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On the link between martian total ozone and potential vorticity

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We demonstrate for the first time that total ozone in the martian atmosphere is highly correlated with the dynamical tracer, potential vorticity, under certain conditions. The degree of correlation is investigated using a Mars global circulation model including a photochemical model. Potential vorticity is the quantity of choice to explore the dynamical nature of polar vortices because it contains information on winds and temperature in a single scalar variable. The correlation is found to display a distinct seasonal variation, with a strong positive correlation in both northern and southern winter at poleward latitudes in the northern and southern hemisphere respectively.

The identified strong correlation implies variations in polar total ozone during winter are predominantly controlled by dynamical processes in these spatio-temporal regions. The weak correlation in northern and southern summer is due to the dominance of photochemical reactions resulting from extended exposure to sunlight. The total ozone/potential vorticity correlation is slightly weaker in southern winter due to topographical variations and the preference for ozone to accumulate in Hellas basin. In northern winter, total ozone can be used to track the polar vortex edge.

The ozone/potential vorticity ratio is calculated for both northern and southern winter on Mars for the first time. Using the strong correlation in total ozone and potential vorticity in northern winter inside the polar vortex, it is shown that potential vorticity can be used as a proxy to deduce the distribution of total ozone where satellites cannot observe for the majority of northern winter. Where total ozone observations are available on the fringes of northern winter at poleward latitudes, the strong relationship of total ozone and potential vorticity implies that total ozone anomalies in the surf zone of the northern polar vortex can potentially be used to determine the origin of potential vorticity filaments.

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1. Introduction

While the relationship of ozone and potential vorticity on Mars has never before been investigated, a strong correlation between potential vorticity, a dynamical tracer, and ozone provides several applications. Total ozone observations at the end of northern winter with good spatial coverage, such as provided by the Mars Color Imager (Clancy et al., 2016) on the Mars Reconnaissance Orbiter spacecraft, could be used to study the dynamical behaviour of the polar vortices. Observations of ozone over several Mars years have also now been collected by the Mars Color Imager, and therefore interannual variations or trends in the dynamical state of the polar vortices can be investigated (Clancy et al., 2016). Current satellite observing techniques to retrieve ozone cannot however reach high poleward latitudes in polar night, where the largest amounts of ozone exist (Barth et al., 1973; Lefèvre et al., 2004). If a strong correlation is apparent between potential vorticity and ozone at poleward latitudes in polar night, the spatial distribution of potential vorticity, which can be constrained by observations of temperature as a function of pressure (McConnochie, 2007) or through reanalysis datasets (Mitchell et al., 2015; Montabone et al., 2014), can be used as a proxy for ozone to extend the coverage of total ozone observational datasets.

Potential vorticity (hereafter PV) is a dynamical tracer which is a product of the absolute vorticity and static stability of atmosphere, and can be calculated from satellite observations of atmospheric temperature (Butchart and Remsberg, 1986; McIntyre and Palmer, 1983). PV can be redistributed but neither created nor destroyed (except where the layer terminates at the surface) on an isentropic surface (Haynes and McIntyre, 1987) in the absence of friction and diabatic processes. This principle underlines PV as a highly useful constraint on the large scale motions of the atmosphere, with the redistribution of PV able to deduce the evolving flow patterns. PV is used to study polar vortices on planetary bod-
ies because it contains information on winds and temperature in a single scalar variable and the motion of air lies parallel to contours of PV (Holton and Hakim, 2004). The invertibility of PV is also an important property, since given sufficient boundary conditions PV can be inverted to deduce the flow of the whole atmosphere. Changes in the PV distribution thus ‘induce’ changes in the wind and temperature fields.

The properties of PV mean its evolution on an isentropic surface can be used as an effective replacement to study trace gas transport in situations where there are sparse observations of chemical tracers (Holton and Hakim, 2004). PV is however only quasi-conserved on relatively short timescales of ~7 days above the turbulent boundary layer on Earth. For Mars, the radiative time constant has been calculated to be ~2 sols (Zurek, 1992), although Barnes and Haberle (1996) determined a timescale for PV conservation of around 5 sols in northern winter solstice conditions. For PV to effectively be used as a substitute chemical tracer therefore requires that the chemical tracer must also be quasi-conserved on similar timescales.

On Earth, studies have found a significant positive ozone-PV correlation in both global maps of total ozone from satellite observations (Vaughan and Price, 1991) and local profiles of ozone at multiple observatories (Beekmann et al., 1994; Rao et al., 2003), particularly at mid to high latitudes in the winter hemisphere. Randall et al. (2002) used the ozone-PV correlation to ‘fill in’ northern hemisphere maps of ozone from satellite observations, where the ozone had not been observed. The ozone column inferred from PV maps rather than observed by satellites was referred to as ‘proxy ozone’. A comparison of proxy ozone to measurements made by ozone sondes and other instruments indicated an agreement to better than 3% above 30°N in winter, where ozone is dynamically controlled. This technique was also extended to the southern hemisphere by Randall et al. (2005) and is further proven for Mars in this study, suggesting it can also be applied to other planetary bodies.

When compared to Earth, the martian atmosphere displays many similarities. A similar axial tilt provides seasons on Mars akin to those experienced on Earth albeit at much lower temperatures. Hadley cells and jet streams provide the primary mode of transport with polar vortices apparent in winter. Their characteristics have been explored by Mitchell et al. (2015), in which they find the residual meridional overturning circulation on Mars is comparable to the stratospheric residual circulation on Earth during winter. PV is seen to display an annular nature in polar winter on Mars, in contrast to Earth, with a stronger polar vortex in the northern hemisphere. The annular nature was also noted by Banfield et al. (2004) and McConnochie (2007), with the latter using temperature retrievals from the Thermal Emission Spectrometer (TES) as a function of pressure to derive PV assuming zero winds at a fixed pressure level. They also found the northern winter polar vortex is better organised than the corresponding feature in the southern and is therefore likely to be a greater barrier to mixing.

