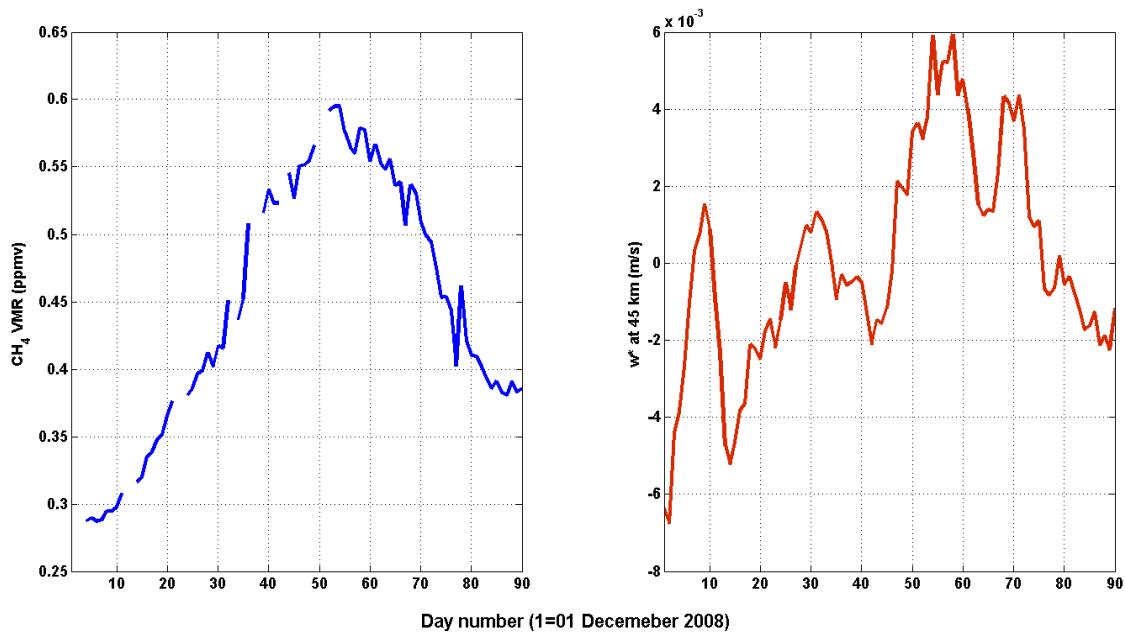
Indeed, in their Figure 2, they show this to be true for 2004, one of the periods discussed in the present paper. With faster upwelling, more CH_4 is transported upwards (i.e. younger air) and less can be oxidized to form H_2O . The present authors already show colder temperatures over the tropical upper stratosphere, this is consistent with increased upwelling. They correctly identify the increased ozone which responds to the lower temperatures.

We agree with the Reviewer that tropical upwelling plays a major role in transporting methane to the higher heights. As per the Reviewer's suggestion we have calculated residual meridional circulation as well as residual vertical velocity over equator which are shown below (R2fig.4)



R2fig4. Height-time cross section of residual meridional(top panel) and vertical velocities

As expected, we have seen enhanced northward flow between 20°S and 80°N during the build-up to the SSW event. And the residual vertical velocity is also high around 2 hPa pressure level over equatorial region which suggests tropical upwelling of methane in upper stratosphere. In the below figure (R2fig5) we have plotted the methane volume mixing ratio and w^* at 45 km height to show the simultaneousness of the variation-enhancement of CH_4 VMR and increase in residual vertical velocity. We have shown it at 45 km because the observed variations in methane and water vapour are found to be more around 45 km.



R2fig5. Daily variation of CH₄ VMR (left panel) and residual vertical velocity (right panel)

But their arguments about CH₄ oxidation are “hand waving” at best and most likely wrong given that transport is the underlying explanation. There were a pair of papers by Nedoluha et al [1998, both GRL and JGR] which showed the link between decreasing CH₄ and increasing H₂O in the few years of the UARS mission. There is also a substantial body of work by authors such as WJ Randel on the relationship of tracers and transport in the tropical stratosphere, none of which is discussed in this paper.

