\documentclass{article}

\usepackage[affil-it]{authblk} % to use the author affiliation tags

\usepackage{graphicx}

\usepackage[space]{grffile}

\usepackage{latexsym}

\usepackage{textcomp}

\usepackage{longtable}

\usepackage{multirow,booktabs}

\usepackage{amsfonts,amsmath,amssymb}

\usepackage{url}

\usepackage{hyperref}

\hypersetup{colorlinks=false,pdfborder={0 0 0}}

\usepackage[utf8]{inputenc}

\usepackage[english]{babel}

\usepackage{natbib}

\bibliographystyle{plainnat}

\begin{document}

%\title{Stratospheric ozone intrusion events, characterisation and distribution over high southern latitudes using ozonesondes.}

\title{Characterising stratospheric ozone intrusions at high southern latitudes}

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\date{\today}

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\maketitle

\begin{abstract}

We develop a quantitative method to identify Stratosphere to Troposphere Transport events (STTs) from ozonesonde profiles.

Using this method we estimate the quantity of ozone transported across the tropopause over Melbourne ($38^\circ$S), Macquarie Island ($54^\circ$S), and Davis ($69^\circ$S).

STT seasonality is determined from a 7--9 year long time series of ozone profiles from each site.

STT events primarily occur during summer above Melbourne and Macquarie Island, while there is little seasonal cycle in STT events above Davis.

The majority of tropospheric ozone due to STT events occur within 3~km below the tropopause at Melbourne and Macquarie Island, and within 2~km below the tropopause at Davis.

Overall, the fraction of total tropospheric ozone attributed to STT events is 2 ‚Äì 4\% at each site, however, during individual events, an STT event can contribute more than 10\% of the total tropospheric ozone at that time.

We use the GEOS-Chem model to understand out point-source ozonesonde results in a 3-dimensional context.

The GEOS-Chem model run with active stratospheric chemistry is too coarsely resolved in the vertical dimension to determine STTs.

Simulated seasonal cycles of tropospheric ozone are well matched at all three sites although vertical profile averages have some bias in the troposphere compared with ozonesondes.

A conservative estimate of yearly tropospheric ozone flux due to STTs is calculated using the simulated tropospheric ozone column between 35$^\circ$S and 75$^\circ$S of $2.2\times10^{16}$ molecules cm$^{-2}$ yr$^{-1}$ (TODO: update number once model finishes).

\end{abstract}%

\section{Introduction}

Tropospheric ozone, which constitutes only 10\% of the total ozone column, is an important oxidant, greenhouse gas and is toxic to biological life.

Over the industrial period, increasing tropospheric ozone, has been estimated to exert a radiative forcing equivalent to a quarter of the CO$\_2$ forcing \citep{IPCC\_Chapter2}. Tropospheric ozone increases above pre-industrial levels are estimated to result in global losses up to \$USD$\_{2000}$ 35 billion per annum until 2030 due to food crop impacts \citep{Avnery2011} and up to \$USD$\_{2000}$ 580 billion by 2050 ($\sim$11.8 billion per year) due to health impacts \citep{Selin2009}. Tropospheric ozone is produced anthropogenically by fossil fuel and biomass combustion emissions (NO$\_x$ and volatile organic compounds) that subsequently undergo photochemistry. Natural sources of tropospheric ozone include the downward transport from the ozone-rich stratosphere, wildfires and lightning photochemical production (\citet{Jacobson2000} and references therein).

Stratosphere to troposphere transport (STT) of ozone can increase regional surface ozone levels above air quality standard thresholds \citep{Danielson1968, Lefohn2011, Langford2012, Zhang2014}. A review of photochemical models by \citet{Stohl2003} (STACCATO) concluded that between 25-50\% of tropospheric ozone can be attributed to SST events. A lower estimate was derived from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), \citep{Stevenson2006} with $5100\pm600$ Tg/yr ($\sim$ 90\%) and $550\pm170$ Tg/yr ($\sim$ 10\%) of tropospheric ozone is due to chemical production and STT, respectively. Models are challenged to correctly represent STT, and process studies are key in determining the relative role of SST in the tropospheric ozone budget.

STT events are due to deep overshooting convection \citep{Frey2015}, tropical cyclones \citep{Das2016} and mid-latitude synoptic scale disturbances (e.g. \citet{Stohl2003,Mihalikova2012}). STT events observed over the Mediterranian region estimate a 10\% contribution to tropospheric ozone budget between 2000 and 2003 \citep{Galani2003}, with other observational studies noting significant occurrences and strong seasonal dependance (i.e. \citet{Lefohn2011}), contributing up to 30\% of the surface ozone over the Western US in spring \citep{Lin2012}. To date, while this topic has received significant attention in the tropics and Northern Hemisphere, observational estimates from the southern hemispheric extra-tropics is noticeably absent in the literature.

In the extra-tropics, ozone has a longer photochemical lifetime and STT events most commonly occur during synoptic-scale tropopause folds \citep{Sprenger2003, Tang2012} which are characterised by tongues of high Potential Vorticity (PV) air descending to low altitudes. These tongues become elongated and filaments disperse away from the tongue and mix irreversibly into the troposphere. STT events have been observed in tropopause folds around both the polar-front jet \citep{Vaughan1994, Beekmann1997}, and the subtropical jet \citep{Baray2000}. They are also observed near cut-off lows \citep{Price1993, Wirth1995}, which are often accompanied by turbulent weather. A high correlation is found between lower stratospheric and tropospheric ozone \citep{Terao2008} with the highest STT associated with jet-streams over the oceans in winter.