The distribution of ozone differs on Mars when compared to Earth, largely due to the lack of a tropopause on Mars. In contrast, Earth experiences a substantial ozone layer in the stratosphere. Modelling studies of the ozone cycle on Mars began with one-dimensional photochemical models such as Krasnopolsky (1993) which gave a comprehensive overview of chemical processes in the martian atmosphere. A common problem with 1-D models is that the spatial variability and transport-driven processes cannot easily be assessed. Latitudinal and diurnal variations of photochemical species including ozone were also investigated with this model (Krasnopolsky, 2006; 2009). The models generally use a fixed temperature profile which is also not indicative of the variations over a martian year. Moreau et al. (1991) used a two-dimensional model to describe vertical profiles of ozone, but this was in a dust-free atmosphere and also neglected cloud effects. To investigate the combined dynamical, physical and chemical processes affecting the ozone distribution requires ideally a three-dimensional model.

The first 3-D model simulations of ozone on Mars (Lefèvre et al., 2004) were performed by coupling a photochemical package to the LMD Global Circulation Model (GCM) and could represent the anti-correlation between ozone and water vapour convincingly. The destruction of ozone occurs due to the existence of the odd hydrogen group HO₂ and O(1D), thus an anti-correlation between ozone and water vapour is apparent. Ozone is more abundant at high latitudes in winter as the winter atmosphere is too cold for much water vapour to be present in equilibrium (preventing the formation of odd hydrogen species) and there is a lack of photolysis in the polar night. The lack of destruction mechanisms at this time of year potentially allows studies of the atmospheric dynamics by treating ozone as a quasi-passive tracer (Lefèvre et al., 2004). This indicates a significant correlation could exist between total ozone and PV on Mars due to the quasi-conservative nature of PV (Holton and Hakim, 2004).

In this study, a Mars global circulation model (MGCM), detailed in Section 2, is used to investigate the link between total ozone column and potential vorticity on Mars. The zonal mean PV and total ozone is first assessed in Section 3. Section 4 calculates the PV-total ozone correlation and explores the variability of the correlation over a Mars year. Finally, the ozone/PV ratio is calculated for Mars in Section 5 and used to investigate the creation of total ozone maps and identification of dynamical features in the surf zone.

2. Atmospheric modelling

For this investigation the UK version of the LMD GCM (hereafter LMD-UK MGCM) is used. The LMD-UK MGCM has been developed in a collaboration of the Laboratoire de Meteorologie Dynamique, the Open University, the University of Oxford and the Instituto de Astrofisica de Andalucia. This model uses physical parameterisations (Forget et al., 1999) shared with a past version of the LMD GCM. Effects due to CO₂ and dust advection and emission, thermal conduction in the soil, CO₂ condensation and sublimation, sub-grid scale dynamics, vertical diffusion and convection are all included in the LMD-UK MGCM. These are coupled to a spectral dynamical core and semi-Lagrangian advection scheme (Newman et al., 2002) with mass conservation (Priestley, 1993) to transport tracers. Using a spectral model, spatial derivatives are calculated exactly, and so the potential vorticity calculation is more accurate than previous attempts using temperature observations which use interpolated values (McConnochie, 2007).

The dust distribution is prescribed horizontally using an interpolation of numerous sets of observations from orbiters and landers using a kriging method (Montabone et al., 2015) and vertically using a modified Conrath dust profile (Forget et al., 1999). The model is truncated at wavenumber 31, resulting in a physical grid of 5° latitude by 5° longitude, with 32 vertical sigma levels extending to an altitude of ~105 km.

Ozone, along with 14 other tracers, is adjusted chemically by the LMD photochemical model (Lefèvre et al., 2004) which is included with the LMD-UK MGCM. The LMD photochemical model provides an extensive analysis of photochemical and chemical interactions in the martian atmosphere, with rate coefficients currently implemented for 36 chemical and 14 photochemical reactions. Chemical species are updated every 10 minutes cycling over each atmospheric column, computing the tendencies for each chemical species at each level in the column. The chemical species are then transported by the semi-Lagrangian advection scheme. The advection scheme uses wind fields updated by
the dynamical core to determine the ozone concentration at each model grid point every 30 minutes. The chemical fields are exchanged between the LMD-UK MCMC and photochemical model each timestep for a fully interactive coupling between dynamics, physical parameterisations and chemical species.

3. Zonal mean distribution of PV/ozone

Potential vorticity (PV) is a conserved dynamical tracer on isentropic surfaces under adiabatic conditions. Following Mitchell et al. (2015), we define PV as

$$\xi = -g(f + \zeta_0 \frac{\partial \theta}{\partial p})$$  \hspace{1cm} (1)

where \(g\) is the gravitational acceleration on Mars, \(f\) is the planetary vorticity, \(\theta\) is potential temperature (in K), \(\zeta_0\) is the vertical component of relative vorticity on a \(\theta\) surface and \(p\) is atmospheric pressure. The planetary vorticity \(f\) is dependent on latitude and equal to \(252 \sin \phi\), where \(\Omega = 7.088 \times 10^{-5}\) rad s\(^{-1}\) is the angular velocity of Mars and \(\phi\) is latitude. Potential temperature is the temperature a fluid parcel would acquire if brought to the surface under adiabatic processes and is defined as

$$\theta = T \left( \frac{P_a}{p} \right)^{R/c_p}$$  \hspace{1cm} (2)

where \(T\) is absolute temperature (in K), \(R\) is the gas constant of air, \(c_p\) is the specific heat capacity at constant pressure and \(p_a\) is the surface pressure at the model grid point.

The distribution of potential temperature at different seasons on Mars is displayed in Fig. 1. Equator-to-pole temperature gradients are increased in the polar winter of both hemispheres. The altitude of the 260 K surface increases poleward in both hemispheres for northern spring \((L_s = 0^\circ\), Fig. 1a) and autumn \((L_s = 180^\circ\), Fig. 1c).