The Reviewer mentioned about the papers of Nedoluha et al. (Nedoluha et al., 1998, JGR and Nedoluha et al., 1998, GRL). The JGR paper investigated the water vapour for the 7 years (1991-1997) using HALOE data and ground-based WVMS measurements. They studied the H₂O trend for the middle atmosphere for all latitudes where they found an increasing trend around the height region 40-70 km. They inferred it perhaps due to the increase in temperature in region of STE processes resulting in enhancement in saturation mixing ratio of water vapour. But our paper is not dealing with long-term changes in either water vapour or methane. It is about the influence of SSW on these chemical constituents.

Regarding the authors’ speculations about chemistry, they admit that they find no change in OH and thus have to rely on the O (¹D) oxidation mechanism. This is too slow. For a rate coefficient of 1e-10 cm³/sec and a typical order of magnitude abundance of O (¹D) of 1e3 cm⁻³, the time constant for this reaction is found to be many months. Thus we can completely rule out the authors’ mechanism and indeed, there is no requirement for it given the well known relationship between tropical CH₄ and transport. Once the authors’ speculations on chemistry are removed from the paper, there is little left. If we accept that the decrease in temperature is due to upwelling which is based upon their earlier work (Nath et al., 2015) and which is quite plausible, the response of O₃ which is anti correlated with temperature and which is also covered in their 2015paper, the CH₄, and H₂O follow straightforwardly. The details of the CH₄ and H₂O response due also depend upon altitude dependent vertical gradients- to simulate that

they would require a model. In the absence of either that or any other quantitative analysis, in my opinion, this paper does not offer sufficient correct new science to merit publication.

While methane increase is shown to be due to tropical upwelling, the decrease of water vapour is explained as follows.

The source of water vapour in upper stratosphere is none other than methane oxidation which goes via two ways:



And for destruction of water vapour in stratosphere, the reaction is:



[All the reaction rates are for the temperature range 200-300 K]

We are taking back our hypothesis of the temperature dependence of ozone variation to be responsible towards the observed decrease in water vapour volume mixing ratio. The reaction rate (of the order 10⁻³³) is too slow to be effective in short term scale variation.

The oxidation of methane can happen via two ways: reaction with OH radicals and reactions with O (¹D) (reactions mentioned above). Both the reactions are very slow (of the order 10⁻¹⁵ for OH and 10⁻¹⁰ for O (¹D)). Whereas the destruction of water vapour molecules in stratosphere occurs by reaction with O (¹D). The rate of the reaction 3 is almost double of that of reaction 2. The respective residence time of H₂O, CH₄ and O (¹D) in upper stratosphere (40-50 km) are few days, few months [Brasseur and Solomon, 2005] and few sec [Seinfeld and Pandis, 2006]. In the upper stratosphere, the time scales for formation of ozone (O₃) from atomic oxygen and oxygen molecules (O + O₂ + M => O₃ + M, where M is the third body) and photolysis of O₃ (O₃ + hν => O + O₂, k=10⁻³ s⁻¹) are short compared to the time scales for reactions such as recombination of atomic oxygen and O₃ (O + O₃ => 2O₂, rate constant of the order 10⁻¹² [k=(8x10⁻¹²)exp(-2060/T) cm³molecule⁻¹s⁻¹]). The rate of the O (¹D) production reaction is of the order 10⁻³. Moreover the lifetime of O (¹D) is around ~10⁻⁷ s. The excited state atomic oxygen gets stabilized very fast by reacting with neutral molecules like N₂, O₂. Out of the two methane oxidation reactions, that one via hydroxyl radical pathway is much slower than that via O (¹D). If we compare all the reaction rates of the three reactions the oxidation of methane by hydroxyl radical can be neglected and in between the production reaction and destruction reaction of water vapour by O (¹D), the later one is faster. So over all a reduction in water vapour volume mixing ratio can be observed during SSW.