%Move to discussion / conclusion ... \citet{Hegglin\_2009} estimate that climate change will lead to increased STT of the order of 30 (121) Tg yr$^{-1}$ relative to 1965 in the Southern (Northern) Hemisphere due to an acceleration in the Brewer Dobson circulation. Tropospheric ozone is lost via chemical destruction and dry deposition, estimated to be $4700\pm700$ Tg/yr and $1000\pm200$ Tg/yr, respectively \citep{Stevenson2006}.

%Hegglin, M. I., and T. G. Shepherd (2009), Large climate-induced changes in ultraviolet index and stratosphere-to-troposphere ozone flux, Nature Geosci, 2(10), 687‚Äì\selectlanguage{english}691, doi:10.1038/NGEO604.

% AIMs paragraph

In section 2, nearly a decade of ozonesonde flight recordings from three locations spanning latitudes from 38$^{\circ}$S - 69$^{\circ}$S are used to characterise the seasonal cycle of STT events and determine their contribution to the total amount of tropospheric ozone.

We examine the depth and frequency of the intrusions and use case studies to relate these STTs to meteorological events.

Lastly, the fraction of total tropospheric column ozone attributable to STT events is calculated and an estimate of how much ozone this represents is made using a global chemical transport model.

\section{Data and Methods}

\subsection{Ozonesonde record in the Southern Ocean}

Ozonesondes are weather balloons which measure ozone concentrations from the surface to around 35km.

These ozonesondes provide a high vertical resolution profile of ozone, along with temperature, pressure, and humidity.

Ozonesondes use an electrochemical concentration cell which senses the proportional electrical current from ozone's reaction to a solution of potassium iodide.

Most ozonesondes are new and independant, since retrieval of a used ozonesonde can be difficult.

Standardised procedures are followed when constructing, transporting, and releasing the ozonesondes.

Ozonesondes are estimated to provide around 2\% precision in the stratosphere, which improves at lower altitudes \citep{noaasondes}, although the accuracy has been shown to be around 5-10\% which increases if standardised procedures are not followed \citep{Smit2007}.

Ozonesondes are launched approximately weekly from Melbourne (38$^{\circ}$S, 145$^{\circ}$E), Macquarie Island (55$^{\circ}$S, 159$^{\circ}$E) and Davis (69$^{\circ}$S, 78$^{\circ}$E).

For this study, we use the data collected from 2004-2013 for Melbourne and Macquarie, and 2006-2013 for Davis.

Around twice as many ozonesonde launches occur at Davis prior to and during the ozone hole season (June-October) than at other times of the year \citep{Alexander2013}.

%The ERA-I data we used for synoptic weather was of one degree horizontal resolution with pressure levels at 200, 300, 400, and 500 hPa.

%For individual cases ERA-I data was downloaded at .25 degree horizontal resolution with the full 34 pressure levels from 1000 to 1 hPa.

\subsection{Characterisation of STT events and associated fluxes}

\label{Section:CharacterisationOfSTTs}

Stratospheric ozone typically mixes irreversibly down (vertically and horizontally) into the troposphere in kilometres-scale tongues of air.

The strength (ozone enhancement above background levels), size, vertical depth, and longevity of these intruding ozone tongues vary due to weather, landscape, and season.

While ozonesondes are released every week or so, ozone intrusion events may only be detectable for a matter of hours \citep{Tang2012}.

This makes the vertical ozone profile recorded by the ozonesonde highly dependent on the time of launch \citep{Sprenger2003}, and it cannot be guaranteed that detected ozone enhancements are fully separated from the stratosphere.

In order to characterise tropospheric ozone events a clear definition of where the stratosphere begins is necessary.

Two common tropopause height definitions are the standard lapse rate tropopause \citep{WMO1957} and the ozone tropopause \citep{Bethan1996}.

The lapse rate is the negative altitudinal temperature gradient, and the lapse rate tropopause is defined as the lowest altitude where the lapse rate is below 2$^\circ$~C~km$^{-1}$, provided the lapse rate between this altitude and all subsequent altitudes within 2~km is also below 2$^\circ$~C~km$^{-1}$.

The ozone tropopause is defined as the lowest altitude satisfying these three conditions \citep{Bethan1996}:

\begin{enumerate}

\item Vertical gradient of ozone mixing ratio (OMR) is greater than 60~ppbv km$^{-1}$

\item OMR is greater than 80~ppbv

\item OMR between 500~m and 2000~m (1500~m in the Antarctic) above exceeds 110~ppbv.

\end{enumerate}

One of our sites (Davis) uses the Antarctic OMR altitude threshhold.

The ozone tropopause can be less robust during stratosphere-troposphere exchange, however it is more robust than the lapse rate tropopause at polar latitudes in winter and near jet streams in the lower stratosphere \citep{Bethan1996, Tomikawa2009, Alexander2013}.

In this work the lower of these two tropopause altitudes is used, as both are calculated for each ozonesonde release.

This choice avoids occasional unrealistically high tropopause heights due to perturbed ozone or temperature measurements in the ozonesonde records.

Figure \ref{fig:seasonaltpheights} shows the monthly mean tropopause altitudes at each location (solid lines).

The mean tropopause altitude for ozonesondes which detected an STT is also shown (dashed lines).