This distribution differs to the polar winter season in both hemispheres, with a decrease in altitude of the 260 K surface moving from the winter to summer hemisphere at both \(L_s = 90^\circ\) (Fig. 1b) and \(L_s = 270^\circ\) (Fig. 1d). The winter season of the southern (defined as \(L_s = 45^\circ-135^\circ\)) and northern (defined as \(L_s = 225^\circ-315^\circ\)) hemisphere display an increase in static stability \((\partial \theta/\partial p)\) at poleward southern and northern latitudes respectively. The steepening of isentropes at the respective poleward latitudes indicate an increase in baroclinicity (i.e. increased misalignment of surfaces of constant pressure and temperature), with a more rapid increase in potential temperature over a given vertical depth. This results in an increase in static stability and therefore an increase in PV in the winter season, when compared to northern and southern spring (Fig. 1a and c respectively). The static stability throughout the atmosphere in the northern hemisphere winter is also increased when compared to the southern hemisphere winter, also suggesting an increased PV in the northern hemisphere winter.

The zonally-averaged daily-mean distribution of PV and total ozone is now compared for MY 29, displayed in Fig. 2. PV is seen to decrease tracing a path from either pole to the equator over the whole year, as expected due to the decrease in \(f\) and static stability at lower latitudes. The largest values of PV are seen in the polar winter of each hemisphere, with the northern hemisphere winter slightly increased (maximum of \(9.24 \times 10^{-4}\) K kg\(^{-1}\) m\(^2\) s\(^{-1}\)) when compared to the southern hemisphere winter (maximum of \([-8.79 \times 10^{-4}\] K kg\(^{-1}\) m\(^2\) s\(^{-1}\)) as suggested from the potential temperature surfaces in Fig. 1b and d. For the majority of the respective winter season in each hemisphere, the distribution of PV is also seen to display an annular nature, as reported by Mitchell et al. (2015). Maximum PV anomalies are seen away from the pole at a latitude of between 75–85° in both southern and northern winter.

The ozone cycle on Mars is thoroughly explored in Lefèvre et al. (2008, 2004) and briefly detailed here. Maximum total ozone values are found in polar winter due to the lack of sunlight preventing photolysis of ozone. The primary destructors of ozone, odd hydrogen species, are also largely absent with the cooler temperatures meaning much less water vapour (the primary source of odd

![Fig. 1. Zonally-averaged potential temperature from the surface to a pressure of 0.4 Pa (~75 km altitude) for the four different seasons of Mars. For each season, the zonal mean is averaged over 60 sols, centred on (a) \(L_s = 0^\circ\), (b) \(90^\circ\), (c) \(180^\circ\) and (d) \(270^\circ\) respectively. The 260 K surface is emphasised with a thicker contour.](image-url)
hydrogen species) is present in the atmosphere. Increased values of total ozone are apparent in northern winter when compared to southern winter due to the weaker wave activity of the southern high latitudes (Lefèvre et al., 2004). Since ozone is predominantly located near the surface at poleward latitudes in northern winter (see Fig. 3), PV on the 260 K surface (~10–15 km altitude at the equator) is chosen for the zonal comparison.

At lower latitudes, there is increased total ozone in the first half of the martian year as a result of the vertical distribution of water vapour. The cold and dust-free atmosphere results in a low saturation altitude of water vapour around 10–15 km, allowing ozone to build above this hygropause (Lefèvre et al., 2004). The hygropause level increases in the second half of the martian year, resulting in less ozone at higher altitudes and therefore decreased total ozone. Heterogeneous uptake of odd hydrogen species (included in the simulation) on water ice clouds also contributes to the increased total ozone in the first half of the year due to the presence of the aphelion cloud belt. The inclusion of heterogeneous uptake of odd hydrogen species has been shown to improve the match of simulated total ozone to observations over the whole martian year (Lefèvre et al., 2008). The summer season in both hemispheres is dominated by minimal total ozone since photolysis of ozone rapidly decreases the column total during the day, with slightly increased values at nighttime. Total ozone is at a minimum in southern summer ($L_S = 225–315^\circ$) at poleward southern latitudes since this region is in almost constant daylight and Mars is at perihelion meaning a shorter but more intense summer with maximal heating from the Sun.

### 4. Ozone-PV correlation

When calculating the correlation of the zonal mean of PV and total ozone, data points at which the amount of total ozone is dominated by photolysis are excluded by using a minimum cut-off value of 2 µm-atm for total ozone. Inclusion of the excluded data points produces a bias in the calculated correlation ($r = 0.77$, $p < 0.01$ for all 24,804 data points in the year, where $r$ is the Spearman’s rank correlation coefficient and $p$ is the p-value or significance level of the test). The data retained represents the total ozone in the winter season of each hemisphere and the mid-latitude increased total ozone towards the start of the year and makes up 46% of the original data set.

A fairly strong average correlation of $r = 0.68$ ($p < 0.01$) is obtained using the restricted data set described above. The PV-ozone correlation is well established on Earth despite the sources and sinks for ozone and PV not being identically distributed (Rishøjgaard and Källén, 1997). This statement is also true for ozone and PV on Mars due to the identified strong correlation. Whereas total ozone in polar winter is likely to be dynamically controlled, the mid-latitude total ozone towards the start of the year is primarily chemically controlled and highly influenced by the vertical distribution of water vapour (Lefèvre et al., 2004). Also, UV radiation is able to penetrate through the whole atmosphere on Mars. On Earth, the stratospheric ozone layer absorbs UV radiation which prevents it from reaching the surface. The presence of the ozone layer, along with its passive nature, results in a strong correlation between ozone and PV at particular levels of the terrestrial atmosphere. Beekmann et al. (1994) calculated $r = 0.83$ ($p < 0.01$) at 225 hPa (lower stratosphere) for all seasons at a particular observatory location on Earth. The PV-ozone correlation on Mars is likely to display a larger variation in season on any particular temperature surface due to the lack of a permanent...
source of ozone comparable in size to Earth’s ozone layer. In polar winter, total ozone has been shown to have large variations over short timescales (Lefèvre et al., 2004), so determining when and where it is plausible for PV to be used as a proxy for total ozone (and vice versa) requires looking at the spatial correlation on a sol-to-sol basis.

Fig. 4 displays the day-to-day PV-total ozone correlation for the whole MY for poleward northern and southern latitudes (Latitudes from 35–90°N and 35–90°S respectively). For poleward northern latitudes, a very strong PV-total ozone correlation of r = 0.8 or greater is found for 274 sols in the year (a Mars year contains ~669 sols). In northern summer, the PV-total ozone correlation decreases as expected, and in some cases even goes negative. Over this time period (Ls = 75–150°), small amounts of total ozone and PV are found (Fig. 2), but PV is still increased poleward primarily due to the planetary vorticity being largest at this location. Total ozone is more abundant away from the pole causing the negative correlation. A steady decline in the PV-total ozone correlation is seen at the start of the year heading towards northern summer as the subsolar point moves northward and total ozone is increasingly affected by photochemical reactions.

In the southern hemisphere, the variation in topography at latitudes further south than 35°S provides preferential sites for the accumulation of ozone. Ozone will reach high levels in the Hellas and Argyre basins due to the high surface pressure (hence large atmospheric column mass) at these locations providing an ideal setting for the accumulation of ozone near the ground (Lefèvre et al., 2004). The northern plains on Mars are more zonally uniform with much reduced topographical variation than in the southern hemisphere. In an attempt to eliminate the topographical effect of the Hellas and Argyre basins, the total ozone is referenced to a pressure level of 450 Pa. This pressure surface has been selected by calculating the average surface pressure at high southern latitudes over southern winter.

For southern latitudes poleward of 35°, the seasonal correlation is the opposite to the northern hemisphere PV-total ozone correlation temporally. The correlation peaks across the winter season of the respective hemisphere. A very strong positive PV-total ozone correlation is seen over southern polar winter (r = 0.8 or greater for 258 sols), although the time window of the very strong correlation is slightly less than seen for the northern hemisphere domain. With southern winter being longer in time than northern winter due to the elliptical orbit of Mars, this suggests there would be less skill at predicting total ozone from PV in southern winter. From Ls = 75–150°, the PV-total ozone correlation decreases slightly in the south even though it is the middle of polar winter. Total ozone is concentrated directly over the pole over this time period, whereas PV is displaying an annular nature with the maximum PV shifted further away from the pole at around 75–80°S (Fig. 2). Again, the lowest correlation is seen around southern summer, with negative correlation evident due to the same reasoning as noted for the northern hemisphere. The strong heating from the Sun in southern summer provides a total ozone minimum at the pole for Ls = 235–305° whereas PV is low but still at a maximum around the south pole. The strong positive PV-total ozone correlation for both northern and southern winter suggests total ozone can be used as a possible proxy for PV and vice versa. A correlation value of greater than 0.8 indicates that greater than 64% of the variance in total ozone is shared with PV (through calculation of the r² value).

4.1. Northern winter (Ls = 225–315°)

Fig. 5 displays northern polar azimuthal equidistant projections of total ozone and PV on the 260 K surface for select days over northern winter. The PV-total ozone correlation over the time period is very strong and over 0.8 for the majority of the time period (See Fig. 4).

The strong correlation results from the fact that both PV and total ozone are materially conserved on short timescales for which diabatic and chemical processes can be seen as negligible compared to advective processes, as found also for Earth (Hood et al., 1999). The maximum values of PV and total ozone do not always spatially match, but on several sols in northern winter they match well (see Fig. 5a). The shifting of maximum PV away from the pole, as seen also in the annular nature of PV displayed in northern winter by Mitchell et al. (2015), more often than not coincides with a corresponding shift in maximum total ozone away from the pole. The match is particularly strong for the zonal average of total ozone and PV (Fig. 2), but day-to-day variations indicate that the
Fig. 5. Total ozone (left) and Ertel potential vorticity on the 260 K surface (right) for (a) $L_5 = 221^\circ$, (b) $L_5 = 241^\circ$, (c) $L_5 = 292^\circ$ and $L_5 = 330^\circ$. The PV-total ozone correlation coefficient for each figure is displayed adjacent to the figure heading. The bounding latitude on each figure is $35^\circ$N and black contour lines indicate topography. The dashed contour mark the 12 μm-atm and $4 \times 10^{-4}$ K kg$^{-1}$ m$^2$ s$^{-1}$ value for total ozone and Ertel potential vorticity respectively.

location of the maximum total ozone and PV can differ slightly in longitude (Fig. 5b,c,d).

Filaments of PV can explicitly be seen from 45–165°W in Fig. 5b, 0–135°W in Fig. 5c and 180–215°W in Fig. 5d. In each case, corresponding filaments of total ozone are seen which match the PV filaments, further strengthening the possibility of using PV as a proxy for total ozone (and vice versa). Clancy et al. (2016) indicate that the filaments of total ozone during northern winter are formed by wave-2 and wave-3 transient eddies. The strong PV-total ozone correlation on a short daily time scale and correspondence in filaments of PV and total ozone seen in this work give further evidence that the variations in total ozone are largely due to dynamical influences, as to be expected for winter when chemical reactions are at a minimum.

PV has been used on Earth to track the polar vortices and has recently been used equivalently for Mars (Mitchell et al., 2015). The martian polar vortex also provides an excellent barrier for the mixing of chemical tracers, suggesting that ozone in the winter season, when it is quasi-passive, can potentially be used to track the shape of the polar vortex. Passive tracers on Mars such as argon and nitrogen would initially seem to provide a better candidate for this purpose, however these species are too well-mixed over a timescale longer than the timescale of PV conservation and lack a distinct boundary inside and outside the polar vortex region unlike ozone. Also, they have only so far been observed infrequently (Sprague et al., 2007). The close agreement between total ozone and PV, as indicated by the dashed contour of 13 μm-atm for total ozone and $5 \times 10^{-4}$ K kg$^{-1}$ m$^2$ s$^{-1}$ for PV in Fig. 5, suggests that total ozone can indeed be used to track the polar vortex in northern winter. The specific contour value of total ozone and PV is consistent throughout the majority of northern winter with Fig. 5 displaying examples from $L_5 = 221^\circ$ (Fig. 5a), leading up to northern winter, right the way through until $L_5 = 330^\circ$ (Fig. 5d) and the onset of northern spring.