The seasonal cycle in tropopause altitude at Melbourne is exhibited, showing a maximum in summer, and a minimum is winter.

This cycle is much more sublte at Macquarie, and almost reversed at Davis, which has a minimum during autumn and maximum from winter to spring.

The decreasing tropopause altitude which occurs at higher southern latitudes is also apparent, as lower mean tropopause heights occur with more southern latitudes.

The tropopause recorded by sonde is generally higher during an STT event at all three sites.

%Tropopause altitudes at Davis may exceed 11~km altitude under certain synoptic conditions \citep{Alexander2013}; the relation of tropopause altitude with individual STT events is investigated in detail below.

\begin{figure}[!htbp]

\begin{center}

\includegraphics[width=0.8\columnwidth]{figures/tpheights}

\caption{Monthly mean tropopause altitudes (minimum of lapse-rate and ozone defined tropopause at 3 sites) determined from ozonesondes.

Dashed lines show the average monthly altitude when only considering dates when STTs occured.)

}

\label{fig:seasonaltpheights}

\end{center}

\end{figure}

Figure \ref{fig:seasonaltropozone} shows seasonally averaged ozone as recorded over the three stations.

Increased ozone extending down through the stratosphere is apparent during December to March and September to November over Melbourne.

These increased tropospheric ozone months are due to STTs (in summer), and possible fire smoke plume influence (in winter).

Over Davis and Macquarie Island the tropospheric ozone is higher between March and October, although the effect is subtle compared to Melbourne.

This is due to less photochemical destruction when the sun is lower (TODO: read and cite S. Oltmans antarctic papers - re Andrews comment).

\begin{figure}[!htbp]

\begin{center}

\includegraphics[width=0.8\columnwidth]{figures/seasonaltropozone}

\caption{

Seasonal cycle of ozone over Davis, Macquarie, and Melbourne measured by ozonesondes, where measurements are binned monthly.

Black solid lines show seasonal tropopause heights, defined as described in the text.

}

\label{fig:seasonaltropozone}

\end{center}

\end{figure}

%One important factor of STT characterisation was the height of the tropopause, which can be defined in several ways.

%Using only the ozonesonde datasets, the tropopause from ozone and lapse rate definitions are easy to calculate.

%While the ozone tropopause can be less robust during stratosphere-troposphere exchange, it performs better than the lapse rate tropopause at polar latitudes in winter and near jet streams in the lower stratosphere \citep{Bethan1996}.

%For many of the sonde profiles ozone disturbances occur between the lapse rate and ozone defined tropopauses, and since it is not clear that this area is actually the troposphere we only characterise events bound by the lower of the lapse rate and ozone tropopause heights.

\citet{Tang2010} define one method of detecting these stratospheric tongues (or tropospheric ozone folds) as follows: From 5~km altitude, if the ozone level exceeds 80~ppb and then within 3~km decreases by 20~ppb or more to a value less than 120~ppb, then a tropopause fold has occurred.

Their definition is based on subjective analysis of sondes released from 20 stations in the latitudinal range from 35$^\circ$S to 40$^\circ$N.

We also characterise STT events using the ozonesondes vertical profiles, looking for tropospheric ozone enhancement above a local background (in moles per billion moles of air, or ppb).

In this paper, tropospheric ozone events are characterised based on a subjective analysis of ozonesonde profiles at three sites at 38$^\circ$S, 55$^\circ$S, and 69$^\circ$S.

Part of the characterisation involves using a Fourier filter which removes high and low frequencies along the vertical dimension (the vertical scale), this filter is called a bandpass, since it retains a band of scales or frequencies.

To identify STT events, the vertical profiles of ozone volume mixing ratio are linearly interpolated to a regular grid with 20~m resolution up to 14~km altitude and are then bandpass filtered to retain perturbations with vertical scales between 0.5~km and 5~km.

From here onwards the filtered vertical profile is referred to as the perturbation profile.

The choice of band limits was set empirically; for an event to qualify as STT, a clear increase above the background ozone level is needed, and a vertical limit of $\sim 5$~km removes seasonal-scale effects.

We exclude from analysis perturbations at altitudes below 4~km above the surface to avoid surface pollution events and those occuring within 0.5~km of the tropopause to avoid the sharp transition to stratospheric air producing spurious false positives.

Then using ozone perturbations from 2~km above the surface up to 1~km below the tropopause, we create a threshhold for each launch site at the 99th percentile.

Profiles with perturbations exceeding this threshhold are classified as STT events, subject to one more check.

The ozone peak is defined as the altitude where the OMR is greatest within the lowest range of altitudes where the perturbation profile exceeds the percentile based threshhold.

If the OMR between this ozone peak and the tropopause drop below 80~ppb and are more than 20~ppb lower than the peak ozone then the event is confirmed, otherwise the profile is rejected as a non-event.

This confirmation is only required if the perturbation profile does not drop below zero between the event peak and the tropopause.

This happens in order to remove `near tropopause' anomalies for which there is no evidence of detachment from the stratosphere.

We conservatively estimate the ozone flux into the troposphere associated with each event.

The estimate is conservative since it does not take into any secondary ozone enhancements which may have been caused by the STT, as well as ignoring any heightened ozone background levels which may be due to synoptic-scale stratospheric mixing into the troposphere.

The ozone flux calculation is made by integrating the ozone concentration enhancement vertically over the altitude range for which an STT event is identified.