Multiple orbiters have now retrieved total ozone on Mars with very good coverage (Clancy et al., 2016; Perrier et al., 2006), but they are restricted in the winter poleward latitudes due to the lack of sunlight. The strong PV-total ozone correlation suggests that PV can be used as a total ozone proxy, increasing the coverage of observations by ‘filling’ in the northern winter polar region.
Southern polar azimuthal equidistant projections of total ozone and PV on the 260 K surface are displayed in Fig. 6 for select days over southern winter. The PV-total ozone correlation for southern winter is generally strong, but less so than in northern winter, with a decrease in correlation after \( L_S = 75^\circ \). This decrease is related to two differences in total ozone and PV. Firstly, as mentioned previously, PV maintains an annular nature after \( L_S = 75^\circ \) (Fig. 2) whereas total ozone is largely situated at a more poleward latitude. This can be seen in Fig. 6a–d.

Secondly, as mentioned previously, the variation in topography at latitudes further south than \( 35^\circ S \) provides two preferential sites for the accumulation of ozone. Even with the modification procedure, the Argyre and Hellas basins contribute (but much less compared to without the modification) to a weakening of the PV-total ozone correlation in the middle of southern winter. At the start and end of southern winter there is decreased total ozone in Hellas basin (Fig. 6d for example) and so the PV-total ozone correlation is stronger (See Fig. 4). Using the total ozone to track the southern polar vortex is also more difficult, primarily due to the increased total ozone in the Hellas basin in southern winter. The specific contour value of total ozone used in an effort to track the polar edge seems to have a similar small variation in southern winter (ranging from 5–6 \( \mu \text{m-atm} \)) compared to the consistent level of 12 \( \mu \text{m-atm} \) which can be used effectively for the northern winter.

The degree of match over the time period is less consistent than in northern winter. The dashed contours for total ozone and PV in Fig. 6a have a good spatial match apart from over Hellas basin. This statement can be made for Fig. 6b–d, indicating the topographical variation in the southern hemisphere results in reduced skill for total ozone to track the polar vortex edge in the winter season of this hemisphere. The structure of PV is much less variable on a day-to-day basis when compared to northern winter, with fewer filaments of PV evident over this time period suggestive of fewer wave-breaking events. PV and total ozone both experience large distortions of their structure in northern winter (see Fig. 5).

5. Ozone/PV ratio

A strong PV-total ozone correlation provides several applications. As previously mentioned, PV can be used as a dynamical proxy to provide derived ozone abundance at poleward latitudes in winter, where ozone cannot be observed by satellites. A PV proxy...
can also be used to initialise chemistry transport models. Total ozone can be used to derive proxy PV and potentially to investigate the dynamics of the atmosphere, especially at smaller scales where the calculation of PV is less precise due to the required calculation of derivatives. For these applications, the ratio between total ozone and PV is necessary.

The ozone/PV ratio has been calculated on numerous occasions for Earth. Gidel and Shapiro (1980) calculate net vertical flux of ozone by relating zonal mean potential vorticity in a GCM to values of the zonal mean observed ozone. Beekmann et al. (1994) calculate the ozone/PV ratio at a particular observatory and suggest it more appropriate to use actual PV values obtained over particular region rather than a zonal mean value due to discrepancies with the values calculated by Gidel and Shapiro (1980). Rao et al. (2003) extend the ozone/PV ratio dataset at the same observatory as used by Beekmann et al. (1994) and show a similar pattern with a discrepancy noted with the values presented by Gidel and Shapiro (1980) but agreement with the values reported by Beekmann et al. (1994) at this specific location.

With the ozone/PV ratio on Earth at particular times being found to be robust, it has subsequently been used to determine a proxy ozone using PV which is found to agree well with actual observations (Randall et al., 2002; 2005). Due to their correlation, vertical profiles of PV measured by a satellite on different potential temperature surfaces can be used to create a proxy ozone in regions where ozone is unobservable by satellites (to an accuracy of 5%), extending the data set. The present study is the first calculation of the ozone/PV ratio for Mars and an investigation of the variability of the ozone/PV ratio over northern and southern winter.

The mean ozone/PV ratio for Mars on a daily basis in northern and southern winter is displayed in Fig. 7a and b respectively. The ozone/PV ratio is calculated over the spatial domain covering all latitudes north of 35°N in northern winter and south of 35°S in southern winter, as used for the previous section. This ratio is only valid when comparing total ozone to PV on the 260 K surface. The mean ozone/PV ratio is fairly consistent in northern winter, ranging from 1.98–2.85 μm-atm / 10⁻⁴ K kg⁻¹ m² s⁻¹ over this time period. A short and sharp decrease in the mean ozone/PV ratio is seen toward the end of northern winter primarily due to decreasing total ozone at poleward latitudes (See Fig. 2).

For southern winter, the mean ozone/PV ratio is fairly constant at the beginning and end with a peak in the middle. The southern winter mean ozone/PV ratio also displays similar variation to the northern winter mean ozone/PV ratio, with a minimum value of 1.30 and peak value of 2.26. The ozone/PV ratio is lower than in northern winter due to the decreased total ozone present in this region, with PV at a similar level to northern winter. The peak mean ozone/PV ratio is a consequence of the increase in total ozone at poleward latitudes around Ls = 90° and decrease in PV at poleward latitudes as it displays a more annular shape than seen at the beginning or end of southern winter (see Fig. 2). Mitchell et al. (2015) found that the winter-mean zonal-mean PV had an increased annular nature for PV when temperature retrievals were assimilated into the MGGM. Assimilation of temperature in southern winter could potentially provide an elevated mean ozone/PV ratio at the beginning and end of southern winter reducing the variability throughout the season.

The spread of the ozone/PV ratio at any particular sol in both northern and southern winter is generally large. 13 sols in northern winter and 4 sols in southern winter are not displayed in Fig. 7 due to their large standard deviation of 2.5 or greater. At these points in time, a localised region (equivalent to one model grid point or 5° × 5° in longitude and latitude) of extremely low PV at latitudes on the boundary of the domain (35–40°N/S for northern(southern winter respectively) causes an extremely large ozone/PV ratio which skews greatly the standard deviation of the data. Misalignment of small scale features in total ozone and PV (over the North Pole in Fig. 5c for example) also act to provide increased ozone/PV ratios in the domain. For any of these sols, only one model grid point in the calculated dataset (0.11% of the data for the sol) displayed the extreme ozone/PV ratio, and so these

Fig. 7. Mean ozone/PV ratio (solid line) every one sol for a) the 35–90°N domain in northern winter and b) the 35–90°S domain in southern winter. Northern winter is classified here as Ls = 225–315° and southern winter is classified as Ls = 45–135°. The dashed lines mark one standard deviation from the mean in northern and southern winter. The unit of ozone/PV ratio is μm-atm / 10⁻⁴ K kg⁻¹ m² s⁻¹.
data points are removed. The mean ozone/PV ratio for the sols removed from the dataset due to the extreme calculated values still fell within the range for northern and southern winter stated above.