Figure~\ref{fig:filterEG} shows an example ozone profile, and how the algorithm detects an STT event, defines the event boundaries, and calculates the ozone flux.

\begin{figure}[!htbp]

% Figure created in getevents.pro, edited in inkscape

\begin{center}

\includegraphics[width=0.8\columnwidth]{figures/filtereg.png}

\caption{ Left: an example illustrating methods used for STT identification and flux estimation using an ozone profile from 2km to the tropopause (dashed vertical line).

At Melbourne on the 8th of January 2004, the flux area shows the estimate of stratospheric impact on tropospheric ozone.

Right: bandpass filtered O$\_3$ ppb perturbation profile.

Coloured lines show the 99th percentile of filtered ozone perturbations (purple dashed) and the technique for determining the vertical extent of the event (orange dashed) is outlined in the text.

}

\label{fig:filterEG}

\end{center}

\end{figure}

\subsection{Sensitivities and limitations}

There are several observationally defined threshholds and limits which have an effect on how many events are detected, what altitude within which they can be detected, and how strongly the events are separated from the stratosphere.

The cut-off threshhold (defined locally to each site) is determined from the 99th percentile of the filtered ozone profile between 2~km and the tropopause height minus 1 kilometer.

If an ozonesonde's filtered profile (between 4~km and the tropopause minus 500~m) goes above this threshhold then the profile is flagged as an event.

Changing either of these altitude ranges, or the cut-off threshhold, changes how many events are detected.

For example, using the 98.5th percentile increased detected events by 26 at Melbourne, 18 at Macquarie Island, and 9 at Davis.

We use the 99th percentile because at this point the filter locates clear events with no obvious false positives.

The altitude range for flagging filtered profiles is set from 4~km above the surface to 500~m below the tropopause .

This range removes possible ground pollution effects as well as local fire smoke plumes which are not likely to ascend above 4~km, as well as allowing event detection up to 500~m from the tropopause.

Some events, including the storm-caused event examined in figure \ref{fig:Melbourne20050203} are within one kilometer of the tropopause.

The altitude range used to determine the 99th percentile is set from 2~km up to 1~km below the tropopause.

This range removes any anomalous edge effects of the Fourier bandpass filter, as well as discounting the highly variable ozone concentration which occurs near the tropopause.

TODO: Check and mention bandpass scale sensitivity.

\subsection{Removal of biomass burning influence}

Other sources of tropospheric ozone profile perturbation need to be analysed and excluded before drawing any conclusions about STTs based on recorded ozone profiles.

The major possible ozone influence other than STTs in the troposphere above 4~km is smoke plumes from biomass burning.

Ozone production from biomass burning is complex and affected by photochemistry, fuel nitrogen load, time since emission, and atmospheric plume chemistry both during transport and at the point of measurement.

%Ozone precursors include nitrogen oxides ($NO\_x = NO + NO\_2$) and non methane volatile organic compounds (NMVOCs). % too basic for here..

Large biomass burning events emit substantial ozone precursors, some of which are capable of being transported far from their origins.

Peroxyacetyl Nitrate (PAN) is a reservoir of NO$\_x$ which can lead to enhanced ozone far from the source of a fire \citep{Jaffe\_2012}.

Biomass burning influence in the Southern Hemisphere comes mostly from Southern Africa and South America, however Australian fires from the midlatitudes, and Indonesian fires can also influence the ozonesonde release sites.

Transported biomass burning plumes influence the southern mid-latitudes generally between July and December \citep{Pak2003}.

Biomass burning smoke plumes can lead to enhanced ozone, however this is not always the case.

Due to the chance of smoke plume influence on STT characterisation, events which occur near smoke plumes are flagged and not included in STT flux calculations.

Removal of any possible influence from biomass burning smoke plumes is performed by detection of smoke plumes through global CO measurements.

Here we identify transported smoke plumes through enhanced carbon monoxide (CO) levels.

CO has a long enough lifetime to be an effective tracer of transport.

The primary source of atmospheric enhancement of CO is fires, making CO a good indicator of fire plumes.

Using high CO levels as a proxy for smoke plumes is a well established method (eg: \citet{Edwards2003,Sinha2004,Edwards2006,Mari2008}).

We use data from the AIRS (Atmospheric Infrared Sounder) instrument on board the Aqua satellite \citep{AIRS3STD}.

A visual inspection of AIRS' vertical columns of CO over the Southern Hemisphere is performed in order to exclude events with possible smoke influence at our three sites.

We diagnose smoke plumes where high ($\sim 2 \times 10^{18}$ molecules cm$^{-2}$ or higher) CO columns appear and when these occur near our sites during a sonde-detected ozone event, the event is flagged.

Figure \ref{fig:excludedeg}(top) shows a day where smoke plumes are near the Melbourne sonde launch site on the day of a detected event.

An event preliminarily detected on this day through the ozonesonde data is flagged as possibly due to fire.

In the figure elevated CO levels can be seen over Australia, likely due to long-range transport from African and/or South American biomass burning.

This day can be contrasted with the example in figure \ref{fig:excludedeg}(bottom) where low CO levels are observed over the entire Southern Hemisphere.

We screened all days at all three sites where an STT event is detected except for one event that coincided with missing AIRS data (January 2010).

We flagged 15 of 72 events over Melbourne, 8 of 48 events over Macquarie island, and none from 45 over Davis.

Nearly all of the flagged events occur within the burning season of the Southern Hemisphere.

\begin{figure}[!htbp]

\includegraphics[width=\textwidth]{figures/AIRS\_compare.png}

\caption{AIRS total column CO.

The top panel (17 October 2007) is a day when ozone above Melbourne (purple dot) could have been caused by a transported biomass burning plume, and so was excluded from analysis.

The bottom panel (3 February 2006) shows an example of a day when Melbourne ozone was likely not influenced by transported smoke plumes and was retained for analysis.}

\label{fig:excludedeg}

\end{figure}

STT events flagged in this way are included in Figures \ref{fig:SummarySeasonality} to \ref{fig:SummaryTPDepths}, they are coloured red and do not contribute to STT flux calculations.

These flagged events are concentrated in spring at Melbourne and Macquarie Island, and don't have any otherwise notable characteristics.

%TODO: JESSE CURRENLY UP TO HERE IN READTHROUGH OF WHOLE TEXT

\section{Synoptic conditions during STT events}

We examine two case studies in detail to illustrate the synoptic-scale conditions in which STT events occur over Melbourne.

Data from the European Center for Medium-range Weather Forecasts (ECMWF) Interim Reanalysis (ERA-I) \citep{Dee2011} product are used for synoptic-scale examination of weather patterns over our three sites on dates matching detected STT events.

Figure \ref{fig:Melbourne20050203} (left) shows the ozonesonde profile above Melbourne on 3 of February 2005.

The tropopause was between 400 and 500 hPa and ozone in the upper troposphere was anticorrelated with relative humidity, suggesting the ozone enhancements derived from dry stratospheric air.

An ozone intrusion into the troposphere at $\sim520$~hPa was identified by our detection algorithm.

Figure \ref{fig:Melbourne20050203}(right) shows the concurrent synoptic weather system, a cut-off low pressure system that caused a large storm and lowered the local tropopause height for several days.

The flux of stratospheric ozone into the troposphere associated with this event was at least $3.1 \times 10^{11}$ molecules cm$^{-3}$ , or 8\% of the tropospheric ozone column.

\begin{figure}[!htbp]

% these IMAGE CREATED BY show\_profile.py, EDITTED IN INKSCAPE

\begin{center}

\includegraphics[width=1.0\columnwidth]{figures/Melbourne20050203.png}

\caption{(Left) Vertical profile of ozone (black), relative humidity (blue), and temperature (red) measured by ozonesonde over Melbourne on 3 February 2005.

The detected ozone STT event is highlighted in pink.

Tropopause heights using both the ozone definition (black dashed line) and lapse rate definition (red dashed line) are also shown.

(Right) Geopotential heights at 500 hPa from the ERA-Interim reanalysis, with wind vectors overplotted.

Also shown are contours of potential vorticity units with 1 PVU in purple.}

\label{fig:Melbourne20050203}

\end{center}

\end{figure}

Figure \ref{fig:Melbourne20100113} (left) shows the ozonesonde profile over Melbourne on 13 January 2010.

The tropopause was higher on this date (100-150 hPa). Using our algorithm, we detected an ozone intrusion centred around 200~hPa.

As before, ozone anticorrelation with relative humidity provides further evidence that the elevated ozone was stratospheric in origin.

In this profile, there was clear separation between the detected intrusion (highlighted in pink) and the ozone tropopause (black dashed line), which indicates that the sonde passed through regular tropospheric air after hitting a stratospheric intrusion but before reaching the tropopause.

Figure \ref{fig:Melbourne20100113}(right) shows that this event was associated with a trough of low pressure (front) passing over southeastern Australia.

This front traveled from west to east and caused a wave of lowered tropopause height. Frontal passage is a known cause of STT as stratospheric air descends and streamers of ozone-rich air break off and mix into the troposphere \citep{Sprenger2003}.

\begin{figure}[!htbp]

% these IMAGE CREATED BY show\_profile.py, EDITTED IN INKSCAPE

\begin{center}

\includegraphics[width=1.0\columnwidth]{figures/Melbourne20100113.png}

\caption{Same as Figure \ref{fig:Melbourne20050203} but for 13 January 2010.

Also shown in this figure is the 2 PVU contour (white), often used to determine dynamical tropopause height.}

\label{fig:Melbourne20100113}

\end{center}

\end{figure}

An investigation of the ERA-I synoptic weather during STT events above Melbourne, Macquarie Island, and Davis are performed and are used to subjectively classify the events based on their likely cause.

Similar characteristics to the case studies presented here occur over Macquarie Island: i.e. a prevalence of frontal and low pressure activity during STT events.

Typically during STT occurrence, the upper troposphere is not calm, with low pressure fronts or cut-offs nearby at coincident time.

Over Davis the weather systems are harder to distinguish, and the stratospheric polar vortex may create ozone folds without other sources of upper tropospheric turbulence.

\section{STT event climatologies}

Figure \ref{fig:SummarySeasonality} shows the seasonal cycles of STT events detected at Melbourne, Macquarie Island, and Davis. STT events in Figures \ref{fig:SummarySeasonality}-\ref{fig:SummaryTPDepths} are coloured based on the meteorological classification described in Section \ref{Section:WeatherClassifications}, with events classified as either low pressure fronts (“frontal”, dark blue), cut-off low pressure systems (“cutoff”, teal), or indeterminate (“misc”, cyan). Events that may have been influenced by transported smoke plumes (Section XX) are shown in red.

There is an annual cycle in the frequency of STT events (Fig. \ref{fig:SummarySeasonality}) with a summertime peak above Melbourne and Macquarie Island.