The large standard deviation in mean ozone/PV ratio for northern and southern winter is a result of the spatial differences in the ozone/PV ratio for each sol. Fig. 8a and b display the winter-mean northern and southern ozone/PV ratio respectively across the calculated domain, with both displaying a wide range in winter-mean ozone/PV ratio from 0.14–5.52 (northern winter) and 0.75–10.68 (southern winter).

The northern winter spatial map displays a clear distinction in topography, with a higher surface elevation coupled with lower winter-mean ozone/PV ratio. Total ozone is lowest at specific longitudes corresponding to the higher terrain as seen in Fig. 5a–d, linked to the pressure dependence of the three-body reaction producing ozone (Lefèvre et al., 2004), whereas PV has less of a distinction. The highest winter-mean ozone/PV ratio is seen between 90–135°E at latitudes close to the boundary (35–40°N). With 12 p.m. local time at 0° longitude, the total ozone over this region is characteristic of total ozone from 6–9 p.m. local time and therefore total ozone is increasing as a consequence of the diurnal cycle. At nighttime, photolysis is negligible and water vapour condenses from the atmosphere (the two main destruction mechanisms for ozone) and total ozone is decreased. Whereas total ozone at 35–40°N latitude displays a longitudinal variation (See Fig. 5b and d for example), the PV does not result in a higher winter-mean ozone/PV ratio. Inside the polar vortex region, the winter-mean ozone/PV ratio is quite consistent, ranging from 2.4 to 3.2 for the majority of the region. This suggests that at poleward latitudes inside the polar vortex, a proxy ozone calculated from the observed PV (or vice versa) will be fairly accurate.

The winter-mean ozone/PV ratio in southern winter (Fig. 8b) displays a quite different pattern. The lowest winter-mean ozone/PV ratio is located around 50–70°S in an annular shape. Directly over the pole, the winter-mean ozone/PV ratio is increased as a consequence of the increased total ozone around Λs = 90° and the annular nature of PV for much of southern winter. A much more distinct latitudinal dependence on the winter-mean ozone/PV ratio is evident for southern winter. The highest winter-mean ozone/PV ratio is seen at lower latitudes (35–40°S). The diurnal cycle of total ozone results in a lower winter-mean ozone/PV ratio at latitudes from 0–45°E and 0–45°W where the local time is between 9 a.m. and 3 p.m. and so destruction of total ozone by photolysis is increased.

Higher winter-mean ozone/PV ratios are seen in southern winter when compared to northern winter as a result of the latitudinal spread of total ozone. In Fig. 2, the higher values of southern winter PV are generally restricted to latitudes below 60°S, whereas increased total ozone is present up to 30°S and even further northward from Λs = 75–105°. As mentioned previously, the vertical distribution of water vapour is the main contributor to the observed increased total ozone over this time period (Lefèvre et al., 2004). The increased winter-mean ozone/PV ratio is located at 40°E, 40°S is a result of a local PV minimum and can be seen in Fig. 6a and d.

5.1. Construction of proxy ozone using ‘observed’ PV

The winter-mean ozone/PV ratio is capable of capturing the gross spatial distribution of both total ozone and PV, although the variability of the ratio over the whole period is generally large for any given time. The mean ozone/PV ratio on any given day is therefore not appropriate for constructing maps of total ozone using PV. Randall et al. (2002) used the relation between ozone and PV on Earth to approximate ozone over locations distant from any actual observations. This could be a valuable tool to provide approximations of ozone at high latitudes in the polar night on Mars which are directly unobservable, whereas PV could potentially be retrieved using atmospheric temperature profiles. To test the creation of proxy ozone at poleward latitudes in polar winter using PV, this investigation uses the PV calculated from the MGCM simulation. In the future, the PV distribution (and also ozone distribution) can be further constrained using assimilation of temperature
profiles into the MGCM as already demonstrated by Mitchell et al. (2015).

The method used here is very similar to Randall et al. (2002), and is conducted over northern winter where the correlation between ozone and PV is generally greater than 0.8. To calculate the proxy ozone on a particular sol, a 3-sol interval centred on the sol of interest is used to determine the relation between ozone and PV. Randall et al. (2002) use a 7-day interval primarily due to the sparse observations available from the instrument to create the fit and the correlation of ozone and PV is reasonably unchanged over this timescale.

The PV and ozone from the MGCM are used to create the fit here, meaning meaningful statistics can be made over a shorter time window due to the increased number of pseudo-observations (model grid points akin to nadir observations are used here to test the method, as opposed to vertical profiles in Randall et al. 2002). A shorter time window is also preferred since the quasi-passive nature of ozone on Mars means over longer timescales the distribution of PV and ozone are likely to diverge due to chemical alteration of ozone. Any grid points in the MGCM north of 60° are not used to create the fit to mimic the inability of instruments to observe in this region. PV can be used for any grid point in the MGCM since this is able to be calculated in the polar night. If this method is eventually used for actual ozone and PV observations on Mars, the time interval can be varied to deduce the optimal time window to create the fit (based on noise and error reductions due to varying ozone/PV relations over longer timescales).