This summertime peak is due to an increased prevalence of summer low-pressure storms and fronts, which increase turbulence and lower the tropopause \citep{Reutter2015}.

\begin{figure}[!htbp]

% these IMAGE CREATED BY non\_transport\_summary.py, labels edited IN INKSCAPE

\begin{center}

\includegraphics[width=1.0\columnwidth]{figures/summary\_season.png}

\caption{Seasonal cycle of STT events detected at Davis (top), Macquarie Island (middle), and Melbourne (bottom).

Events are categorised by associated meteorological conditions as described in the text, with low pressure fronts (“frontal”) in dark blue, cut-off low pressure systems (“cutoff”) in teal, and indeterminate meteorology (“misc”) in cyan.

Events that may have been influenced by transported smoke plumes are shown in red (see text for details).}

\label{fig:SummarySeasonality}

\end{center}

\end{figure}

At Davis, the frequency of STT events is relatively constant throughout the year, with a slight increase during Antarctic winter. STT events associated with cut-off low pressure systems are more prevalent during winter, while STT events associated with frontal passage occur throughout the year. The polar vortex and associated lowered tropopause may be partially responsible for the STTs detected in winter. We were unable to meteorologically classify most summertime events at Davis.

The slightly increased winter time frequency of STT events at Davis may be attributable to the increased frequency of sonde releases from June to October (see Section XX).

It is also possible that the sample of only 45 detected events over 10 years is too small to detect any seasonality.

Figure \ref{fig:SummaryAltitudes} shows the altitudes of detected events, based on the altitude of peak (maximum) tropospheric ozone in the ozonesonde profile.

STT event peaks most commonly occur at 6 -- 10~km above Melbourne and 6 -- 9~km at Davis but are distributed more evenly at Macquarie Island from ~4 -- 7.5 kilometres altitude. There is no clear relationship between meteorological conditions and event altitude.

Figure \ref{fig:SummaryTPDepths} shows the distance from the tropopause of the peaks of detected events, based on the distance between the peak ozone peak associated with the detected STT event and the tropopause (using the lowest of the two tropopause definitions), as described in Section XX.

The majority of STT events occur within 3~km of the tropopause at both Melbourne and Macquarie Island, and within 2~km of the tropopause at Davis. Again, there is no clear relationships between meteorological conditions and event depth.

For both Melbourne and Macquarie Island, the STT events which are unlikely to be fire-related occur mostly in summer and mostly during low pressure synoptic systems which can increase convection and upper tropospheric turbulence.

\begin{figure}[!htbp]

\begin{center}

\includegraphics[width=0.99\columnwidth]{figures/summary\_altitude.png}

\caption{The distribution of STT event altitude at Davis (top), Macquarie Island (middle), and Melbourne (bottom), determined as described in the text.

Events are coloured as described in Fig. \ref{fig:SummarySeasonality}.}

\label{fig:SummaryAltitudes}

\end{center}

\end{figure}

\begin{figure}[!htbp]

\begin{center}

\includegraphics[width=0.99\columnwidth]{figures/summary\_depth.png}

\caption{The distribution of STT event distance from the tropopause at Davis (top), Macquarie Island (middle), and Melbourne (bottom), determined as described in the text.

Events are coloured as described in Fig. \ref{fig:SummarySeasonality}.

}

\label{fig:SummaryTPDepths}

\end{center}

\end{figure}

\section{Comparison with GEOS-Chem}

GEOS-Chem is a global chemical transport model \citep{Bey2001}, which includes transport, emission, deposition, chemical production and destruction of ozone and 103 other trace gases throughout the troposphere along with stratospheric chemistry, including photolysis.

Stratosphere-troposphere coupling is calculated using the stratospheric unified chemistry extension (UCX) \citep{Eastham2014}, which includes a further 28 trace gases.

For comparison to ozonesonde observations, we use GEOS-Chem version 10-01 (including UCX) run from 2005-2012, following a 1-year spin-up for 2004.

Transport is driven by assimilated meteorological fields from the Goddard Earth Observing System (GEOS-5) maintained by the Global Modeling and Assimilation Office (GMAO) at NASA.

Our simulation was modified from the standard v10-01 to a fix a bug in the treatment of the Total Ozone Mapping Spectrometer (TOMS) satellite data used to calculate photolysis (see \citet{TomsFix2016}).

The simulation uses 2$^{\circ}$ latitude by 2.5$^{\circ}$ longitude horizontal resolution, with 72 vertical levels from the surface to 0.1~hPa.

Biogenic emissions of organic chemicals are determined by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.1 extended by Guenther et al \citep{Guenther2012}.

Anthropogenic emissions are given by the Emissions Database for Global Atmospheric Research (EDGAR) version 4.2.

Ozonesondes are useful for looking at specific locations with high resolution, and in this work they provide an estimate of both STT occurrence rates and STT ozone flux.

At these discrete locations, this information can be used in conjunction with regional-scale information in order to estimate large-scale impacts of STT on tropospheric ozone. Here, the

GEOS-Chem CTM is used to provide the regional-scale ozone concentrations.

Following this, an extrapolation is performed and the stratospherically sourced ozone is estimated over the latitude range from 35$^{\circ}$S to 75$^{\circ}$S.

This range is used as it includes all three sites, a change of 5$^{\circ}$ in either direction at either end of the range changes the average tropospheric ozone by -8 to 9\%.

Examination of the GEOS-Chem output also gives us an insight as to whether the simulation can be used on its own in order to estimate STT event distribution and magnitude.

\begin{figure}[!htbp]

\includegraphics[width=\textwidth]{figures/StationSeries.png}

\caption{Tropospheric ozone column ($\Omega\_{O3}$, in molecules cm$^{-2}$) at daily resolution simulated by GEOS-Chem (red dots) from January 1 2004 to December 31 2013. For each plot, the model has been sampled in the grid square containing the site.

The GEOS-Chem outputs are respectively at 7AM, 11AM, and 11AM for Davis, Macquarie, and Melbourne.

Columns calculated from ozonesondes are shown as black stars, each representing one measurement. (TODO: Update once fixed model run finishes)}

\label{fig:StationSeriesGEOSChem}

\end{figure}

Figure \ref{fig:StationSeriesGEOSChem} compares the time series of tropospheric ozone column ($\Omega\_{O\_3}$) in molecules cm$^{-2}$ simulated by GEOS-Chem (red dots) to the measured tropospheric ozone columns (black stars).

Sonde tropospheric columns are calculated using the GPH and ozone partial pressure recorded by the ozonesondes, using TODO: equation here.

The seasonal cycles are well correlated, with similar timing and magnitude (paired r$^2$ values of TODO: run script when model run finished).

In both observations and model, the maximum ozone column at Melbourne occurs in summer, with a minimum in winter, while

Macquarie and Davis show the opposite seasonality.

The model shows more day-to-day variability than the ozonesondes, although there are daily simulated values for the model while only weekly or less for the ozonesondes.

\begin{figure}[!htbp]

\includegraphics[width=\textwidth]{figures/seasonalprofiles00.png}

\caption{Observed and simulated tropospheric ozone profiles over Davis, Macquarie, and Melbourne, averaged seasonally.

Model means (2005-2013 average) is shown as red solid lines, with red dashed lines showing one standard deviation.

Ozonesonde means () are shown as black solid lines, with coloured shaded areas showing one standard deviation.

The horizontal dotted line shows the mean tropopause heights from the model (red) and the observations (black).

TODO: Update once fixed model run finishes.}

\label{fig:GEOSChemSeasonalProfiles}

\end{figure}

Figure \ref{fig:GEOSChemSeasonalProfiles} shows the observed and simulated ozone profiles at all sites, averaged seasonally.

The model generally underestimates ozone at low altitudes (up to 6~km) at both Davis and Macquarie, although this bias is less pronounced during summer.

Over Melbourne, ozone in the lower troposphere is well represented, but the model overestimates ozone from around 4~km to the tropopause.

Also notable is the lower tropopause height simulated by the model, which on average is $\sim$ 1~km lower than observed (TODO: mean bias, updated when model finishes).

The effect of local pollution can be seen over Melbourne, mostly during the austral summer months (DJF), as the increased mean mixing ratios and enhanced variance near the surface.

While GEOS-Chem can generally reproduce both the measured tropospheric ozone columns and the seasonal mean behaviour in the upper troposphere / lower stratosphere, it does not have the vertical resolution required to capture the individual STT events detected from the ozonesonde measurements.

Figure \ref{fig:event\_profile\_comparison} compares modeled (red) and observed (black) ozone profiles on three example days when STT events were detected using the ozonesondes. The leftmost plot (Macquarie Island, 20040519) shows the profile with the closest match between model and observations; the middle plot (Davis, 20070115) shows an average comparison, and the rightmost plot (Melbourne, 20050203) shows the worst comparison found in our dataset.

The model output is shown in red, and is the average over 2$^{\circ}$ latitude by 2.5$^{\circ}$ longitude which contain the respective sonde release site.

As shown in the figure, GEOS-Chem includes few levels in the tropopause (compared to more than 100 for the ozonesondes). This low vertical resolution precludes detection of STTs, which are typically <1km in extent.

\begin{figure}[!htbp]

\includegraphics[width=\textwidth]{figures/event\_profile\_comparison.png}

\caption{Example comparisons of ozone profiles from ozonesondes (black) and GEOS-Chem (red) from three different dates during which STT events were detected from the measurements.

The dates were picked based on subjective visual analysis. The examples show: (left) the best match, on 19 May 2004 over Macquarie Island; (middle) an average case, on 15 January 2007 over Davis, and (right) the worst match, on 3 February 2005 over Melbourne.}

\label{fig:event\_profile\_comparison}

\end{figure}

\section{Stratosphere-to-troposphere ozone flux from STT events}

We quantify the mean stratosphere-to-troposphere ozone flux due to STTs at each site based on the integrated ozone amount associated with each STT event (see section \ref{Section:CharacterisationOfSTTs}). Events that may have been influenced by transported biomass burning are excluded from this calculation.

This estimate is a conservative lower bound as our algorithm ignores secondary ozone peaks which may also be transported down from the stratosphere and ignores potential ozone dispersion from the ozone peak.

Figure \ref{fig:fluxsummary} shows the mean fraction of total tropospheric column ozone at each site attributed to stratospheric ozone intrusions, averaged over days when an STT event occurred.

At all sites, the mean fraction of tropospheric ozone attributed to STT events is 2--4\%. On individual days, this value can exceed 10\% at Macquarie and Melbourne.

Figure \ref{fig:fluxsummaryabs} shows the STT-induced ozone flux in absolute terms. We find that the mean ozone flux associated with STT events is $1$ to $2 \times 10^{16}$~molecules/cm$^2$.