Fig. 9 displays an example of the fitting method at $L_s = 221^\circ$ and $292^\circ$ (corresponding to Fig. 5a and c). The goodness of the fit to the data can be represented using the coefficient of determination, which is calculated as $r^2 = 0.45$ for Fig. 9a and $r^2 = 0.51$ for Fig. 9b. A quadratic fit determines the ozone/PV relation, consistent with the method used by Randall et al. (2002). A quadratic fit was used by Randall et al. (2002) due to a 2-to-1 mapping of ozone to PV (chemical loss of ozone inside the polar vortex on Earth), however this relation is not as clear for Mars. Throughout northern winter, the fit indicates that total ozone generally monotonically increases with PV. This fit is to be expected, as the vortex edge acts as a barrier to the mixing of high total ozone into regions further south. In the region sampled to create this fit (45–60°N) most of the pseudo-observations record lower PV values than obtained inside the polar vortex. The maximum PV sampled in the fit is $\sim 7 \times 10^{-4}$ K kg$^{-1}$ m$^2$ s$^{-1}$ with maximal PV values at poleward latitudes exceeding $10 \times 10^{-4}$ K kg$^{-1}$ m$^2$ s$^{-1}$ in certain regions. Extrapolating the fit to higher PV values could therefore result in an under or overestimation of the total ozone.

The proxy ozone, calculated by applying the fits in Fig. 9 to the calculated PV from the MGCM, are displayed in Fig. 10a and 10c along with their deviations from the actual total ozone in the MGCM (Fig. 10b and d). The total ozone at latitudes north of 60° is the region that this method is aiming to predict accurately since this is the unobserved region (inside the thick black contour of Fig. 10). The largest deviation is an overestimation of total ozone east of Alba Mons ($\sim 110^\circ$W,40°N) which is an artifact due to an anomalous structure in the MGCM PV field. Photolysis of ozone at this location would quickly reduce the overestimated total ozone if an MGCM simulation were initialised with the proxy ozone distribution for this sol. The total ozone east of Alba Mons does not necessarily need to be predicted well, since it has been assumed that total ozone is observed here (it is used to calculate the fit) and assimilation of the total ozone observations would supersede the proxy ozone.

Inside the region where no observations have initially been made, the general trend is a slight underestimation of the actual total ozone by up to $\sim 4$ μm-atm (or up to $\sim 40\%$ of the absolute ozone value) for $L_s = 221^\circ$ (Fig. 10b) and slightly more in the other test case (Fig. 10d). For the majority of the unobserved region, the absolute error in total ozone is less than 20%. If a 5-sol interval is used to calculate the fit the underestimation is increased further since the 5-sol fit relates higher PV values to slightly reduced levels of total ozone, when compared to a 3-sol interval. The peaks in PV match reasonably well with total ozone for Fig. 10a (see Fig. 5a) but less so for Fig. 10c (see Fig. 5c), resulting in further underestimation of total ozone by the proxy ozone at $L_s = 292^\circ$ in Fig. 10d.
Fig. 10. Spatial distribution of proxy ozone (a,c) and deviations of proxy ozone from total ozone (b,d) over the 35–90°N domain at $I_o = 221°$ and $292°$ respectively. The proxy ozone is calculated using a quadratic fit to the ozone/PV relation. The thick black contour marks the 60°N latitude boundary.

The underestimation could potentially be alleviated by instead comparing the PV on the 260 K surface to an equivalent surface of ozone. For instance, the underestimation in the 45–180°W, 60–80°N region of Fig. 10b is due to the total ozone including increased amounts of ozone toward the surface at altitudes below the 260 K surface, whereas ozone on the 260 K surface has less ozone in this region (only a portion of the atmosphere is sampled). The majority of actual ozone observations currently available for Mars (Clancy et al., 2007; Perrier et al., 2006) are however nadir total ozone, with vertical profiles of ozone much less frequent. Using vertical profiles would require a longer time interval to provide a fit which is statistically significant (as a result of the sparse current data set of ozone vertical profiles in time), but the short timescale of consistency in the ozone/PV relation would limit this approach. The NOMAD instrument on the ExoMars TGO spacecraft will retrieve numerous high latitude vertical profiles of ozone which could therefore allow for a robust comparison of PV and ozone on equivalent surfaces to become available in future.

5.2. Capturing dynamical features in the surf zone

On the fringes of northern winter ($I_o = 0°–30°$ and 150–180°), where a strong correlation is still seen between total ozone and PV (see Fig. 4), total ozone observations with good spatial coverage are available (Clancy et al., 2007). If observational maps of total ozone are to be used to accurately identify dynamical features the variability in ozone/PV ratio displayed in Fig. 7 ideally needs to be reduced. In an effort to reduce the aforementioned variability, the latitudinal coverage is reduced to covering the ‘surf zone’ region outside the polar vortex. The surf zone is defined as the region of weak PV gradients surrounding the main polar vortex (McIntyre and Palmer, 1983). In the surf zone region, interesting dynamical features such as wave-breaking events occur frequently creating isolated thin filaments of high PV away from the main polar vortex. Events such as these have been observed on Earth and shown to correlate well with total ozone (McIntyre and Palmer, 1983; Vaughan and Price, 1991). The filaments of PV and matching filaments in total ozone are also seen to occur on Mars (see Fig. 5b,c and d), suggesting the filaments of ozone are of primarily dynamical origin.

The analysis here focuses on the region covering the surf zone of the northern winter polar vortex, where isolated filaments of PV are seen to occur much more frequently than in southern winter. Due to the shape and positioning of the northern polar vortex over winter, analysing the total ozone data in the vicinity of the surf zone cannot be simply performed by reducing the latitudinal coverage across all longitudes to a particular latitude band. Firstly the northern winter polar vortex on Mars is generally elliptical in shape (consistent with Mitchell et al., 2015) which results in the surf zone beginning at different latitudes across the longitudinal axis. Secondly, the centre of the polar vortex is often shifted from directly over the pole on multiple sols in northern winter, again resulting in a latitudinal difference for the surf zone region at different longitudes.

To calculate the ratio in the surf zone requires only using pseudo-observations southward of the polar vortex edge. This dataset is created by taking total ozone values at each longitude in turn and, starting from the north pole, finding the first pseudo-observation lower than 12 μm-atm. The 12 μm-atm contour is used in northern winter since it has been seen to provide the best
Fig. 11. Spatial distribution of total ozone in the calculated surf zone region at a) \( L_s = 241^\circ \) and b) \( L_s = 292^\circ \). The dashed black contour marks the \( 4 \times 10^{-4} \) K kg\(^{-1}\) m\(^2\) s\(^{-1}\) value for PV, an estimation of the polar vortex edge. Solid black contours indicate topography.

match in the GCM simulation to define the polar vortex edge in a comparison with PV (Fig. 5). The surf zone region is then defined as the region covering 30° latitude south of the 12 \( \mu \)m-atm contour. 30° of latitude is chosen since further coverage in latitude is likely to include territory where chemical alteration of ozone has an increased effect on its relation to PV. The pseudo-observations provided by this method are displayed in Fig. 11. The pseudo-observations are much more consistent with the boundary of the main polar vortex than simply taking a latitude band across all longitudines. A closer match to the polar vortex edge is limited at some longitudines by the resolution of the GCM in this study, but would not be true if real observations are used instead. Real observations should therefore provide an even better match to the polar vortex edge.