Our flux estimates are relatively insensitive to our biomass burning filter: including smoke-influenced days changed the mean flux by less than 0.25\% (5\% relative change).

\begin{figure}[!htbp]

\begin{center}

% Flux plot from

\includegraphics[width=0.8\columnwidth]{figures/flux\_relative.png}

\caption{Fraction of total tropospheric column ozone attributed to STT, derived from ozonesonde measurements as described in the text.}

\label{fig:fluxsummary}

\end{center}

\end{figure}

\begin{figure}[!htbp]

\begin{center}

\includegraphics[width=0.8\columnwidth]{figures/flux\_absolute.png}

\caption{Tropospheric ozone attributed to STT, derived from ozonesonde measurements as described in the text.}

\label{fig:fluxsummaryabs}

\end{center}

\end{figure}

We use simulated tropospheric ozone columns from GEOS-Chem to extrapolate the sonde-based estimates to the entire Southern Ocean using our estimated enhanced tropospheric ozone, we can create a rough estimate of the STT effect on tropospheric ozone in this region. To do so, we

multiply the monthly likelihoods of STTs (fraction of sonde releases for which an STT event was detected, per month) by the monthly mean tropospheric ozone column over the Southern Ocean (from the GEOS-Chem multi-year mean) and by the monthly mean fraction of the ozone column attributed to STT (as in Fig. \ref{fig:fluxsummary}, but separated by month). The monthly values of each term in this equation are shown in Figure \ref{fig:SOExtrapolation} (lower panel).

Figure \ref{fig:SOExtrapolation} shows the extrapolated monthly mean ozone flux from STT events over the Southern Ocean.

We find that STT events may be responsible for at least (TODO:update once fixed model is finished) $2.2\times10^{16}$ molecules cm$^{-2}$ yr$^{-1}$, of the tropospheric ozone over the Southern Ocean, TODO: this is around X:TG/yr ozone.

\begin{figure}[!htbp]

\includegraphics[width=\textwidth]{figures/SO\_extrapolation.png}

\caption{(Top) Estimated contribution of STT to tropospheric ozone columns over the Southern Ocean. (Bottom) The three quantities used to calculate the flux estimates shown in the top panel. The tropospheric ozone column (left axis) is from GEOS-Chem, while the STT fraction and likelihoods (right axis) are from the ozonesonde measurements.}

\label{fig:SOExtrapolation}

\end{figure}

Our estimate is ( todo: greater/smaller/completely different) to other estimates of southern hemisphere STT flux.

\citet{Olsen2003} use PV and winds from the GEOS reanalysis combined with ozone measurements from the TOMS satellite to estimate that around 210~TG yr$^{-1}$ of ozone flux occurs in 2000 between 30$^{\circ}$S and 60$^{\circ}$S.

Their estimates show peak ozone flux from winter to early spring (JJAS). At this time of year, we find from the GEOS-Chem simulation the highest overall tropospheric $\Omega\_{O3}$, but a relatively low overall STT flux. Instead, our results suggest that the STT flux is largest in austral summer (DJFM), primarily due to an increased frequency of STT detections during these months.

Global STT flux estimated from an ensemble of models suggests values around 550~Tg yr$^{-1}$ \citep{Stevenson2006}.

Global net flux (transport from the stratosphere to the troposphere minus opposite transport) is estimated to be 75~Tg yr$^{-1}$ \citep{Sprenger2003}.

Considering the individual event contributions, \citet{Terao2008} estimate much higher STT impacts; where 30--40\% of the tropospheric column is due to STT.

Although this figure is based on the Northern Hemisphere during the seasonal STT peak.

\section{Conclusions}

Ozonesonde data in the Southern Hemisphere provides a satellite-independant quantification of STT ozone transport.

The frequency and amount of ozone descending from the stratosphere into the troposphere can be estimated from the long time series of tropospheric ozone profiles.

Using almost ten years of ozonesonde profiles over the southern high latitudes, a clear summer peak is seen for STT occurences at both 38$^{\circ}$S and 55$^{\circ}$S, although not at 69$^{\circ}$S.

We use a Fourier bandpass filter to determine STT ozone transport events.

The filter removes seasonal tropospheric ozone influences and allows clear detection of ozone-enhanced tongues of air in the troposphere.

By setting empirical checks, ozonesonde vertical profiles can clearly show tropospheric ozone enhancement which is separated from the stratosphere.

The cause of these ozone enhancements is examined through the use of satellite and reanalysis datasets on case studies above Melbourne.

The major causes of STT events found over Melbourne are turbulent weather in the upper troposphere due to low pressure fronts and cut-off low pressure systems.

TODO: Discuss Davis,Macq here

Integration of the ozone enhancement along the altitude of the ozone profile allows a rough estimate of stratospheric transport for each event.

Events typically cause a 3\% enhancement of the tropospheric ozone column.

This is around $2 \times 10^{15}$ molecules cm$^{-2}$ (TODO: Update when model run finishes) ozone enhancement over the southern high latitudes caused by STTs.

GEOS-Chem performs fairly well when compared to ozonesondes at our three sites, with vertical profile averages and seasonal cycles of tropospheric ozone conforming to within $\sim 10$\% (TODO: update when model finishes) of the data, even though the model is looking at the average over 2$^{\circ}$ latitude by 2.5$^{\circ}$ longitude grid boxes.

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\bibliography{bibliography/Ozone.bib}

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