The filaments of ozone and PV in the surf zone region, from 90°–150°W and 40°–145°W in Fig. 11a and b respectively, are nicely captured by this selection method. Calculating the mean ozone/PV ratio with the above stated selection method also decreases the variability when compared to using the whole northern domain above 35°N but not to a significant level. For example, at \( L_s = 241^\circ \) the mean ozone/PV ratio calculated over the 35–90°N domain is 2.506 with a standard deviation of 1.334. Using only pseudo-observations in the surf zone region, and implementing a quadratic fit on the data using the exact same fitting method as in Section 5.1, the mean ozone/PV ratio is 2.763 with a standard deviation of 1.116. Using a quadratic fit to define the ozone/PV relation over the surf zone region, rather than the mean ozone/PV ratio, resulted in a similar outcome to the proxy ozone calculated in Section 5.1, with the overestimation of PV further increased when only the mean value is used.

To understand why the variability in ozone/PV ratio is difficult to reduce, the proxy PV calculated from the total ozone in the surf zone region is displayed in Fig. 12a and b for \( L_s = 241^\circ \) and 292° along with the actual PV from the GCM (Fig. 12c and d). Fig. 12e and f show the deviations of the proxy PV from the actual PV. The region in which PV is underestimated by the proxy PV is on the northern ridge of Alba Mons (45–135°W, 45–60°N). This is due to the spatial discrepancy between the sharp gradient of total ozone and PV. Since the majority of total ozone is close to the surface, it is restricted by the topographical boundary. PV on the 260 K surface is higher in the atmosphere and unaffected by the same boundary. Selecting ozone volume mixing ratio (instead of total ozone) on a corresponding potential temperature surface could alleviate the PV underestimation in this region but is beyond the scope of this investigation.

The other regions in which PV is underestimated are located at the fringes of the data closest to the north pole at particular longitudines. These regions are primarily inside the 4 \( \times 10^{-4} \) K kg\(^{-1}\) m\(^2\) s\(^{-1}\) contour (Fig. 12f at 70–110°E, 55–60°N for instance) and so therefore not technically in the region of interest. An improved method to prevent data from inside the main polar vortex being included in the surf zone analysis could help to reduce the variability of the ozone/PV ratio.

The important result is that where PV filaments occur, the proxy PV reproduces well the strength and location of this event. Total ozone observations can therefore be of use to identify the location of midlatitude frontal weather systems, as indicated by Clancy et al. (2016), but not to provide accurate spatial maps of PV in the surf zone region. Using vertical profiles of ozone as a proxy PV instead of total ozone should be able to alleviate the underestimation, and potentially the overestimation, of PV in the regions identified.

6. Conclusions

In this paper, the strong relationship between total ozone and PV on isentropic surfaces is demonstrated for Mars. A link between ozone and PV for Earth is widely established, but this relationship has never before been looked at for another planet. Comparing the zonal-mean total ozone and PV, a strong positive correlation of \( r = 0.68 \) (\( p < 0.01 \)) is identified, with elevated levels of total ozone and PV at poleward northern/southern latitudes in northern/southern winter. An annular shape in PV is seen in the
winter season of both hemispheres, consistent with previous studies (Banfield et al., 2004; McConnochie, 2007; Mitchell et al., 2015).

The PV-total ozone correlation, studied on regional domains covering latitudes 35–90°N in the northern hemisphere and 35–90°S in the southern hemisphere for a whole Mars year on a daily basis, shows a distinct seasonal variation. The strength of the PV-total ozone correlation is greatest at northern/southern latitudes in northern/southern winter, where variations in total ozone are dominated by advective processes due to the lack of sunlight in polar winter. Little or no correlation is seen for the majority of the rest of the Mars year since ozone is instead dominated by chemical processes which create a diurnal cycle in total ozone. The strong spatial match in northern winter suggests total ozone can be used to track the vortex edge and be used as an effective tracer to study the dynamical nature of the polar vortices on Mars as an alternative to PV. In southern winter, the preferential accumulation of ozone in the Hellas and Argyre basin reduces the skill for total ozone to be used for this application.

Focusing on the northern and southern winter, where the strongest PV-total ozone correlation is found, the ozone/PV ratio is then calculated. In northern winter, the mean ozone/PV ratio over the domain is reasonably time invariant, whereas the mean ozone/PV ratio in southern winter displays a peak midwinter as a result of increased total ozone over the pole at \( L_\phi = 90° \). The standard deviation is large for both northern and southern winter due to the spatial variations in winter-mean ozone/PV ratio across the domain. In northern winter, the winter-mean ozone/PV ratio displays little variation inside the polar vortex suggesting PV can be used as an effective proxy ozone. In southern winter, a strong latitudinal dependence on the ozone/PV ratio is evident. This is due to a steady reduction of total ozone as you move to lower latitudes in comparison to PV which has an increased negative gradient over the same latitudinal space. The decreased slope in total ozone results from the vertical distribution of water vapour allowing increased total ozone at lower latitudes when compared to similar northern latitudes in northern winter.

Fig. 12. Spatial distribution of proxy PV (a,b), pseudo-observed PV (c,d) and deviations of proxy PV from pseudo-observed PV (e,f) in the surf zone region at \( L_\phi = 241° \) and 292° respectively. The dashed black contour marks the \( 4 \times 10^{-4} \text{ K kg}^{-1} \text{ m}^2 \text{ s}^{-1} \) value for PV, an estimation of the polar vortex edge. Solid black contours indicate topography. The grey shaded area in e and f indicate where no pseudo-observations are located.
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